

Interaction Potentials of Atom-Molecule and Molecule-Molecule
Systems From Crossed Beam Experiments

Thesis by
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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1979

(submitted September 29, 1978)

To my patient, tolerant,
and understanding family

Acknowledgments

I wish to thank my research adviser, Professor Aron Kuppermann, who has been friend, adviser, and teacher. His guidance and understanding are gratefully remembered; but, most of all, his scientific integrity stands out as a model. To him, I am more than grateful.

A great debt exists to many at Caltech: to Mark Keil who was lab partner and with whom I shared many moments of frustration and of success--it was a pleasure to work with Mark; to Wayne Flicker, Oren Mosher, Mike Coggiola, Jon Burke, and Don Mintz who offered aid and encouragement as they were completing their experimental investigations; to Joel Bowman and George Schatz who offered much needed aid in Ch 125; to my contemporaries in the Kuppermann group who worked and suffered and prevailed, Bob Frueholz, Jeff Sell, John Dwyer, Bob Reiner, and Ron Rianda; and especially to the men in the shops who made research possible, Bill Schuelke, Toni Stark, Guy Duremberg, Jim Olson, Irv Moskovitz, and Tom Dunn.

I am grateful for many of the friendships made here at Caltech. People like Adria and Tom are always remembered.

Special thanks go to my family: to my parents for their love and encouragement and for implanting the desire for education; and to Maggie and the boys who have tolerated and loved their husband/daddy through a trying period. Thanks go also to friends in the heights, especially Doug, who have shown me much about life and myself.

Finally, thanks go to the Air Force for my support over the $3\frac{1}{2}$ years of residence at Caltech and thanks go to the Air Force Weapons Laboratory for the opportunities afforded me over the past year-and-a-half to continue work and finish my thesis.

Abstract

The text of this thesis is comprised of eight chapters and six appendices.

The first chapter is an introduction, overviewing the purpose of the experiments and outlining the remainder of the thesis. Chapters 2 and 3 survey the theory of intermolecular potentials and of elastic scattering and provide the basis for interpreting the results obtained. Chapter 4 reviews the investigations and optimizations/characterizations made to the apparatus and procedures.

Chapters 5, 6, and 7 present the results. Chapter 5 details studies on the $\text{H}_2(\text{D}_2) + \text{Ar}$ system. Essentially three independent experiments were performed on this system to check internal consistency. The results obtained were also consistent with other laboratories, some using different techniques. The effects of the non-spherical part of the intermolecular potential were found to be negligible, within error of the experiment. A potential model with five independent parameters, the Simmons-Parr-Finlan-modified Dunham (SPFD), was found to provide the best representation of the intermolecular potential. In Chapter 6, studies on the $\text{He} + \text{CH}_4$, NH_3 , H_2O , SF_6 systems are described. Central-field SPFD potentials were found to provide satisfactory descriptions of the intermolecular potential for these systems. The potentials described for the $\text{He} +$ isoelectronic hydride series (CH_4 , NH_3 , H_2O) are physically reasonable; however, the $\text{He} + \text{SF}_6$ system is shown to have an anomalously deep potential well which can not be readily explained.

Central-field SPFD potentials were found to provide satisfactory descriptions of the intermolecular potential for all these systems. Chapter 7 presents the results of studies on the $\text{H}_2(\text{D}_2) + \text{NH}_3$, H_2O systems. Results for H_2 and D_2 with each hydride molecule were found to be in agreement with each other, as expected. Again, the five-parameter central-field SPFD potentials provided satisfactory descriptions of the intermolecular potential. In Chapter 8 we present a summary of the results and conclusions of the intermolecular potential studies performed.

Appendices 1, 2, 3, and 4 outline changes to and tests of the apparatus which represent considerable effort. They were essential to establish the reliability and quality of the experimental data and, furthermore, to increase the capabilities of the apparatus.

Appendices 5 and 6 present the results of two additional experiments on which the author played a major role. Each represents a paper in press.

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CHAPTER 1

Introduction

1. INTRODUCTION

Crossed molecular (atomic) beams may be defined as two directed beams of molecules (atoms), interacting with each other at such low pressures that only single collisions between the species of each beam need be considered. The scattering patterns resulting from such collisions provide valuable information about intermolecular forces between the colliding partners.

Ideally the crossed molecular beam experiment involves two monoenergetic, collimated beams whose molecules are in well-defined internal quantum states. The two beams are directed to intersect with a known relative energy; and the scattered species are analyzed for changes in velocity, internal quantum states, and chemical composition. Collisions in which only the direction (but not the magnitude) of the relative velocity are changed are termed "elastic collisions." Those in which internal-state quantum numbers are changed are termed "inelastic collisions." Those which involve structural changes are termed "reactive collisions."

Regardless of which type collision is considered one of the fundamental objectives is to determine the intermolecular forces at play. This represents the goal of this thesis. The interactions examined are the van der Waals forces for atom-molecule and molecule-molecule interactions. Although the long-range potential for such systems has been accurately defined through both experimental and theoretical studies, the short-range repulsive potential and the intermediate-range attractive minimum are as yet not well known.

Because of the importance that these van der Waals forces have for other properties (gas equilibrium and transport properties, crystal structure and behavior, collisional energy transfer, and chemical reactions, to give some examples), any additional understanding of these forces will provide physical insight which may be then applied to more complicated systems. In other words, our studies of simple systems at the microscopic level can be used to increase our understanding of much more complicated systems.

In the first part of this thesis we survey the present theoretical knowledge of intermolecular potentials and digress into some of the more common representations of spherically-symmetric (central-field) potential forms and also of non-spherically-symmetric potential forms. The theory of elastic scattering is then reviewed, and the determination of intermolecular potentials from molecular scattering data is examined. Next, the experiment is described: an overview of the hardware is given followed by detailed discussion of improvements/optimizations of the apparatus; experimental procedures are then summarized.

Having reviewed the theory, apparatus, and procedures of the experiments, we are now ready to discuss the experiments. In Chapter 5, investigations of the $\text{H}_2(\text{D}_2)$ -Ar system are presented. Previously, the He-Ar system which may be modelled validly with the central-field assumption had been studied by this research group (see Appendix E). A logical extension of that work was the investigation of the $\text{H}_2(\text{D}_2)$ -Ar system which represents only a small step

from the central-field noble gas pairs. Additionally, this system was amenable to detailed experiment and also had been studied by a number of different laboratories using a variety of experimental techniques.

A further extension of the intermolecular potential studies was the investigation of He-molecule systems. Both He-diatomic molecule (see Appendix F) and He-polyatomic molecule systems were addressed. In Chapter 6 the investigations of He + CH₄, NH₃, H₂O, SF₆ are described and the validity of the central-field assumption is addressed. In Chapter 7, the studies of intermolecular potentials finally address molecule-molecule interactions, H₂(D₂)-NH₃ and H₂(D₂)-H₂O. This represents further exploration into the validity of the central-field assumption as the He atom in the He + NH₃ and the He + H₂O systems addressed in Chapter 6 is replaced by the H₂(D₂) molecule. In Chapter 8 we summarize the results of our experimental investigations and present our conclusions.

In the first four Appendices, details of modifications of the apparatus are given which represent considerable effort and are essential to establishing the validity of the results obtained.

Appendix 1 reviews work done on the data acquisition and processing system, including not only a checkout test of its linearity but also a detailed analysis of the minicomputer program used to acquire and process the raw experimental data. Appendix 2 examines work done to introduce a pulse counting capability in the apparatus. Appendix 3 presents a detailed analysis of a 1024 multichannel buffer (along with

a brief discussion of its purpose) necessary to do velocity analysis of the scattered beam and, hence, inelastic scattering. Finally, Appendix 4 describes work done to effectively utilize a nominal one-liter liquid helium dewar as a cryopump; also discussed are thermal analyses applicable to the use of liquid nitrogen.

The last two appendices represent journal articles on research in which this author was an active participant. Appendix 5 is the results of considerable effort in studying the atom-atom He + Ar system. Appendix 6 is the results of investigations of the He + N₂, O₂, CO, and NO systems.

CHAPTER 2

Theory of Intermolecular Potentials

2. INTERMOLECULAR POTENTIALS

Since the days of the ancient Greek atomist philosophers in the fifth century BC, man has speculated upon the manner in which molecules (atoms) might interact. A somewhat later expositor of atomism was Lucretius¹ who noted the differences in the flow properties of oil and wine and speculated that the respective sizes or the interactions of the particles was responsible for them. Much later in 1743, Clairault² made the first attempt to understand in a semi-quantitative manner the nature of intermolecular forces. He noted the "strange effects of capillary" and considered the explanation in his description of fluids in small portions: "whose parts are animated by forces the direction of which vary in the most general way." In 1763, Boscovich proposed that molecules could be regarded as point centers of forces which were both attractive and repulsive in nature with strong repulsions at very small separations; Clausius in 1857 postulated the imperfection of gases could be attributed to the finite size of molecules and to molecular attraction; and Van der Waals used these concepts as the basis for his famous equation of state.³

Intermolecular forces play a large role in the world around us; but, before entering into discussion of such roles and of such forces, it is worthwhile to explain the concepts of "molecule" and "force." Following the example of Longuet-Higgins,⁴ a molecule is defined as a group of atoms (or a single atom) with a binding energy that is large in comparison with the thermal energy kT . Thus the molecule will not lose its identity as it interacts with its environment, i.e., it will

not normally dissociate during collisions with neighboring molecules. Interactions between molecules are most conveniently represented by potential energy surfaces whose gradient furnishes the force on each molecule. For interacting molecules, the forces are dependent upon the electronic, vibration, and rotational states of the molecules. In principle, intermolecular forces can be calculated from a knowledge of the fundamental constants and the Schrödinger equation. Unfortunately, however, even for systems with only a few electrons this approach bogs down in mathematical complexity, forcing compromise and approximation.

The intermolecular potential of closed-shell systems plays an important role in determining their physical properties. As an example, helium does not liquify under standard pressure until a few degrees Kelvin is reached ($\sim 4^\circ\text{K}$) while water liquifies at 373°K and freezes then at 273°K . The equations of state of dilute gases often are described by the virial expansion where the second coefficient represents the mean contribution of interacting pairs of molecules, the third coefficient represents the mean contribution of triplets, etc. Since often the third coefficient can be ignored, good approximations describing dilute gases can be made if the intermolecular forces are known. Also, the theory of transport processes required consideration of the dynamics of molecular collisions and, hence, of the intermolecular potential. Insight into such processes as viscosity and heat conduction can thus be obtained. Intermolecular forces furthermore are reflected in the structure of crystals. Properties such as size

and structure of the unit cell, sublimation energy, compressibility, heat capacity, elastic constants, and lattice vibrations all depend upon the intermolecular potentials. Perturbations arising from intermolecular interactions in the spectra of many gases systems are important. Changes in linewidth and shape due to such interactions play a major role in the operation of many gas lasers (such as DF chemical, CO₂ electrical) which are finding more uses every day. Finally, the molecular environment in which a given chemical reaction occurs can affect it profoundly, as illustrated in surface chemistry, catalysis, and solvent studies. In summary, understanding of intermolecular potentials provides physical insight into the behavior of the world around us.

As mentioned above, an exact description of the intermolecular potential from first principles is extremely difficult and essentially impossible for all but the simplest systems. Over the past forty-odd years since the pioneering work of London on dispersion forces,⁵ a very large volume of research has been done to improve our knowledge and understanding of intermolecular (atomic) forces.^{6, 7, 8} For the purposes of describing and analyzing the experimental results presented in this work, only a survey of the most critical points to our understanding will be reviewed. Some of the more common model potentials will be examined; and, finally, a short discussion on the inclusion of anisotropy in the models will be made.

2.1 Theoretical Considerations

In a system composed of two neutral atoms or molecules, attractive forces of completely different orders of magnitude can arise. If the two interacting partners can form a stable molecule, an extremely strong attractive potential will occur at small distances of approach (say, 1-2 eV at an equilibrium distance of about 1 Å separation). This potential which we will term the "chemical potential" will dominate our observations out to very large separations. On the other hand, if the electron spins of two approaching atoms are parallel, if one or both atoms are rare gas atoms, or if the interacting molecules (molecule/atom) cannot form a chemical bond, a much weaker attractive potential will exist; i.e., a Van der Waals attractive potential of the order of a few meV at its minimum. It is this weak attractive potential and the close repulsive potential with which we are concerned in the present studies.

The forces between molecules (atoms) are electric in origin. Both short-range and long-range forces can be thus explained, but detailed calculations for short-range forces cannot easily be performed at an equivalent level of accuracy to those for long-range forces. A simple physical picture can be obtained for the short-range forces in terms of the Hellmann-Feynman electrostatic theorem and the Pauli exclusion principle. The Hellmann-Feynman theorem basically states that the force acting on any one nucleus is just the classical Coulomb interaction between it and the other nuclei and the electronic charge distribution. The Pauli exclusion principle requires that the

wavefunction of the system be antisymmetric with respect to the exchange of electrons between the two interacting molecule. Thus, at distances short enough for appreciable overlap of the charge clouds to occur, large distortions must take place in these distributions (distortions due purely to the Coulomb repulsion among the electrons appears to be a secondary effect). The decreased screening of the nuclei by the electron clouds results in a net repulsion. (In the case of interaction of atoms or molecules with incomplete shells, an enhancement of the electron distribution can occur in the region between the nuclei leading to the formation of a chemical bond.) The resulting energies for these short-range interactions may be calculated by first-order perturbation theory. For atoms and molecules with closed shells, these first-order exchange energies may be approximated over a wide range of separations by the following expression

$$V(r) = A \exp(-br) \quad (2.1)$$

where A and b are constants and r is the intermolecular separation.

For long-range interactions, the overlap of electron clouds is negligible with the consequence that the first-order exchange energies also are. This results in eliminating the requirement for antisymmetrizing the wavefunction with respect to change of electrons between the two molecules. The consequence of these conditions is that highly accurate semiempirical calculations can be made in the theory of long range forces. Long-range interactions can be considered to be

classed into four categories: (1) electrostatic, (2) induction, (3) dispersion (London forces), and (4) resonance forces. Electrostatic forces are those caused by interaction of permanent electric moments (charge, dipole; quadrupole, etc.). Induction is caused by the permanent electric moments of the first. Dispersion forces arise from the mutual perturbation of electronic structures creating electric moments which then interact. Resonance forces occur between two identical molecules, when the quantum numbers of the two molecules are such that the optical selection rules permit the free exchange of a photon from one molecule to another. While the electrostatic and induction forces can be understood from classical arguments, the dispersion and resonance forces have strictly quantum mechanical origins.

The most important of these interactions in the present studies are the London dispersion forces (refer to chapter 5). A simple semiclassical description attributes them to the interaction between the instantaneous dipole moment of the fluctuating dipole in one molecule and the dipole it induces in the other. These dipoles are in phase, producing a net attraction, although the average dipole moment vanishes. London⁵ has made an accurate second-order perturbation calculation between two atoms which has the form

$$V_{12}^{(2)}(\text{dispersion}) = - (C_6/r^6) - C_8/r^8 - (C_{10}/r^{10}) + \dots \quad (2.2)$$

where the first term represents dipole-dipole interaction, the second term represents dipole-quadrupole interaction, etc. The first term on the right-hand-side of (2.2) may be written

$$-\frac{C_6}{r^6} = -\frac{3}{2r^6} \frac{e^4 \hbar^4}{m_e^2} \sum_{i,j \neq 0} \frac{f_{1i} f_{2j}}{(E_{10} - E_{1j})(E_{20} - E_{2j})(E_{10} + E_{20} - E_{1i} - E_{2j})} \quad (2.3)$$

where E_{ki} is the energy of the i^{th} electronic state of the k^{th} atom and f_{ki} is the corresponding dipole oscillator strength of the transition from the ground state to the i^{th} electronic state.

The short-range forces appear in a first-order perturbation calculation with antisymmetrized wavefunctions, whereas the long-range forces first appear in a second-order perturbation with unsymmetrized wavefunctions. At some intermediate separation distance, the sizes of the two calculated energies will be comparable. In this range also the second-order exchange energies can be significant although they are negligible in the short and in the long ranges.^{7c} Since the long- and short-range forces have been obtained using different approximations, it would be a dubious procedure merely to add the forces.⁹ Consequently, theoretical characterization of the van der Waals attractive minimum where the forces are balancing is more difficult than either the long- or short-range regimes.¹⁰ For closed-shell atoms and molecules Gordon and Kim¹¹ have developed a model which assumes that the interatomic interaction is evaluated from additive atomic densities where no rearrangement or distortion of the separate atomic densities has taken place. Agreement was quite good for all systems studied except for the helium system.

2.2 Model Potential Functions

Because of the many difficulties inherent in the ab initio calculations of intermolecular potentials, especially in the well minimum regime, the use of model functions is necessary. These model potential functions have a varying number of adjustable parameters which can be optimized to fit experimental data. (Fitting procedures are discussed in Chapter 3). The major objection to such fits is one of whether the optimized-parameter model potential function is unique; a second objection is one of how sensitive the fits are to the data. Keil and Kuppermann¹² have made a study of fitting data generated from an assumed potential with a number of different model potential functions. The potential assumed was for a quantum system (nominally He + Ar) that had a collision energy thirty times the depth of the potential well. They concluded that a suitable potential form had to have at least four parameters and that up to five independent parameters could be justified, with the SPFD and M^2SV (Eqs. (2.13) and (2.14) below) potentials the most suitable in combining flexibility and uniqueness. They further determined that unique potentials could be obtained by proper analyses using such potential forms. These conclusions were strongly supported by the experimental results given in Chapters 5, 6, and 7 as well as in Appendices 5, 6, and 7 in which the fits with M^2SV and SPFD potentials were found to be essentially identical (within experimental error) while more simple potential forms gave similar but, nevertheless, different potentials.

The simplest potential model function, which describes hard sphere collisions, is

$$V(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (2.4)$$

Here, only repulsive forces are considered through use of a rigid wall. The only parameter is σ , the distance of closest approach. Another model which considers only repulsive forces is the line-of-center model

$$V(r) = \alpha r^{-\delta} \quad (2.5)$$

Here, both the exponent δ and the constant coefficient α are used to adjust the magnitude of the potential.

Realistic intermolecular interactions have both attractive and repulsive forces. The square well potential often is used for a first-order representation for simple model investigations.

$$V(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \alpha\sigma \\ 0 & r > \alpha\sigma \end{cases} \quad (2.6)$$

The three adjustable parameters in this function are the range, σ ; the depth of the well, ϵ ; and the well width parameter, α .

Obviously more sophisticated potentials can be used. These range from the two-parameter Lennard Jones 12-6 (LJ12-6) potential to the Simons-Parr-Finlan-Dunham third-order potential (SPFD).

The potential model functions which we used in our experiments were written in the reduced form

$$f(\rho) = \frac{V(r)}{\epsilon} , \quad \rho = \frac{r}{r_m} \quad (2.7)$$

where r_m is the radius of the attractive minimum and ϵ is its depth.

The zero of the potential, occurring at $r = \sigma$, may be related to r_m and the potential shape $f(\rho)$.

Potential model functions considered are:

a) Lennard-Jones 12-6 (LJ12-6)^{6c}

$$f(\rho) = \rho^{-12} - 2\rho^{-6} . \quad (2.8)$$

Here the first term accounts for the repulsive forces, and the second accounts for the attractive forces. The potential zero, σ , may be readily shown to equal $r_m / (2^{\frac{1}{6}})$. The second term represents the attractive forces using the r^{-6} dependence discussed earlier.

b) Lennard-Jones n-6 (LJn-6)^{6c}

$$f(\rho) = \frac{6}{n-6} \left\{ \rho^{-n} - \frac{n}{6} \rho^{-6} \right\} . \quad (2.9)$$

The difference with the LJ 12-6 potential is that the r^{-12} repulsive dependence is recognized as merely a mathematical convenience; and, hence, the repulsive exponent is allowed to vary.

c) Klein-Hanley n-8-6 (n-8-6)¹³

$$f(\rho) = \frac{\rho^{-n}}{n-8} (8 - 2c_6) - c_6 \rho^{-6} - \frac{\rho^{-8}}{n-8} (6c_6 + n - nc_6) . \quad (2.10)$$

Shape parameters designed to primarily govern the short- and long-range regions are n and c_6 ,¹⁴ respectively. The second dispersion term in ρ^{-8} is included; but, obviously, its coefficient is fixed.

d) Double Lennard Jones (DLJ)¹⁵

$$\left. \begin{aligned} f(\rho) &= \frac{m}{n_1 - m} \left\{ \rho^{-n_1} - \frac{n_1}{m} \rho^{-m} \right\} \quad \text{for } \rho < 1 \\ f(\rho) &= \frac{6}{n_2 - 6} \left\{ \rho^{-n_2} - \frac{n_2}{6} \rho^{-6} \right\} \quad \text{for } \rho \geq 1 \end{aligned} \right\} \quad (2.11)$$

Available shape parameters are n_1 , n_2 , and m . n_1 determines the slope of the repulsive potential wall; n_2 can be used to determine the leading dispersion term independent of the repulsive regime.

(e) Morse-Spline-van der Waals (MSV)¹⁶ and M^2SV ¹²

$$\begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2], \quad \text{for } \rho \leq \rho_1 \\ f(\rho) &= (\rho_2 - \rho)[s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1)[s_2(\rho - \rho_1)^2 + s_4], \quad (2.12) \\ &\quad \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= -\sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho \geq \rho_2 \end{aligned}$$

The s_i ($i = 1, 2, 3, 4$) are cubic spline coefficients, which are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 . The first spline point is taken as the inflection point of the Morse curve, $\rho_1 = 1 + \beta^{-1} \ln 2$. The second spline point may be treated as a fitted parameter but, as a result of the computer simulation studies for He + Ar,¹² was held fixed at $\rho_2 = 1.6$. Remaining shape parameters are β_1 , governing the

shape of the repulsive and well regions, and the dispersion series coefficients. We may modify this potential (MSV) by using a second Morse function for $n < \sigma$, joined smoothly to the first at $n = \sigma$. This M^2SV potential then has the additional parameter β' and differs from above as

$$f(\rho) = \frac{1}{\omega} e^{(\beta' - \rho\beta\omega)} [e^{(\beta' - \rho\beta\omega)} - 2] \quad \text{for } \omega = \frac{\beta' - \ln 2}{\beta - \ln 2} \quad \text{and} \\ \rho < 1 - \beta^{-1} \ln 2 \quad (2.13)$$

$$f(\rho) = e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] \quad \text{for } 1 - \beta^{-1} \ln 2 \leq \rho \leq \rho_1$$

This potential effectively decouples the attractive well region from the near repulsive wall region, a very desirable feature for flexibility in fitting experimental data.

(f) Simmons-Parr-Finlan-Dunham (SPFD)¹⁷

$$f(\rho) = b_0 \lambda^2 \left(1 + \sum_{i=1}^N b_i \lambda^i\right) - 1 \quad \text{for } \lambda = 1 - \frac{1}{\rho}, \quad N=3, \quad \text{and } \rho < \rho_f \\ f(\rho) = - \sum_{i=1} c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho \geq \rho_f \quad (2.14)$$

Smoothness conditions at $\rho = \rho_f$ are used to fix the highest-order coefficients b_2 and b_3 . ρ_f may be treated as a variable, but it is fitted at $\rho_f = 1.6$;¹² the b_0 and b_1 coefficients determine the shape of the potential; and the dispersion coefficients are also independent parameters. Since the SPFD potential often shows a spurious maxima or

oscillations below $\rho = 0.65$, and exponentially repulsive wall, i.e., $f(\rho) = Ae^{-b\rho}$ is joined to the potential at $\rho = 0.7$ (A and b are not independent but, rather, are fixed by smoothness conditions. This is a very flexible potential energy form.

A few attempts have been made in the recent literature to represent non-spherical intermolecular potentials. Generally, the form of the potential is assumed to be

$$V = V_I + V_A P_2(\cos \theta) . \quad (2.15)$$

Zandee et al.¹⁸ have made total cross section measurements applying state selection to the H_2 molecule to determine the magnitude of the anisotropic part of the intermolecular potential. In fitting their data, they employ an LJ n-6 in the general form of eq. (2.15),

$$V = c_n R^{-n} [1 + q_n P_2(\cos \theta)] - c_6 R^{-6} [1 + q_6 P_2(\cos \theta)] \quad (2.16)$$

with $c_n = [6/(n-6)] \epsilon R_m^n$ and $c_6 = [n/(n-6)] \epsilon R_m^6$. Here q_n and q_6 are adjustable parameters called the anisotropy parameters which describe the position and depth of the anisotropic minimum,¹⁹ i.e., the minimum of the function $V_2 (= c_n R^{-n} q_n P_2(\cos \theta) - c_6 R^{-6} q_6 P_2(\cos \theta))$ one finds the anisotropic depth $\epsilon_a = (\epsilon q_6^{n/(n-6)})/q_n$ and the anisotropic well minimum $R_{m,a} = R_m (q_n/q_6)^{1/(n-6)}$. LeRoy and Van Kranendonk²⁰ have employed the same potential in their fit of $H_2(D_2) + Ar$ spectroscopic data. (For their data fit, n optimized to 12.) LeRoy et al.²¹ later used another potential that was a generalization of the Buckingham-Corner potential with the C_6 coefficient held constant at its semi-

empirically-determined value.²² Dunker and Gordon have also fit the same data, again with an anisotropic potential of the form in eq. (2.15) but using an MSV potential model.

For scattering experiments, the recent work of Parker, Keil, and Kuppermann²³ for fitting anisotropic intermolecular potentials for the He + CO₂, N₂O, and C₂N₂ systems is most promising. Utilizing the infinite-order sudden approximation, the investigators have obtained physically reasonable anisotropic intermolecular potentials with excellent data fits -- the spherical averages of the empirical anisotropic potentials are quite different from the potentials obtained by central-field analysis of the data. The potential forms recommended all are an elliptical modification to central-field types of potentials

$$V(r, \gamma) = \epsilon(\gamma) f[\rho(r, \gamma)] \text{ where } \rho(r, \gamma) = \frac{r}{r_m(\gamma)} \quad (2.19)$$

and

$$r_m(\gamma) = r_{m\perp} \left[\frac{1 + r_q \sin^2 \gamma}{1 + r_q} \right]^{\frac{1}{2}}; \quad \epsilon(\gamma) = \epsilon_0 + \epsilon_2 P_2(\cos \gamma).$$

For arbitrary γ , $r_m(\gamma)$ is the distance to the potential minimum, and $-\epsilon(\gamma)$ is the corresponding potential energy with r the distance of the He atom to the molecule center-of-mass and with γ the angle between r and the molecular axis. Any central-field reduced potential energy function, as those in eqs. (2.8-2.13), can be used for $f(\rho)$, because the anisotropy is introduced through the Legendre polynomial expansion of the well depth and the elliptically shaped well position. This model

is, of course, limited to systems which can be represented by an elliptically-shaped intermolecular potential, i.e., a linear molecule and an inert gas atom.

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CHAPTER 3

Theory of Elastic Scattering

3. THEORY OF ELASTIC SCATTERING

Determination of the intermolecular potential in elastic scattering molecular beam experiments depends upon the fact that the angle of deflection in a binary collision is a function of the relative kinetic energy, the relative angular momentum, and the intermolecular potential. Elastic scattering of two molecules (atoms) can provide a direct method to determine the intermolecular (atomic) potential. In a typical experiment, beam intensities and background pressures are sufficiently low to ensure that either no collision or only one collision occurs. If the scattering angle is scanned by moving the detector around the scattering center and if the intensity of the scattered particles is recorded as a function of deflection angle from the original direction of the primary (detected particle) beam, surprisingly complicated scattering patterns can be obtained.

Thus scattering patterns show a number of interference effects since the intermolecular potential consists of both attractive and repulsive forces. These interferences are most pronounced in the thermal energy range and contain detailed information about the intermolecular potential. In this chapter we restrict ourselves to an overview of the theory necessary to extract information about the intermolecular potential from elastic scattering data.¹ (Elastic collisions are those in which only the direction of the relative velocity is changed, i. e., no translational to internal energy transfer occurs.) First, an overview of classical scattering is made; this is followed by a discussion of semiclassical scattering in which the structure of

the differential cross section (DCS) is examined; next, the quantum mechanical scattering of two particles is reviewed; and, finally, procedures for determining the intermolecular (atomic) potential are surveyed with emphasis on the procedures for data fits used in the results of Chapters 5, 6, and 7.

3.1 Classical Mechanics

The scattering of two particles interacting via a spherically symmetrical (central field) potential, can be reduced to an equivalent one-particle system under the action of this potential.² The first step in the reduction of the two-particle problem is the separation of the center-of-mass motion which is subject only to the constraint that the potential is only a function of the distance separating the particles with no dependence upon external distances. Consider two particles m_1 and m_2 which have a total of six degrees of freedom and hence six independent generalized coordinates. Define the location of m_1 and m_2 as $\underline{r}_1$ and $\underline{r}_2$, respectively, with the origin taken as some arbitrary point. The relative position vector is now defined as

$$\underline{r} = \underline{r}_1 - \underline{r}_2 \quad (3.1)$$

and the center-of-mass vector is given by

$$\underline{R} = (m_1 \underline{r}_1 + m_2 \underline{r}_2) / (m_1 + m_2) \quad (3.2)$$

Inverting these relationships (eqs. 3.1 and 3.2) gives

$$\underline{\underline{r}}_1 = \underline{\underline{R}} + \frac{m_2}{m_1 + m_2} \underline{\underline{r}} = \underline{\underline{R}} + \frac{\mu}{m_1} \underline{\underline{r}} \quad (3.3a)$$

$$\underline{\underline{r}}_2 = \underline{\underline{R}} - \frac{m_1}{m_1 + m_2} \underline{\underline{r}} = \underline{\underline{R}} - \frac{\mu}{m_2} \underline{\underline{r}} \quad (3.3b)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ = reduced mass of the system.

The linear momentum, angular momentum, and kinetic energy are given by

$$\underline{\underline{P}} = m_1 \dot{\underline{\underline{r}}}_1 + m_2 \dot{\underline{\underline{r}}}_2 = (m_1 + m_2) \dot{\underline{\underline{R}}} \quad (3.4a)$$

$$\underline{\underline{L}} = m_1 (\underline{\underline{r}}_1 \times \dot{\underline{\underline{r}}}_1) + m_2 (\underline{\underline{r}}_2 \times \dot{\underline{\underline{r}}}_2) = m (\underline{\underline{R}} \times \dot{\underline{\underline{R}}}) + \mu (\underline{\underline{r}} \times \dot{\underline{\underline{r}}}) \quad (3.4b)$$

$$\underline{\underline{T}} = \frac{1}{2} m_1 \dot{\underline{\underline{r}}}_1 \cdot \dot{\underline{\underline{r}}}_1 + \frac{1}{2} m_2 \dot{\underline{\underline{r}}}_2 \cdot \dot{\underline{\underline{r}}}_2 = \frac{1}{2} m \dot{\underline{\underline{R}}} \cdot \dot{\underline{\underline{R}}} + \frac{1}{2} \mu \dot{\underline{\underline{r}}} \cdot \dot{\underline{\underline{r}}} \quad (3.4c)$$

Since the potential energy does not depend upon $\underline{\underline{R}}$, no force acts on the center of mass and $\underline{\underline{P}}$ is conserved. Furthermore, if we assume that the motion of the center of mass is known, we can define a new coordinate system whose origin is at the center of mass. $\underline{\underline{R}}$ and $\dot{\underline{\underline{R}}}$ thus vanish and

$$\underline{\underline{L}} = \mu (\underline{\underline{r}} \times \dot{\underline{\underline{r}}}) \quad (3.5a)$$

$$\underline{\underline{T}} = \frac{1}{2} \mu \dot{\underline{\underline{r}}} \cdot \dot{\underline{\underline{r}}} \quad (3.5b)$$

Thus, we have reduced the original two-particle problem to two separate one-particle problems: (1) the translational motion of the system as a whole, which simply adds a constant to the total energy

(by our judicious choice of coordinates, this is zero); (2) the internal motion which is now described by a hypothetical particle of mass μ and $\underline{r}$ moving about a fixed center of force.

The equivalent one-particle plus potential system with its three degrees of freedom (three of the original six degrees of freedom describe the motion of the center of mass) can further be reduced. In a spherically symmetric (central-field) system the total angular momentum is conserved, i.e.,

$$\dot{\underline{L}} = \mu \frac{d}{dt} (\underline{r} \times \dot{\underline{r}}) = \mu (\dot{\underline{r}} \times \dot{\underline{r}}) + \mu (\underline{r} \times \ddot{\underline{r}}) = 0 \quad (3.6)$$

since $(\dot{\underline{r}} \times \dot{\underline{r}})$ obviously is zero and since the force $\mu \ddot{\underline{r}}$ by definition is always along $\underline{r}$. As a result, the reduced particle moves in a space-fixed plane and has only two degrees of freedom which can be described by two first-order differential equations in plane polar coordinates

$$L = \mu r^2 \dot{\theta} \quad (3.7a)$$

$$\begin{aligned} E &= \frac{1}{2} \mu (\dot{\underline{r}}^2 + r^2 \dot{\theta}^2) + V(r) \\ &= \frac{1}{2} \mu \dot{\underline{r}}^2 + \frac{L^2}{2\mu r^2} + V(r) \end{aligned} \quad (3.7b)$$

where θ and r are the coordinates.

We now examine a typical trajectory for the particle of mass μ scattered by a fixed scattering center in which the particle moves under the influence of a potential that is attractive at long range and repulsive at short range. Such a trajectory is shown in Figure 3.1.

Here χ is the angle of deflection between initial and final relative velocity vectors and is the quantity of interest since this is the experimental observable. Equations (3.7a) and (3.7b) may be rewritten

$$dr = \left[\frac{2}{\mu} \left(E - V - \frac{L^2}{2\mu r^2} \right) \right]^{\frac{1}{2}} dt \quad (3.8a)$$

$$d\theta = \frac{L}{\mu r^2} dt \quad (3.8b)$$

Elimination of dt from these equations and application of the asymptotically defined relation for L ($L = \mu vb$) gives

$$\theta_c(E, b) = b \int_{r_c}^{\infty} \left(1 - \frac{b^2}{r^2} - \frac{V}{E} \right)^{-\frac{1}{2}} r^{-2} dr \quad (3.9)$$

where r_c and θ_c are the polar coordinates of the point of closest approach, the "turning point" of the trajectory and b is the impact parameter defined as the distance of closest approach in the absence of any interaction. The trajectory is symmetric about the point of closest approach (r_c, θ_c) which leads to the following expression for χ

$$\chi(E, b) = \pi - 2\theta_c = \pi - 2b \int_{r_c}^{\infty} \frac{dr}{r^2 \left(1 - \frac{b^2}{r^2} - \frac{V}{E} \right)^{\frac{1}{2}}} \quad (3.10)$$

The radial distance of closest approach is determined from the condition that r be a minimum, $\frac{dr}{d\theta} = 0$, or equivalently, $\frac{dr}{dt} = 0$ (radial velocity vanishes). From eq. (3.7b) we have

Figure 3.1: Typical classical trajectory for a two-particle system reduced to one particle of mass $\mu = (m_1 m_2 / m_1 + m_2)$ scattering from a potential located at the origin. The incoming particle has velocity v and impact parameter $b = (\ell / \mu v)$. The polar coordinates r and θ (measured from the center of force) describe the motion (eq. 3.10) with r_c and θ_c corresponding to the classical turning point. The center-of-mass scattering angle χ is measured with respect to the asymptotic velocity vectors. Note that the trajectory is symmetric about the turning point.

$$b^2 = r_c^2 \left[1 - \frac{V(r_c)}{E} \right] . \quad (3.11)$$

In the laboratory there is no selection of impact parameters. Examination of a large number of collisions will show that the impact parameters are randomly distributed over a plane normal to the relative velocity that is virtually infinite when compared to atomic dimensions. From Fig. 3.2 we see that the probability of a collision occurring which has an impact parameter between b and $b + db$ is proportional to the area of the shaded ring $2\pi b db$. Applying conservation of particles yields the result that all particles which enter the collision zone with impact parameters between b and $b + db$ must emerge into the solid angle $d\omega$ subtended by the shaded spherical strip lying between χ and $\chi + d\chi$. This number of particles is given by

$$dn = I_0 \cdot 2\pi b |db| \quad (3.12)$$

and we define the differential cross section σ as

$$\sigma(\chi)d\omega = \frac{\text{number of particles scattered into unit solid angle } d\omega \text{ per unit time}}{I_0} \quad (3.13)$$

where I_0 is the incident flux and $d\omega$ is the element of solid angle

$$d\omega = 2\pi \sin\chi d\chi . \quad (3.14)$$

Substituting (3.14) and (3.12) into (3.13) gives

$$\sigma(\chi) \cdot 2\pi \sin\chi d\chi = 2\pi b |db| \quad (3.15a)$$

or

$$\sigma(\chi) = \frac{b}{\sin \chi} \frac{|db|}{d\chi} = \frac{b}{\sin \chi \left| \frac{d\chi}{db} \right|} . \quad (3.15b)$$

In Fig. 3.3, which is a plot of the deflection function vs. impact parameter, we see that the deflection is not necessarily single-valued which means that the observed $\sigma(\chi)$ can have more than one component. The main features of the deflection function $\chi(b)$ are:

- (a) a positive and a negative branch due to the net repulsion and net attraction in the collision as the impact parameter is varied;
- (b) a minimum at $\chi_r(b_r)$ due to the increased effect of the repulsive core of the potential as the impact parameter is decreased;
- (c) a zero where the repulsive and attractive portions of the potential cancel for a finite-valued impact parameter.

The differential cross section thus has a strong classical dependence upon χ (and thus E). The primary effects on the classical DCS include:

a) for $\chi < \chi_r$

$$\sigma(\chi) = \sum_{i=1}^3 \frac{b_i}{\sin \chi \left| \frac{d\chi}{db_i} \right|} . \quad (3.16a)$$

Here three impact parameters contribute to the DCS with the b_3

Figure 3.2: Impact parameter and corresponding scattering angle. Equation (3.15a) gives the relationship between the two derived in terms of the differential cross section.

Figure 3.3: Typical deflection function calculated from a potential with a form similar to the Lennard-Jones 12-6. The shape is typical for a potential that combines both attractive and repulsive regions. b_0 is the impact parameter giving rise to rainbow scattering; and b_1 , b_2 , and b_3 are impact parameters all having the same deflection angle $|\chi|$.

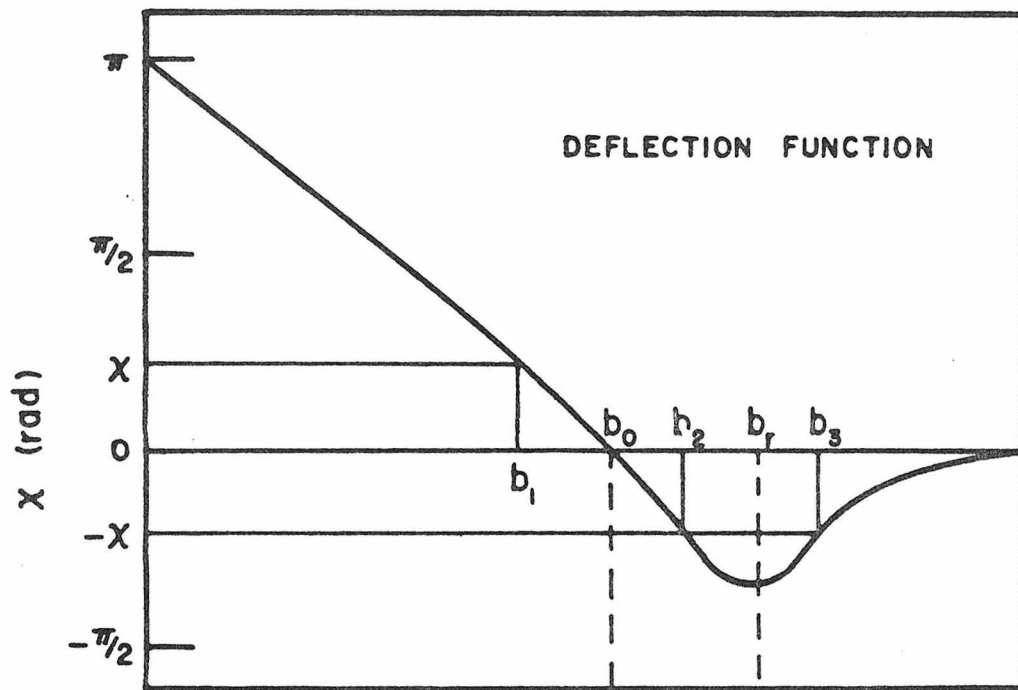


Figure 3.2

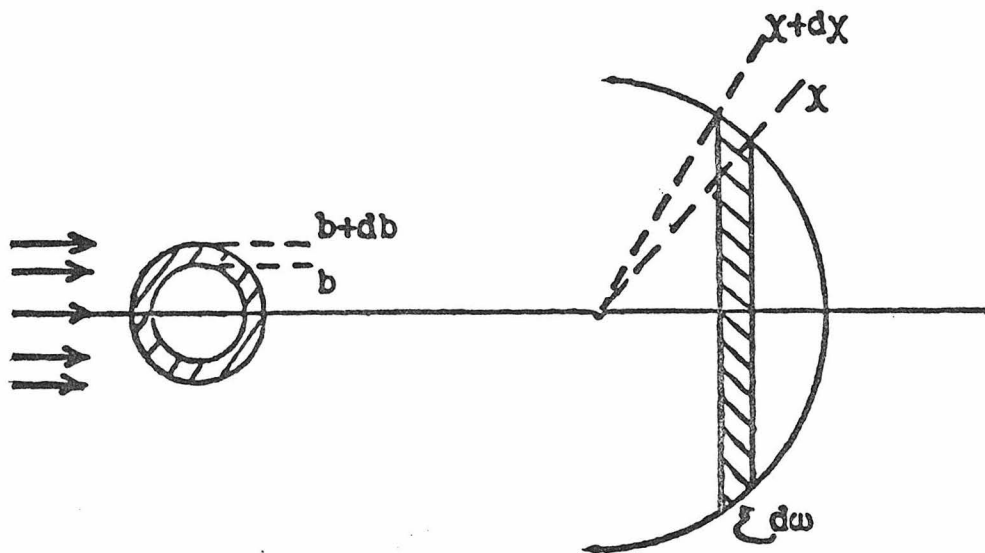


Figure 3.3

contribution the largest,

b) for $\chi \rightarrow \chi_r$, i.e., rainbow scattering

$$\sigma(\chi) \sin \chi \sim [\chi - \chi_r]^{-\frac{1}{2}} . \quad (3.16b)$$

This is obviously a singularity. For thermal scattering, χ has a strong dependence on E ; and as the minimum of χ shifts, the classical singularity in $\sigma(\chi)$ shifts.

c) for $\chi > \chi_r$

$$\sigma(\chi) = \frac{b_1}{\sin \chi \left| \frac{d\chi}{db_1} \right|} . \quad (3.16c)$$

Here only one impact parameter contributes to the DCS. This regime is referred to as the dark side of the rainbow while the previous regime ($\chi < \chi_r$) is known as the bright side. This regime, of course, is sensitive only to the repulsive core of the potential.

d) for $\chi = 0$, i.e., forward glory scattering and

for $\chi \rightarrow \pi$, i.e., backward glory scattering

$$I \rightarrow \infty \text{ as } \sin \chi \rightarrow 0 .$$

e) as E is decreased, $\chi_r(b_r)$ increases and b_r increases until at a critical energy E_c

$$\chi \rightarrow -\infty .$$

Physically the two colliding particles have gone into orbit and have formed a classically bound state.

3.2 Semiclassical Scattering

Because of the wave-like nature of matter, the classical description of scattering fails in cases where the particle wavelength is not much shorter than the range of the potential. Instead, a quantum mechanical description of scattering must be employed. However, often a semiclassical description may be reasonably used -- this has the further value that insight into the phenomena involved may still be gained providing a good compromise between an exact description of the process and the insight of the physical picture. In semiclassical theory the classical particles are replaced by wave packets which are able to interfere but which follow the classical paths.

According to Ford and Wheeler,³ the semiclassical approximation is based on four mathematical assumptions. The first is that the phase shift (see Eq. 3.52, in which the symbol δ_ℓ instead of η_ℓ is used) is determined by the JWKB method, i.e.,

$$\eta_\ell = k \left[\int_{r_c}^{\infty} \left[1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right]^{\frac{1}{2}} dr - \int_b^{\infty} \left[1 - \frac{b^2}{r^2} \right]^{\frac{1}{2}} dr \right] \quad (3.17)$$

where k is the wavenumber. If we apply the deBroglie relationship

$$\lambda = \hbar/mv = \hbar/\sqrt{2mE} = 1/k \quad (3.18)$$

where $\hbar$ = Planck's constant divided by 2π , we are led to a definition for η

$$\eta(E, L) = \lim_{r \rightarrow \infty} \left\{ \int_{r_c}^r \frac{dr}{\lambda} - \int_b^r \frac{dr}{\lambda} \right\} \quad (3.19)$$

Substitution of E from eq. (3.7b) thus leads to eq. (3.17).

Additionally the deflection angle may be expressed in a form analogous to that for the phase shift:

$$-\chi = 2\theta_c - \pi = \lim_{R \rightarrow \infty} \left[\int_{\text{actual path}} d\theta - \int_{V=0 \text{ path}} d\theta \right] \quad (3.20a)$$

or substituting for θ (eq. 3.9)

$$\chi = -2b \left[\int_{r_c}^{\infty} \left[1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right]^{-\frac{1}{2}} \frac{dr}{r^2} - \int_b^{\infty} \left[1 - \frac{b^2}{r^2} \right]^{-\frac{1}{2}} \frac{dr}{r^2} \right]. \quad (3.20b)$$

Using the semiclassical approximation $(\ell + \frac{1}{2}) = kb$ (where ℓ is the angular momentum quantum number) and differentiating χ with respect to ℓ (which is assumed to vary continually) in eq. (3.17), we see that in comparing with eq. (3.20b)

$$\frac{d\eta_\ell}{d\ell} = \frac{1}{2}\chi(\ell). \quad (3.21)$$

This relationship is known as the semiclassical equivalence relationship.

The second assumption for semiclassical scattering is that the Legendre polynomials in the quantum scattering description (see next section) are replaced by either of the following asymptotic expressions

$$P_\ell(\cos\chi) \cong \left[\frac{1}{2}(\ell + \frac{1}{2})\pi \sin\chi \right]^{-\frac{1}{2}} \sin\left[(\ell + \frac{1}{2})\chi + \frac{\pi}{4}\right], \quad (3.22a)$$

$$\sin\chi \geq 1/\ell$$

or,

$$P_\ell(\cos\chi) \cong (\cos\chi)^\ell j_0[(\ell + \frac{1}{2})\chi], \quad \sin\chi \leq 1/\ell. \quad (3.23b)$$

The third assumption is that the summation over ℓ in the quantum expression for the scattering amplitude (again see next section) is replaced by an integral. This assumption implies that η_ℓ is continuous and allows the integral to be written

$$f(\chi) = -\frac{1}{2ik} \int_0^\infty (2\ell + 1) e^{2i\eta} P_\ell(\cos\chi) d\ell \quad (3.24)$$

if $\chi \neq 0, \pi$. This expression may be given as (using the assumption of 3.22)

$$f(\chi) \approx \frac{-1}{k(2\pi \sin\chi)^{\frac{1}{2}}} \int_0^\infty (\ell + \frac{1}{2})^{\frac{1}{2}} \{e^{i\phi_+} - e^{i\theta_-}\} d\ell \quad (3.25)$$

where

$$\theta_\pm(\ell) = 2\eta_\ell \pm (\ell + \frac{1}{2})\chi \pm \frac{\pi}{4}. \quad (3.26)$$

The final assumption for semiclassical scattering is that eq. (3.25) may be evaluated by the method of stationary phase. This assumption recognizes that $\phi_\pm$ can vary widely with ℓ with the result that the integrand will be a rapidly oscillating function of ℓ and will thus only make a negligible contribution to the scattering amplitude results. However, this is not the case if for some ℓ either exponent becomes stationary, i.e.,

$$\frac{d\phi_{\pm}}{d\ell} = 0 \quad (3.27)$$

which applied to eq. (3.26) reduces to the semiclassical equivalence relationship of eq. (3.21),

$$\frac{d\eta_{\ell}}{d\ell} = \frac{1}{2} \chi(\ell) .$$

The semiclassical approximation for scattering leads now into insight of physical phenomena which cannot be described by classical theory. In the stationary phase assumption, it is possible that more than one value of ℓ satisfies eq. (3.27). In particular, three solutions will exist for values of χ less than the rainbow angle, two corresponding to stationary phase in ϕ_{+} and one in ϕ_{-} . Hence, the semiclassical cross section can be written

$$\begin{aligned} \sigma(\chi) &= \left| \sum_n f_n(\chi) \right|^2 = \left| f_1(\chi) + f_2(\chi) + f_3(\chi) \right|^2 \\ &= \sum_n |f_n(\chi)|^2 + \sum_n \sum_{\substack{m \\ n \neq m}} |f_n(\chi)| |f_m(\chi)| \cos(\beta_n - \beta_m) \end{aligned} \quad (3.28)$$

where β is the phase defined to replace ϕ in eq. (3.25) such that the correct phase to $|2\pi|$ is obtained between all three branches. It is obvious that interference terms between all branches exist which allows an oscillatory behavior roughly centered about the classical curve to exist. The periodicity of the undulations is given by

$$\Delta \chi \propto \frac{2\pi}{b_n \pm b_m} \quad (3.29)$$

which leads to the expectation of two main types of oscillations: (1) widely spaced oscillations with an angular spacing inversely proportional to $b_3 - b_2$ and (2) rapid oscillations with an angular spacing proportional to $b_1 + b_2$ and $b_1 + b_3$. The former ($b_3 - b_2$) are referred to as supernumerary rainbows, since they are oscillations centered about b_r and often appear as oscillations superimposed over the maximum caused by the rainbow. The angular spacing of the rapid oscillations provides direct information about σ . Over a large range of angles less than the rainbow, $b_1 + b_2 \sim 2b_0$ where b_0 is the impact parameter corresponding to $\chi = 0$ and where $b_0 = \sigma$. Thus

$$\Delta \chi \propto \frac{\pi}{\sigma} \quad (3.30)$$

and it may be shown⁷

$$\Delta \chi = \frac{\lambda}{2\sigma} . \quad (3.31)$$

For values of χ greater than χ_r , only the repulsive branch of the deflection will contribute to the cross section leading to the classical result with no oscillatory structure. Hence, strong oscillations are predicted for $\chi \leq \chi_r$ but only a smoothly falling DCS is predicted for $\chi > \chi_r$. However, Zahr and Miller⁴ have shown that diffraction from a purely repulsive potential can be described by an extension of semi-classical analysis which allows interference between "classically

allowed" and "classically forbidden" contributions to the scattering amplitude, $f(\chi)$.

3.3 Quantum Mechanics of Scattering

While the semiclassical approximation is valid for a number of molecular (atomic) systems and while the oscillatory structure of the DCS is qualitatively described by it, the semiclassical analysis is not valid for the present studies. Failure of this approach to scattering generally occurs when the incident de Broglie wavelength becomes comparable to the range of the potential.^{1d} If the potential energy changes so slowly that the momentum of the particle is sensibly constant over many wavelengths, the semi-classical approximation is valid. This is not so for the thermal scattering of H_2 , D_2 , $He +$ molecule systems. Also features in the DCS are much different from that predicted by semiclassical analysis.

Semiclassically, the rainbow angle χ_r is located at a scattering angle of approximately 15° in the center of mass system for collisions of H_2 with NH_3 or H_2O (location is $\sim 2\epsilon/E$ in radians⁵). Not only is no rainbow maximum apparent in the observed structure but rapid oscillations continue beyond 15° where the semiclassical results would predict only a smooth classical fall-off. Similar behavior is observed in the $He +$ atom, molecule systems studied: rapid oscillations continue well beyond the rainbow angle with little or no evidence of rainbow structure. Consequently, it appears that only a complete quantum description of scattering will be valid for the systems studied in this work.

Before discussion of the DCS structure from a quantum view and before discussion of quantum mechanical scattering, it would be fruitful to discuss a few points in the breakdown of classical mechanics not addressed in the above discussion of the semiclassical approximation. While interference phenomena have been discussed, the existence of finite cross sections as opposed to the singularities predicted by classical mechanics has been ignored. In classical mechanics, we predict that low-angle scattering is due only to the long-range part of the intermolecular interaction. For the expected long-range r^{-6} attractive potential, the behavior of the DCS is expected at low angles to behave as

$$\sigma(\chi) \propto \chi^{-\frac{4}{3}} \csc \chi \sim \chi^{-\frac{7}{3}}. \quad (3.32)$$

This, of course, has the implication of a divergence at $\chi = 0$, i.e., the forward glory. Quantum treatment, as well as experimental observation, predicts a DCS with a finite limiting value as $\chi \rightarrow 0$. Additionally, it has been observed that rainbow structures have a finite amplitude that becomes independent of resolution -- classical mechanics, of course, predicts a divergence in the DCS at the rainbow angle. The basic reason for the non-infinite values for the glory and the rainbow features of the DCS's, can be explained by the Heisenberg Uncertainty Principle. There is a limit in the precision with which we can specify the impact parameter; this limit causes an uncertainty in the transverse momentum ρ_x of a wave packet chosen to describe the collision. For the classical trajectory to be well-defined,

$\Delta b \ll b$ which thus requires that the wave packet must be constructed from a range of momentum states of width $\Delta p_x \gg \hbar/b$. This leads to an uncertainty in the angle of deflection (from the relation $\Delta p_x \approx \mu v_z \sin \chi$) given by

$$\Delta \sin \chi \approx \Delta p_x / \mu v_z . \quad (3.33)$$

Consequently, a finite limit will always exist on the ability to specify χ , eliminating the classical divergences. Furthermore, at very small angles, the scattered intensity no longer can be attributed to only a narrow range of impact parameters centered around the value corresponding to the classical angle of observation.

Examination of the DCS's for the He and $H_2(D_2)$ systems studied in this work reveals that all the systems studied have diffraction oscillations and in each of the He systems studied a low angle shoulder. The B parameter of Harrison and Bernstein⁶ for the systems studied is always in the quantum regime. ($B = 2\mu\epsilon r_m / \hbar^2$, μ = reduced mass, ϵ = well depth of the potential, r_m = minimum of the potential, and $\hbar = h/2\pi$ with h = Planck's constant.) As a consequence, we are led to determine that the oscillations in our systems are described as a diffractive effect produced at the steep wall of the potential.⁷ The presence of an attractive well intensifies the diffractive oscillations and tends to increase their frequency since r_m rather than σ is considered the appropriate range parameter.⁸ The frequency of these oscillations is

$$\Delta\theta \sim \frac{\pi\hbar}{\mu v r_m} \sim \frac{\lambda}{2r_m} \quad (3.34)$$

where $\Delta\theta$ is the spacing of the oscillations in radians and λ is the de Broglie wavelength $= \hbar/\mu v$ where μ is the reduced mass and v is the relative collision velocity. At low angles in the He systems a shoulder is observed between 4 and 5° which corresponds to the location predicted for such systems by Munn and Smith⁹ of the rainbow. Consequently the shoulder around such angles is ascribed to a quantum-damped rainbow. As mentioned, no evidence of a rainbow is observed in the $H_2(D_2) + NH_3$ or H_2O systems or in the $H_2(D_2) + Ar$ system.

The quantum mechanical description of the scattering process is discussed in the center-of-mass coordinate system with the motion of the center of mass factored out of the wavefunction, leaving the wave function for relative motion $\psi(r, \chi)$ to satisfy

$$\left\{ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right\} \psi = E\psi \quad (3.35)$$

∇^2 is the Laplace operator, μ is the reduced mass, and E is the relative collision energy. By introducing $K^2 = \frac{2\mu E}{\hbar^2}$ ($K = \frac{\rho}{\hbar} = \frac{2\pi}{\lambda}$ where λ is the de Broglie wavelength) and $U(r) = \frac{2\mu}{\hbar^2} V(r)$, eq. 3.35 can be rewritten

$$\nabla^2 \psi + [k^2 - U(r)] \psi = 0. \quad (3.36)$$

Since the effects of scattering are observed far from the scattering center, we may treat the quantum mechanical problem by considering

the asymptotic behavior of the wavefunction. The incident particles are represented by plane wave of the form

$$\psi_{\text{inc}} \sim e^{ikz} \quad (3.37)$$

while the particles scattered after interaction are represented by an outgoing spherical wave

$$\psi_{\text{scat}} \sim f(\chi) \frac{e^{ikr}}{r} \quad (3.38)$$

where $f(\chi)$ is the scattering amplitude and depends upon both k and χ . It is assumed that the potential is spherically symmetric and that thus $f(\chi)$ is independent of ϕ , the out-of-plane angle, and depends only on χ . Hence, $\psi(r)$ must have the following asymptotic form

$$\psi(r, \chi) \xrightarrow{r \rightarrow \infty} A \left[e^{ikz} + \frac{1}{r} f(\chi) e^{ikr} \right] . \quad (3.39)$$

The DCS is related to the scattering amplitude by

$$\sigma(\chi) = |f_{\mathbf{k}}(\chi)|^2 . \quad (3.40)$$

This relationship may be proven as follows. The current density vector is defined by

$$\mathbf{j} = \frac{\hbar}{2\mu i} [\psi^* \nabla \psi - (\nabla \psi)^* \psi] . \quad (3.41)$$

Inserting the incident wavefunction Ae^{ikz} into (3.41) gives the incident intensity

$$I_0 = \frac{\hbar}{2\mu i} 2ik |A|^2 = \frac{\hbar k}{\mu} |A|^2 = v |A|^2. \quad (3.42)$$

Inserting the wavefunction for the scattered wavefunction $\frac{1}{r}f(\chi)e^{ikr}$ into (3.41) gives the intensity of the radially outgoing scattered wave

$$I = |f(\chi)|^2 \frac{v}{r^2} |A|^2 = |f(\chi)|^2 \frac{I_0}{r^2}. \quad (3.43)$$

Comparing eq. (3.43) with the previous definition for the differential cross section in eq. (3.13), we see that

$$\sigma(\chi)d\omega = \frac{Id\omega/r^2}{I_0} = |f(\chi)|^2 d\omega \quad (3.44)$$

where $Id\omega/r^2$ is the number of particles scattered in a solid angle $d\omega$, and I_0 is the incident flux. Thus we have the result for eq. (3.40), the definition of the differential cross section in terms of the scattering amplitude.

In obtaining a solution for the scattering problem defined by eq. (3.35), separation of variables is first carried out where

$\psi(r, \chi, \phi) = R(r) Y(\chi, \phi) = \frac{u(r)}{r} Y(\chi, \phi)$. This gives

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + (k^2 - U(r) - \frac{\ell(\ell+1)}{r^2}) R = 0 \quad (3.45a)$$

$$\frac{1}{\sin \chi} \frac{d}{d\chi} \left(\sin \chi \frac{\partial Y(\chi, \phi)}{\partial \chi} \right) + \frac{1}{\sin \chi} \frac{d^2 Y(\chi, \phi)}{d\phi^2} + \ell(\ell+1) Y(\chi, \phi) = 0. \quad (3.45b)$$

Since symmetry restricts $Y(\chi, \phi)$, the spherical harmonics, to be a function of χ only (central-field potential), the solutions of eq. (3.45b) must be

$$Y_{\ell}^0(\chi) \sim P_{\ell}(\cos \chi) \quad (3.46)$$

where P_{ℓ} is the Legendre polynomial of degree ℓ . For $U(r) = 0$, eq. (3.45a) reduces to a form of Bessel's equation which has the independent solutions, $j_{\ell}(k_r)$ and $\eta_{\ell}(k_r)$, where $j(k_r)$ is the spherical Bessel's function and $\eta_{\ell}(k_r)$ is the spherical Neumann function of degree ℓ . The asymptotic expressions for the values of the argument are

$$j_{\ell}(kr) \xrightarrow{r \rightarrow \infty} \frac{1}{kr} \sin(kr - \frac{\ell\pi}{2}) \quad (3.47a)$$

$$\eta_{\ell}(kr) \xrightarrow{r \rightarrow \infty} \frac{1}{kr} \cos(kr - \frac{\ell\pi}{2}) . \quad (3.47b)$$

The boundary condition requiring $u(r) = 0$, $r \rightarrow 0$ (since otherwise $\psi(r, \chi)$ would diverge at $r \rightarrow 0$) eliminate the Neumann functions leaving as an acceptable solution of eq. (3.45a) near the origin for $U(r) = 0$

$$u_{\ell} = rR = C_{\ell}^0 r j_{\ell}(k\ell) \xrightarrow{r \rightarrow \infty} \frac{C_{\ell}^0}{k} \sin(kr - \frac{\ell\pi}{2}) . \quad (3.48)$$

For the case in which the potential $U(r) \neq 0$, as long as the field decreases faster than $\frac{1}{r}$, the potential may be neglected for sufficiently large r values. The general asymptotic solution for eq. (3.46) ($U(r) \neq 0$) is

$$u_{\ell}(r) \xrightarrow{r \rightarrow \infty} A_{\ell} r j_{\ell}(kr) + B_{\ell} r \eta_{\ell}(kr) . \quad (3.49)$$

Let $-\tan \delta_{\ell} = B_{\ell}/A_{\ell}$, which allows eq. (3.49) to be written

$$u_{\ell}(r) \xrightarrow{r \rightarrow \infty} C_{\ell} r [\cos \delta_{\ell} j_{\ell}(kr) - \sin \delta_{\ell} \eta_{\ell}(kr)] ,$$

$$C_{\ell} = A_{\ell} / \cos \delta_{\ell} . \quad (3.50)$$

By using the asymptotic conditions for j_{ℓ} and η_{ℓ} given in (3.47a), (3.48b) this can be written as

$$u_{\ell}(r) \xrightarrow{r \rightarrow \infty} \frac{C_{\ell}}{k} \sin(kr - \frac{\ell\pi}{2} + \delta_{\ell}) . \quad (3.51)$$

The net effect of the scattering, i.e., the effect of the potential $U(r)$ which falls off rapidly as $r \rightarrow \infty$, is to introduce a phase factor (or phase shift) δ_{ℓ} into the asymptotic radial wavefunction. The solution of eq. (3.35) may be expanded as

$$\begin{aligned} \psi(r, \chi) &= \sum_{\ell=0}^{\infty} b_{\ell} P_{\ell}(\cos \chi) \frac{u_{\ell}(r)}{r} \\ &= \sum_{\ell=0} \frac{b_{\ell}}{kr} P_{\ell}(\cos \chi) \sin(kr - \frac{\ell\pi}{2} + \delta_{\ell}) . \end{aligned} \quad (3.52)$$

In order to compare this result with the asymptotic boundary condition (eq. 3.39), we must also expand e^{ikz} in the $P_{\ell}(\cos \chi)$ basis set. The result is

$$e^{ikz} = e^{ikr \cos \chi} = \sum_{\ell=0} j_{\ell}(2\ell+1) P_{\ell}(\cos \chi) j_{\ell}(kr) . \quad (3.53)$$

If we now compare the asymptotic boundary condition with the asymptotic solution, we get

$$e^{ikz} + \frac{1}{r} f(\chi) e^{ikr} = \sum_{\ell=0}^{\infty} b'_{\ell} \frac{1}{kr} P_{\ell}(\cos \chi) \sin(kr - \frac{\ell\pi}{2} + \delta_{\ell}) \quad (3.54)$$

Using the results of (3.53) and expressing the asymptotic sine solution in terms of exponential functions, eq. (3.54) becomes

$$\begin{aligned} & \sum_{\ell=0}^{\infty} \frac{1}{2ikr} (2\ell + 1) P_{\ell}(\cos \chi) [e^{ikr} - (-1)^{\ell} e^{-ikr}] + \frac{f(\chi)}{r} e^{ikr} \\ &= \sum_{\ell=0}^{\infty} \frac{b'_{\ell}}{2ikr} P_{\ell}(\cos \chi) [e^{ikr} e^{i\delta_{\ell}} (-i)^{\ell} - e^{ikr} e^{-i\delta_{\ell}} i^{\ell}] . \end{aligned} \quad (3.55)$$

Comparing terms containing e^{-ikr} , we get

$$b'_{\ell} = (2\ell + 1) i^{\ell} e^{i\delta_{\ell}} . \quad (3.56a)$$

Introducing this into eq. (3.55) and comparing terms containing e^{ikr} , we get

$$f(\chi) = \sum_{\ell=0}^{\infty} \frac{(2\ell + 1)}{2ik} P_{\ell}(\cos \chi) (e^{2i\delta_{\ell}} - 1) . \quad (3.57)$$

The differential cross section may now be given

$$\begin{aligned} \sigma(\chi) = |f(\chi)|^2 &= \frac{1}{4k^2} \left[\left(\sum_{\ell=0}^{\infty} (2\ell + 1) \sin 2\delta_{\ell} P_{\ell}(\cos \chi) \right)^2 \right. \\ &\quad \left. + \left(\sum_{\ell=0}^{\infty} (2\ell + 1) (\cos 2\delta_{\ell} - 1) P_{\ell}(\cos \chi) \right)^2 \right] . \end{aligned} \quad (3.58)$$

The total cross section is defined as

$$Q = 2\pi \int_0^{\pi} \sigma(\chi) \sin \chi \, d\chi . \quad (3.59)$$

Therefore, the total cross section (quantum mechanical) is given by

$$Q(k) = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_{\ell} . \quad (3.60)$$

Consequently, δ_{ℓ} must be determined in order to solve for $f(\chi)$ and, hence, $\sigma(\chi)$ and $Q(k)$. A wide variety of methods may be employed which include an exact numerical solution of the wave equation (3.35), as well as different approximation techniques. Since approximation techniques are much less time consuming, they are popularly employed. Considerable effort has gone into investigation of the conditions for validity and accuracy of the phase shift calculation.^{10,11} Suffice it to say that for the systems studied here, JWKB phase shifts described earlier in the semiclassical section with Rosen-Yennie corrections¹² give essentially identical results to the exact phase shifts¹¹ calculated from direct numerical integration of the Schrödinger equation. JWKB phase shifts without the Rosen-Yennie corrections give DCS results which are well within experimental error when compared to the JWKB phase shifts with the Rosen-Yennie correction.

3.4 Determination of the Intermolecular Potential From Scattering Data

The actual determination of the intermolecular potential from scattering data is not a trivial task. A number of authors have reviewed this area with perhaps the best surveys of the general problem found in the review of Buck^{1a} or in the thesis of Coggiola.¹⁰ Two approaches can be used to extract information about the intermolecular potential from scattering data. In the first approach, the potential is constructed directly from the measured data. A set of phase shifts is constructed from the cross section followed by determination of the potential from the phase shifts. In practice this method is very difficult and generally requires detailed, high-precision data before any attempt at quantitative fits of the intermolecular potential can be made. Because of these difficulties, the second approach is usually applied. A form for the intermolecular potential which has between two and five adjustable, independent parameters is assumed. (As mentioned previously in Chapter 2, analysis of the typical system encountered in the present studies reveals that a five parameter potential appears necessary and no more than five parameters can be reliably determined.¹³) Then the parameters are varied in a trial and error process so as to obtain the the best fit to the measured cross section.

In addition to the two general reviews mentioned above, excellent reviews specifically on the inversion of molecular beam scattering data are given by Buck¹⁴ and by Sheen et al.¹⁵ Firsov¹⁶ demonstrated

twenty-five years ago that a knowledge of the complete phase shift function would allow for the determination of the unique potential which had generated the scattering. However, his analysis was limited by the use of monotonic potentials and classical mechanics only. Considerable work has been done since then, semi-classically and quantum mechanically, to deduce the intermolecular potential from the phase shifts. Unfortunately, exact quantum mechanical procedures have met with little practical success, although simplified cases and simulated examples have been studied to obtain qualitative behavior trends. Consequently, only semiclassical approaches have been used in practical attempts to "invert" molecular beam scattering data. In fact, the results of semiclassical analyses (see discussion in Chapter 2 on the semiclassical approximation, Ford and Wheeler)¹⁷ have had excellent success in fitting data. The recent quantum mechanical methods of Shapiro et al.¹⁸ for direct inversion of scattering data is however very promising.

Buck et al.¹⁹ have made extensive studies of the inversion of data from the scattering of alkali atoms on mercury. High precision data fits are obtained with error at the well minimum $\sim 0.5\%$ in r_m and $\sim 3.0\%$ in ϵ and with error in the attractive tail at $6.5 \text{ \AA}$ only $\sim 12\%$ in V . These data show a well resolved rainbow structure including supernumerary rainbow oscillations, with the classical rainbow and the superimposed rapid oscillations clearly resolved. Experimental data necessary as input data for the inversion procedure include (i) the positions of the rainbow oscillations; (ii) the separation of the

rapid oscillations; (iii) the background scattering of the differential cross section; (iv) the position of the extrema of the glory oscillations in the velocity dependence of the integral cross section; (v) the van der Waals constant from semiempirical calculations; and (vi) the ratio of the first rainbow oscillation to the backward scattering. As can readily be seen, extensive data are required; and the method is limited to systems which have a semiclassical behavior.

On the other hand, Klingbeil²⁰ has had good success in fitting the differential cross section data of Li + Ar measured by Detz²¹ and Wharton. This system ($B = 360$) displays no rainbow structure but does have well separated rapid oscillations, i.e., a differential cross section structure similar to those observed in this work. In this analysis the phase shifts are treated as individual parameters with the small δ values (large ℓ) approximated by a simple analytical function. Several hundred phase shifts were found from the measurement by the least squares procedure, and a semiclassical approach was utilized to obtain the potential. This entire procedure for obtaining the potential does require significant computational effort because of the large number of phase shifts compounded by the presence of velocity-averaged differential cross section. This method requires a smooth phase shift function and requires a well-behaved starting potential. It does appear to be well suited for systems which display strong quantal behavior -- such systems are not compatible with the other inversion procedures commonly found in the literature.

These two examples do indicate that inversion procedures offer

strong promise in the determination of the intermolecular potential from measured cross sections. The potential obtained in these procedures inherently can only be determined for the region probed by measurement. Because of the direct relationship between the scattering data and the potential, questions of error and of accurate representation can be attacked in a straightforward manner. On the negative side, much work still appears necessary to demonstrate any reliability/use of inversion procedures for the typical molecule systems studied in this work.

Consequently, a fitting procedure was utilized to obtain the intermolecular potential in this work. (For a detailed explanation of the fitting procedure, consult Appendix 5.) The evaluation of high resolution measurements in molecular scattering experiments has indicated that commonly used potential models are not sufficient for a good description of the potential. As previously mentioned, it has been quantitatively demonstrated that a four-parameter model is minimally required and a five-parameter model generally provides the best representation of the actual intermolecular potential.¹³

Functionally, the fitting procedure employed in this effort has three parts. In the first part, initialization of the experimental conditions is set up. Velocity distributions for the primary and secondary beams are calculated; the distribution of beam intersection angles is calculated; the velocity and intersection angle distributions are used to calculate the relative collision velocities; laboratory scattering angles are calculated from the input set of center-of-mass scattering angles -- also the Jacobian factors and relative velocities for each

laboratory scattering angle are calculated; an additional set of lab angles is calculated from the peaks of the beam and angle intersection peaks. In the second part, monoenergetic differential cross sections are calculated in the center-of-mass frame from an assumed inter-atomic potential followed by averaging over the appropriate apparatus parameters. With the calculated relative velocities, phase shifts are calculated from the previously assumed intermolecular potential; differential cross sections are calculated at center-of-mass angles using determined relative collision energies followed by interpolation to yield the cross sections at desired conditions; the differential cross sections desired are transformed to the lab frame; interpolation of the transformed lab differential cross sections is made to yield a set at the peaks of the beam and angle intersection distributions; velocity and angle averaging of the differential cross sections are made followed by an apparatus resolution averaging (empirically determined); the averaged lab cross sections are interpolated to be at the same angles as the experimental intensities; the calculated differential cross section is scaled (the measured DCS is arbitrarily normalized) with a scaling factor adjusted to minimize the following

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2 \quad (3.61)$$

where I_i are the measured cross sections, σ_i are the calculated cross sections, and g_i are weighting factors for each point. In the third and final part of the fitting procedure, a weighted least-squares iterative procedure is utilized to optimize the parameters of the

potential model selected.

The fitting procedure outlined was optimized with regard to averaging beam and angle intersection distributions. Quality-of-fit to the data was based on the expression

$$\frac{\Delta\alpha_{0.95}}{\alpha} = \frac{1}{\alpha} t_{0.05}(n-k) \left[\frac{\chi^2}{(n-k) \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}}, \quad (3.62)$$

where χ^2 , I_i , σ_i , and g_i are as defined in eq. (3.61), n is the number of scattering angles, k is the number of parameters, and $t_{0.05}(n-k)$ is the appropriate Student t -distribution statistic for a 95% confidence level of the scaling factor α . It should be noted that $\Delta\alpha_{0.95}/\alpha$ is independent of the arbitrary normalization used in the experiment and is statistically adjusted for the number of data points, i.e., a more straight-forward comparison can be made in the quality-of-fit.

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22. It is convenient to refer to $I(\chi)$ as a laboratory differential cross section in arbitrary units. However, $I(\chi)$ is really a signal intensity. To transform it into such a laboratory DCS requires multiplication by the laboratory velocity of the scattered beam (which is a function of χ), since the mass spectrometer used in our measurements is a number density detector.

CHAPTER 4

Experimental

4. EXPERIMENTAL

A molecular beam scattering apparatus should have the features which permit the acquisition of meaningful data: (1) pressures low enough to ensure that only single collisions are significant; (2) beams of adequate intensity with minimal angular and velocity spreading to permit resolution/definition of the desired scattering process features; and (3) a detector system sensitive enough to maximize signal while suppressing background.

This chapter will address these criteria with the purpose of showing how the apparatus fits these criteria and of describing the work done to optimize system performance.

4.1 General Description of the Apparatus

Since the crossed molecular beam machine has been described elsewhere in detail,¹ emphasis will be on the modifications and characterizations/optimizations made since. Examination of Figure 4.1, which gives a vertical cut through the axis of the apparatus, shows that the main features of the system are a movable, differentially pumped quadrupole mass spectrometer; a differentially pumped supersonic primary beam; and a capillary-array secondary beam. All are contained in a 1200 liter, stainless steel vacuum chamber with the beams intersecting at right angles to each other at the center of rotation of the detector chamber. The detector chamber is mounted on a semicircular shaped quadrant arm which pivots about the axis of the main chamber -- this permits detection in the in-plane configura-

tion when the detector chamber is in the same plane as the beams. However, the detector itself may be rotated about the scattering center by movement along the rim of the semicircular arm -- this permits detection in the out-of-plane configuration.

The primary beam is of supersonic design and is housed in a double chamber oven. The first chamber contains the source, a simple effusive beam source, 0.070 mm in diameter, and a sharp edged conical skimmer which collimates the beam, 0.640 mm in diameter. This collimation permits only the high Mach number core flow to be transmitted. The second chamber contains a mechanical chopper which modulates the beam for AC signal detection. Also contained in the second chamber is an eight-wheel slotted velocity selector which may be moved in or out of the beam by a pneumatic bellows. In normal experiments, the selector is moved out of the beam since the velocity spread is sufficiently small. Early in the system characterizations, the primary beam was found to have a limitation in both its Mach number and intensity. A motor-driven nozzle mount was placed in the first oven to allow adjustment of the nozzle skimmer. This allowed optimization of the beam Mach number (measure of mean gas velocity in beam's direction to thermal velocity/motion) and of the intensity with the available pumping capacity.² Optimized Mach numbers for the H₂, D₂, and He primary beams were 20.5, 17.5, and 17.5, respectively. The secondary beam, which is a glass capillary array 0.61 mm thick with individual capillary diameters of 0.002 mm and 50% transparency to

Figure 4.1: Cut through the vertical axis of molecular beam apparatus. N - primary beam nozzle source, S - skimmer cone, VS - velocity selector, C - primary beam chopper, F - beam flag, CA - secondary beam glass capillary array, IS - electron bombardment ionizer, MF - quadrupole mass filter, EM - electron multiplier (14-stage Cu-Be multiplier), SEM - spiraltron electron multiplier, CP - liquid helium cryopump, BV - bellows operated bake-out valve, VIPI - Vac Ion 5ℓ/sec pump, VIP2 - Vac Ion 25ℓ/ sec pump, HeV - helium vent line for cryopump, LHeF - liquid helium fill line for cryopump, VP - pyrex view port.

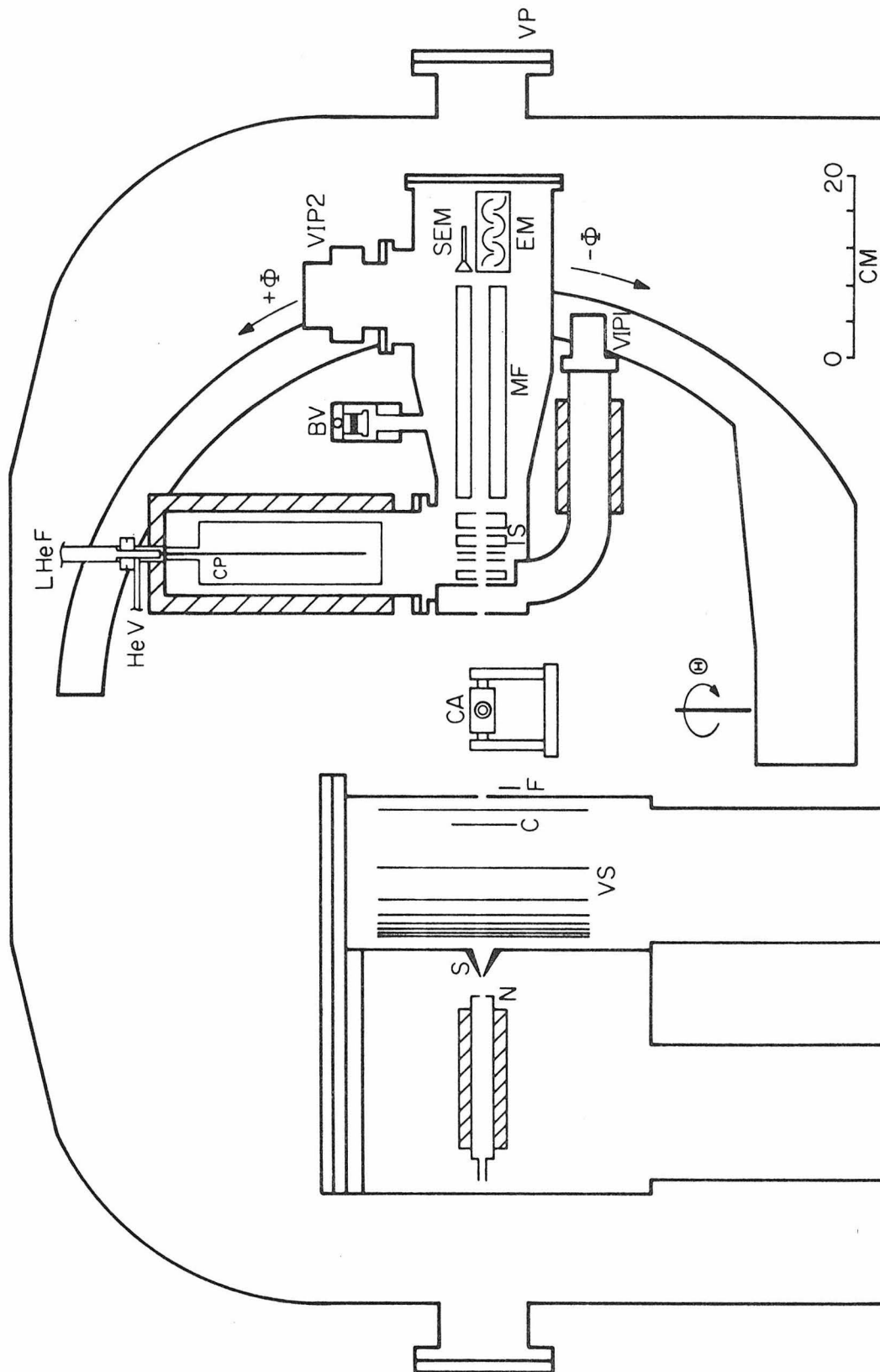


Figure 4.1

gas flow, was inserted in place of the primary beam nozzle. The nozzle skimmer and collimator were taken out of the primary system, and the velocity selector was used to characterize performance of the secondary. Measured velocity distributions on a number of different gases gave a characteristic Mach number of 1.45 with a specific heat ratio of 1.64. Main chamber pressures are kept below 2×10^{-6} torr by regulating the secondary flow; this pressure in the scattering chamber ensures that only single-collision phenomena are observed.

A major improvement in the detection capability of the apparatus came with the introduction of new pumps on the detection chamber. The first pump was a small 5 ℓ /sec Vac Ion pump which provided continuous pumping and which allowed the main chamber to be opened to allow work in the chamber; the second pump was 25 ℓ /sec Vac Ion which allowed both chambers of the detector system to be differentially pumped with relatively high efficiency pumps; the third pump was a cryogenic liquid helium pump. This is the most important pump during experiments; pressures in the ionization region are lowered a factor between 2 and 5, based on uncalibrated gauge readings. Corresponding increases occur in the signal-to-noise ratios which consequently allow the counting (integration) times to be decreased since signal-to-noise is proportional to the square root of counting time. Pumping by the cryopump appears to be conductance-limited at approximately 400. ℓ /s.

4.1.1 Main Chamber/Vacuum System

The main chamber is a bell jar 127 cm in diameter (with a machined flange) and 94 cm high which lifts to provide access to the beams and detector chamber. All electrical connections, all liquid nitrogen (LN₂) cooling lines, all water cooling lines, and all gas flow lines are admitted into the bell jar through Con Flat feedthroughs, 50 of which are positioned on the perimeter of the bell jar and under the machined flange. The bell jar is lowered onto this flange which has a rubber O ring and an aluminum metal washer/spacer to provide the vacuum seal for the bell-jar/scattering chamber. Figure 4-2 provides a top view of the main chamber with the cut made at the machined flange.

The main chamber is pumped by four LN₂-baffled Varian/NRC VHS-6 oil diffusion pumps and by one LN₂-and freon-baffled Edwards 6M3 mercury diffusion pump. Extensive work was done with these pumps to insure maximum performance. Two independent sets of flow measurements were made to assess the effective pump speeds. In the first method both air and dry nitrogen were admitted into the main chamber at a known constant rate determined by a Hastings flowmeter. The system was allowed to equilibrate at a constant pressure which was approximately two orders of magnitude larger than the ultimate pressure with no controlled flow. With an error of only a few percent, the pumping speed is given by eq. 4.1.

$$S_p = \frac{Q}{P} \quad (4.1)$$

S - pumping speed

Q - leak rate or controlled flow rate

P - equilibrium pressure.

In the second method, the rate of evacuation of the main chamber was measured with the initial pressure P_0 much larger (a factor of ~ 100) than the final pressure. Since the effective volume of the main chamber could closely be estimated, eq. 3 could be used to determine the pumping speed S. For constant volume and changing pressure, ideally it may be written

$$Q = V \frac{dP}{dt} \quad (4.2)$$

but $Q = S_p P$

$$\Rightarrow S_p P = V \frac{dP}{dt}$$

$$\frac{P}{P_0} = e^{-S/Vt} \quad (4.3)$$

P - pressure at time t

P_0 - initial pressure

t - time

V - effective volume of bell jar

S, Q, P - defined for eq. (1).

For both methods, the oil pumps were found to have consistent speeds of approximately 400ℓ/sec (with the exception of pump 4 which had a

Figure 4.2: Top view of bell jar. 1,2,3 - mercury diffusion pumps; 4,5,6,7,8 - oil diffusion pumps, 9 - beam chopper, 10 - primary beam nozzle/skimmer, 11 - rotatable mass spectrometer/detector housing, 12 - machined bell jar flange, 13 - secondary beam glass capillary array.

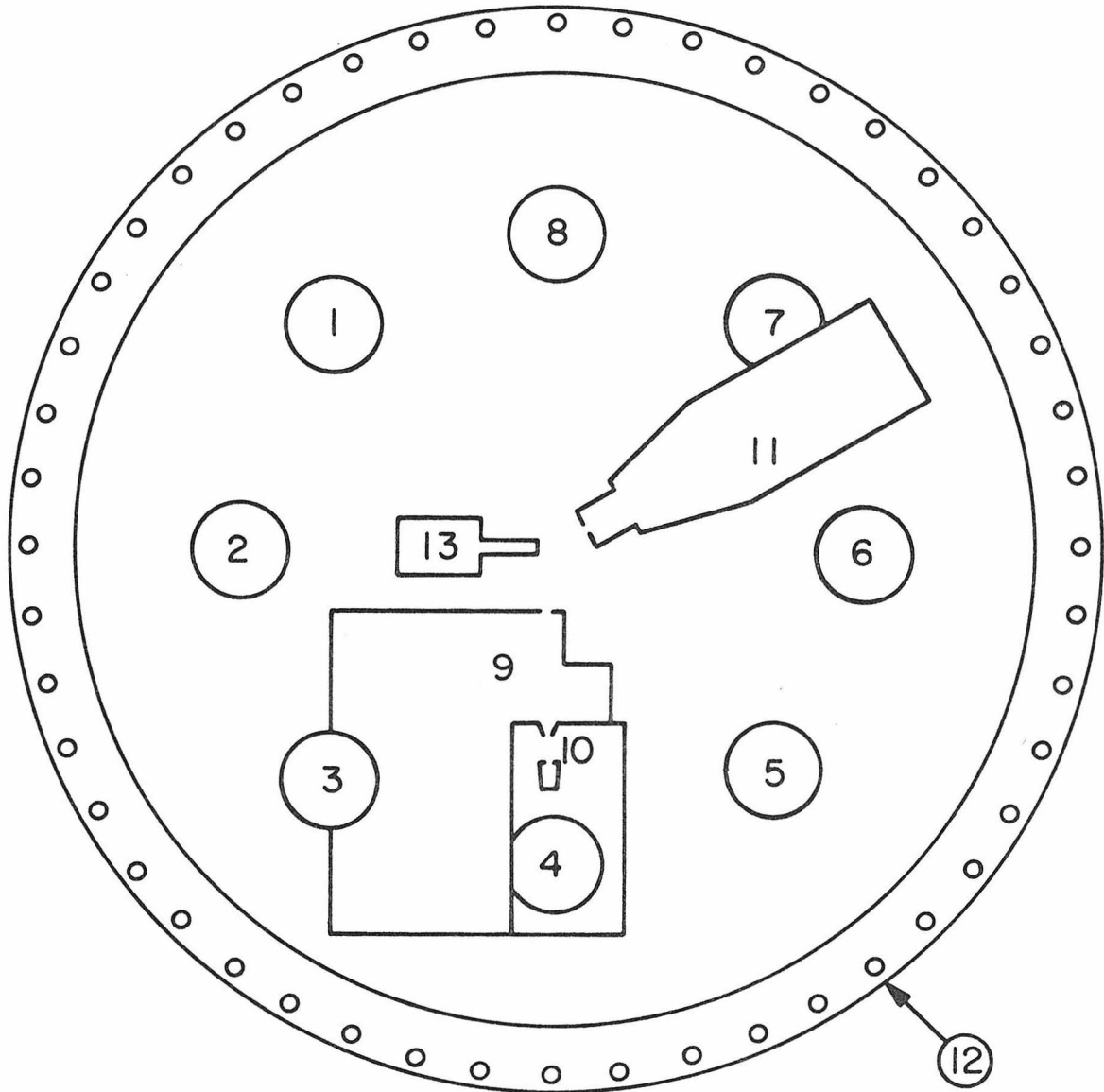


Figure 4.2

lower speed due to increased conductance in the primary beam oven); the mercury pumps had speeds of approximately 130 l/sec. While the speed of the mercury pump agrees closely with the manufacturer's rating, the speeds of the oil pumps were strikingly lower -- by a factor of three. Close examination indicates that the oil pumps are conductance limited. This explanation is supported by: (1) no performance change was seen after completely cleaning and recharging one of the oil pumps; (2) the performance of the backing mechanical pump is exactly that expected; (3) a third set of measurements made by introducing the gas flow in the pumping port shows a significant variation in pump speed as the position of introduction is varied in the port tube, i.e., as the conductance is varied, the pumping speed changes accordingly (care was taken to avoid streamlining; and (4) theoretical pump-speed calculations agree with the measured pumping speeds when the conductance of the port tubes is considered.

As a result of these pump-speed measurements, a thorough investigation of possible leaks was undertaken. Three significant types of leaks were found. The first were in the Conflat electrical feedthroughs. Spraying the outside with Celvaseal compound appeared to remedy this problem. The second concerned leaks in the cooling and gas flow lines. Use of a helium leak detector identified and thus led to the elimination of such leaks. Generally lines were replaced and in some cases connections were rebuilt, especially in water cooling lines where corrosion of the lines had occurred. The third leak type was the most frustrating. For a period of several months,

every time that LN_2 cooling lines were used, a large leak developed. Finally, it was discovered that, although the exhaust flow was six inches from the side of the bell jar and although a person could place his/her hand between the bell jar and the flow with no discomfort, the exiting LN_2 flow was cooling the jar itself sufficiently to cause a thermal contraction. As a result of this work, the operating pressure in the main chamber is now maintained easily in a range less than 2×10^{-6} torr. The ultimate pressure with all diffusion pumps running is found to be less than 2×10^{-8} torr. These operating pressures at less than 2×10^{-6} torr correspond to a mean free collision path always greater than a few meters. Since the largest distance traversed by the primary beam in the main chamber is approximately 0.15 meters, it is readily seen that collision with the background gas are negligible and furthermore that leaks into the main chamber are negligible.

4.1.2 Primary Beam

The primary beam is of supersonic design and is housed in a double chamber oven. The first chamber contains the source, a simple effusive beam source, 0.070 mm in diameter, and a sharp-edged conical skimmer which collimates the beam 0.640 mm in diameter. This collimation permits only the high Mach number core flow to be transmitted. The second chamber contains a mechanical chopper which modulates the beam for AC signal detection. Also contained in the second chamber is an eight-wheel, slotted velocity selector which may be moved in or out of the beam by a pneumatic

bellows. In normal experiments, the selector is moved out of the beam since the velocity spread is considered sufficiently small. The selector then is only used to characterize the primary beam; since the design³ and calibration¹ of the velocity selector have been described previously, discussion here is limited to its use.

During initial system characterizations, the primary beam was found to have a limitation on both its Mach number and intensity. As a consequence, a motor-driven nozzle mount was placed in the first oven. This permitted an adjustment of nozzle-skimmer distance, resulting in the elimination of the previous limitations and in the optimization of the primary beam performance. At this point, a brief discussion of theory is necessary to understand the results of optimizing/characterizing the primary beam.

Kantrowitz and Grey⁴ first proposed that a gas stream in supersonic flow with its molecules in predominantly ordered motion in the direction of the final beam could be used. This technique overcomes major limitations of conventional oven beams: (1) relatively low intensity and (2) wide distribution of velocity of beam molecules. The basic arrangement is similar to a conventional molecular effusion source, with some major changes. The gas jet is produced by a supersonic nozzle which results in a large amount of gas within the jet. To cope with this gas, a hollow truncated cone called a skimmer is used to deflect much of the gas from the beam, allowing only the intense supersonic core of the beam to be passed. Design of the skimmer and its location are critical. If the cone angle is too large, the shock wave which would attach to the cone tip becomes detached.

The result is formation of a shock wave in front of the skimmer hole -- gas now going into the skimmer hole will be in the thermodynamic post-shock state of subsonic Mach number and high temperature.³

The ideal skimmer should have (1) an orifice with as sharp an edge as possible, (2) a small exterior angle at the orifice to ensure that the shock wave is "attached", and (3) a large interior angle to minimize scattering losses inside the skimmer; the orifice should be highly symmetric and perpendicular to the beam axis.⁵ Distance between the nozzle and skimmer has a significant role also, since too large a distance will allow formation of the normal shock between the nozzle and skimmer in front of the skimmer hole.⁶ Again the gas will be in subsonic flow with a high temperature, i.e., the skimmer now acts as a conventional oven beam nozzle does. The narrow velocity spread and the high intensity no longer exist.

Even if the effects of the skimmer are neglected, an analytical model of the flow is extremely complicated. Transitions from hydrodynamic to free molecular flow and the various relaxation processes taking place must be described. As an alternative, a simplified model may be used to present the significant features of the supersonic beam.^{7, 8, 9} Assume that the expansion is isentropic, free of shock waves. Conservation of energy along a flow streamline requires

$$H + \frac{1}{2} v^2 = H_0 \quad (4.4)$$

where H = enthalpy per unit mass along streamline

v = local velocity

H_0 = stagnation enthalpy per unit mass.

We may further note

$$H = C_p T + \text{constant} \quad (4.5)$$

$$C_p = \gamma R / (\gamma - 1) \quad (4.6)$$

$$M^2 = \frac{v^2}{c^2} = \frac{v^2}{\gamma R T} \quad (4.7)$$

where C_p = heat capacity at constant pressure

T = temperature

γ = ratio of specific heats

R = gas constant

M = local flow Mach number.

Substitution of these last equations (4.5-4.7) into the earlier one (4.4), results in the following expression for the ratio of the gas temperatures before and after expansion.

$$\frac{T_0}{T} = \left[1 + \frac{\gamma - 1}{2} M^2 \right] \quad (4.8)$$

where T_0 = initial temperature.

Cooling can be quite large: if the Mach number reaches 20, for a diatomic gas the ratio of T to T_0 is 81, i. e., the temperature decreases a factor of 81.

For continuum isentropic flow, the velocity of the beam at the skimmer entrance (assuming no disturbance of the stream entering the skimmer) is given by⁷

$$v_s = \sqrt{\frac{2kT}{m}} \left(1 + \frac{\gamma-1}{2} M_s^2\right)^{-\frac{1}{2}} \left(\frac{\gamma}{2} M_s^2\right)^{\frac{1}{2}}. \quad (4.9)$$

The subscript s refers to conditions at the skimmer entrance, and again 0 refers to stagnation conditions. The most probable velocity of a molecule of mass m at temperature T is given by $\sqrt{2kT/m}$, i. e., this is also the most probable velocity of an effusive source (conventional beam oven). Hence, the ratio of velocities for the supersonic beam to conventional beam is given by

$$\frac{v_s}{v_{mp}} = \left(1 + \frac{\gamma-1}{2} M_s^2\right)^{-\frac{1}{2}} \left(\frac{\gamma}{2} M_s^2\right)^{\frac{1}{2}}. \quad (4.10)$$

It is obvious that for large Mach numbers, this ratio approaches the value $\left(\frac{\gamma}{\gamma-1}\right)^{\frac{1}{2}}$. This is important in characterizing the primary beam.

As noted above, large cooling effects occur; but internal degrees of freedom (vibration and rotation) have much longer relaxation times than translation, in general. This situation leads to the possibility of "freezing" internal energy and having the gas behave as if it has fewer degrees of freedom; hence, a different γ . Since, in our measurements of the velocity distribution with a velocity selector, the stagnation temperature (and its associated most probable velocity) and the measured velocity (determined by velocity selector calibration) are known, γ may be determined. Indeed, measurement of the optimized hydrogen beam gives a γ value of 1.60; measurement of deuterium gives 1.54; and helium of course gives 1.67. The difference between the two hydrogen isotopes is the difference in

energy spacing of rotational energy levels. Since hydrogen's spacings are much larger, the rotational energy "freezes" earlier with the result that hydrogen acts more like a monotomic gas than does deuterium. (The hydrogen beam also has a higher Mach number, 20.5 vs. 17.5, and thus has a lower temperature.)

For isentropic expansion the velocity distribution is given by

$$f(v) \simeq \frac{1}{\sqrt{\pi}} \left(\frac{\gamma M^2}{2} \right)^{\frac{3}{2}} \left(\frac{V}{\alpha_S} \right)^3 e^{-\frac{\gamma M^2}{2\alpha_S} (v-\alpha)^2} \quad (4.11)$$

where $\alpha_S = \alpha \left(\frac{\gamma}{2} \right)^{\frac{1}{2}} M$.

Immediately, it may be observed that the velocity distribution has been narrowed from the velocity distribution of a gas at temperature T_0 , i.e., a conventional oven source, where the distribution is the familiar Maxwellian:

$$f(v) = \frac{4v^2}{\sqrt{\pi} \alpha^3} e^{-v^2/\alpha^2} \quad (4.12)$$

As a first approximation of the FWHM of the supersonic beam velocity profile, the ratio of the most probable velocity at the local temperature to the most probable velocity in the beam direction may be taken

$$\frac{v_T}{v_S} \simeq \frac{\alpha_T}{\alpha_S} \simeq \left(\frac{2}{\gamma} \right)^{\frac{1}{2}} \frac{1}{M} \quad (4.13)$$

Experimental determination involves measuring the relative intensities as a function of velocity using the calibrated velocity selector. Intensities must be corrected for the method of detection; in this case division by velocity since intensity is a direct function of velocity. Mach numbers are then determined by empirical fit to the following equation:⁷

$$\frac{dI}{dv} = \frac{1}{\sqrt{\pi}} \left(\frac{\gamma M}{2} \right)^{\frac{3}{2}} \left(\frac{v}{v_s} \right)^3 \exp \left[- \frac{\gamma M}{2} \left(\frac{v}{v_s} - 1 \right) \right] \quad (4.14)$$

$$v_s = \frac{2kT_0}{m} \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-1} \frac{\gamma M^2}{2} . \quad (4.15)$$

Figure 4.3 shows an experimental velocity distribution for a hydrogen beam. Figure 4.4 shows the results of optimizing the hydrogen beam at the most favorable nozzle-skimmer distance. After a study of these results, a plenum pressure between 490 and 510 torr was chosen as the operating pressure, since this regime represented a maximization of intensity and of Mach number. The reason for the "knee" in the intensity curve is that the oil diffusion pump no longer maintains a low enough pressure in the first chamber to prevent back-scatter between the beam and the background gas. Further increase beyond pressures investigated probably would result in an abrupt drop in intensity as ultimately a shock wave would be expected to form in front of the skimmer entrance. The reason that Mach number is used as a criterion is merely one of convenience. The real goal, of course, is to minimize the velocity distribution which is decreased by lowering

the local temperature. Since Mach number is the ratio of velocity to the local speed of sound (directly dependent on local temperature), Mach number is in this sense a measure of local temperature--the higher the Mach number, the lower the local temperature. Mach number becomes equivalent to a measure of ordered motion (mean beam velocity) relative to thermal motion.

Intensities and Mach numbers were optimized for hydrogen, deuterium, and helium primary beams. At maximum intensities, Mach numbers were 20.5, 17.5, and 17.5, respectively.

Symmetry of the primary beam was also investigated. Initially, asymmetric profiles were found, but after careful alignment (see Section 4.2.1) the profiles given in Figures 4.5 and 4.6 were obtained.

4.1.3 Secondary Beam

The secondary beam source is a multichannel array source which admits gas directly into the main chamber. The array consists of many tubes 0.002 mm inside diameter and 0.61 mm long, with a quoted transparency to gas flow of 50%;¹⁰ the diameter of the secondary beam is determined by a sealing restraining ring over the array that is 1.6 mm inner diameter. Unlike the primary beam, the secondary beam requires no differential pumping and furthermore can be easily placed close to the scattering center, 6.0 mm. Thus we have relatively intense beam, which results in more collisions and a stronger scattering signal. The disadvantages of this beam compared to the primary supersonic beam are a much wider velocity distribution and a much larger angular spread.

Figure 4.3: Measured Velocity Distribution of H₂ Beam.

Figure 4.4: Optimization of Primary Beam (H₂).

Figure 4.5: Angular Intensity Distribution in Vertical Scan.

Figure 4.6: Angular Intensity Distribution in Horizontal Scan.

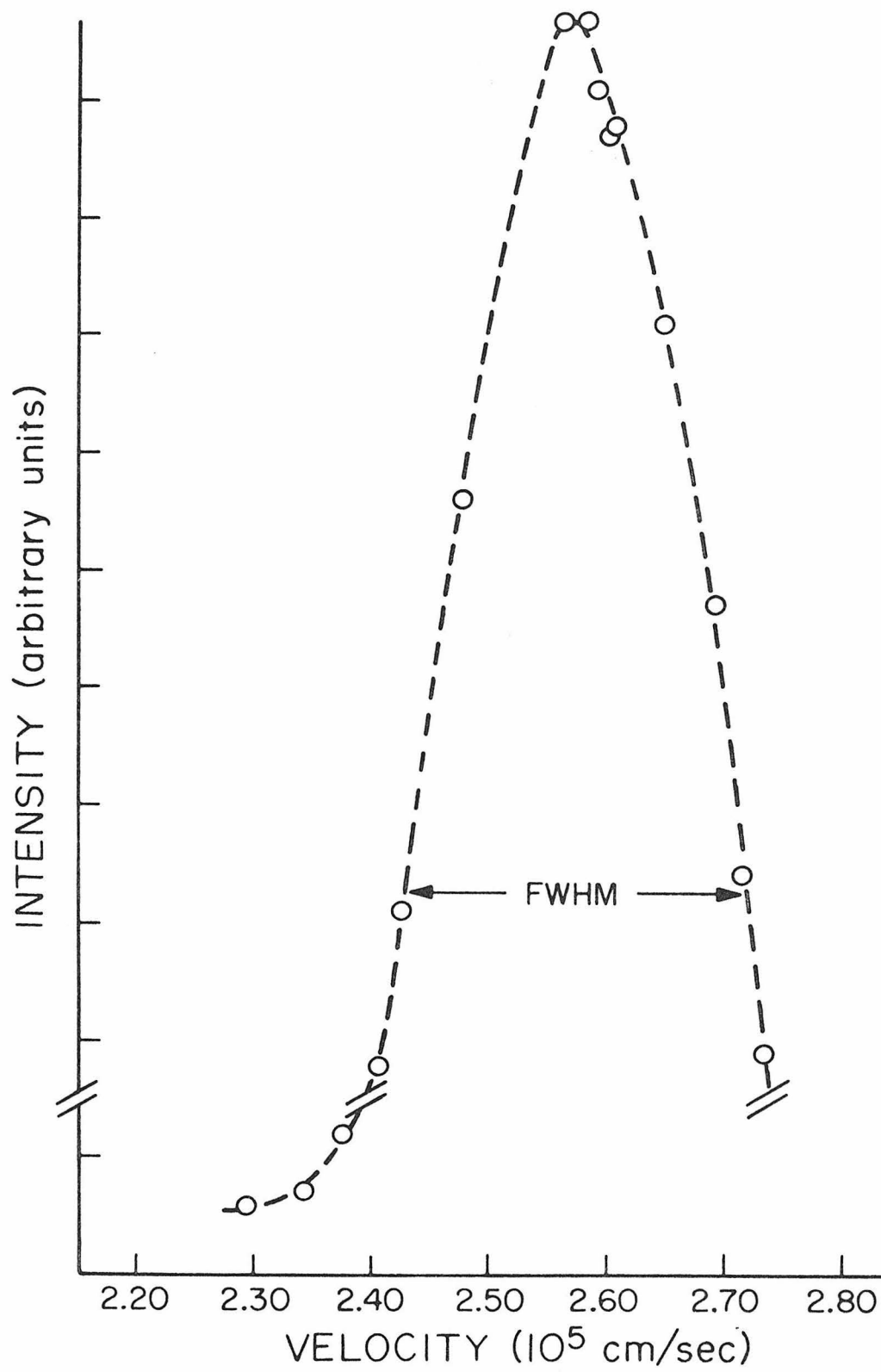


Figure 4.3

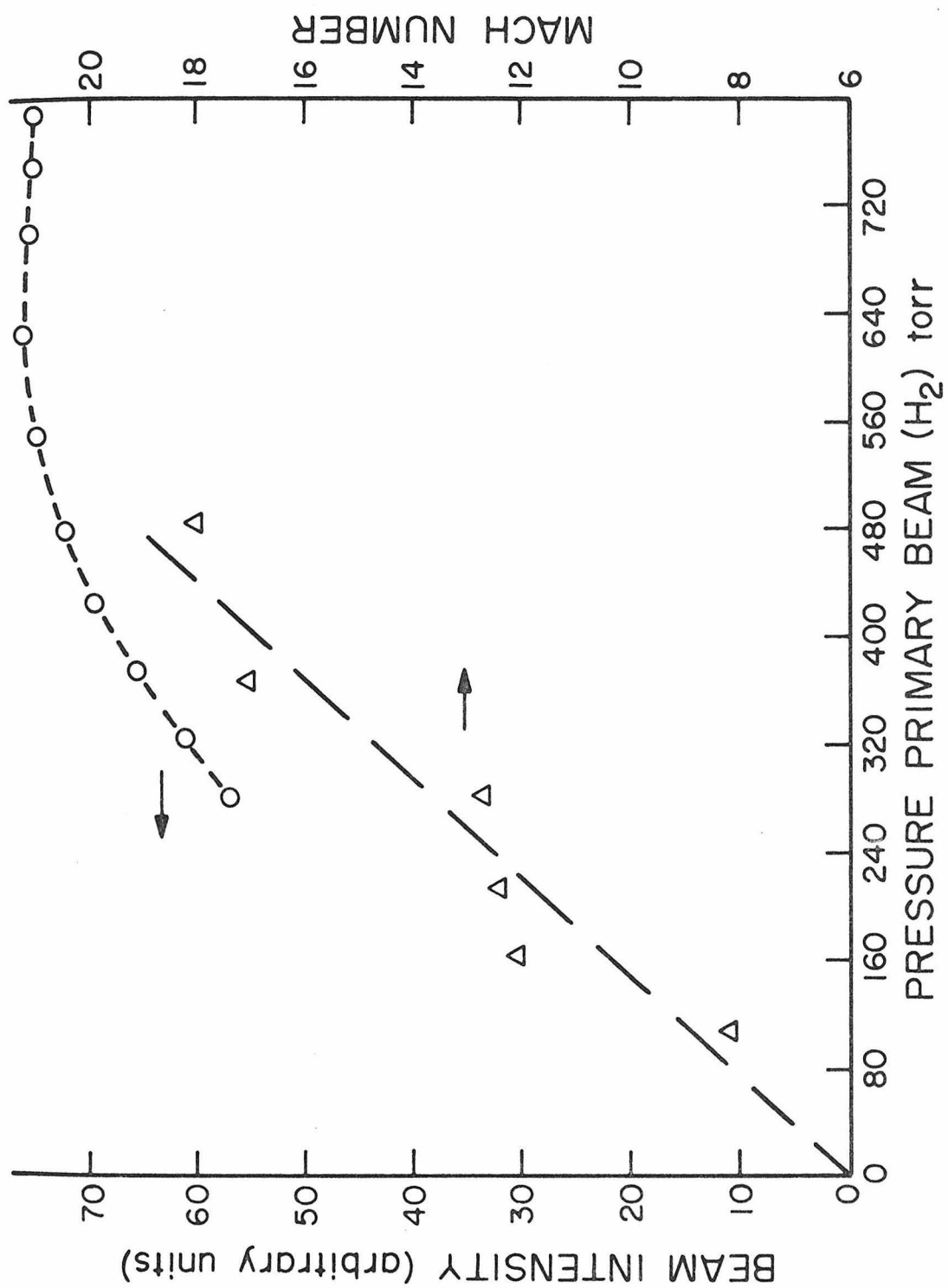


Figure 4.4

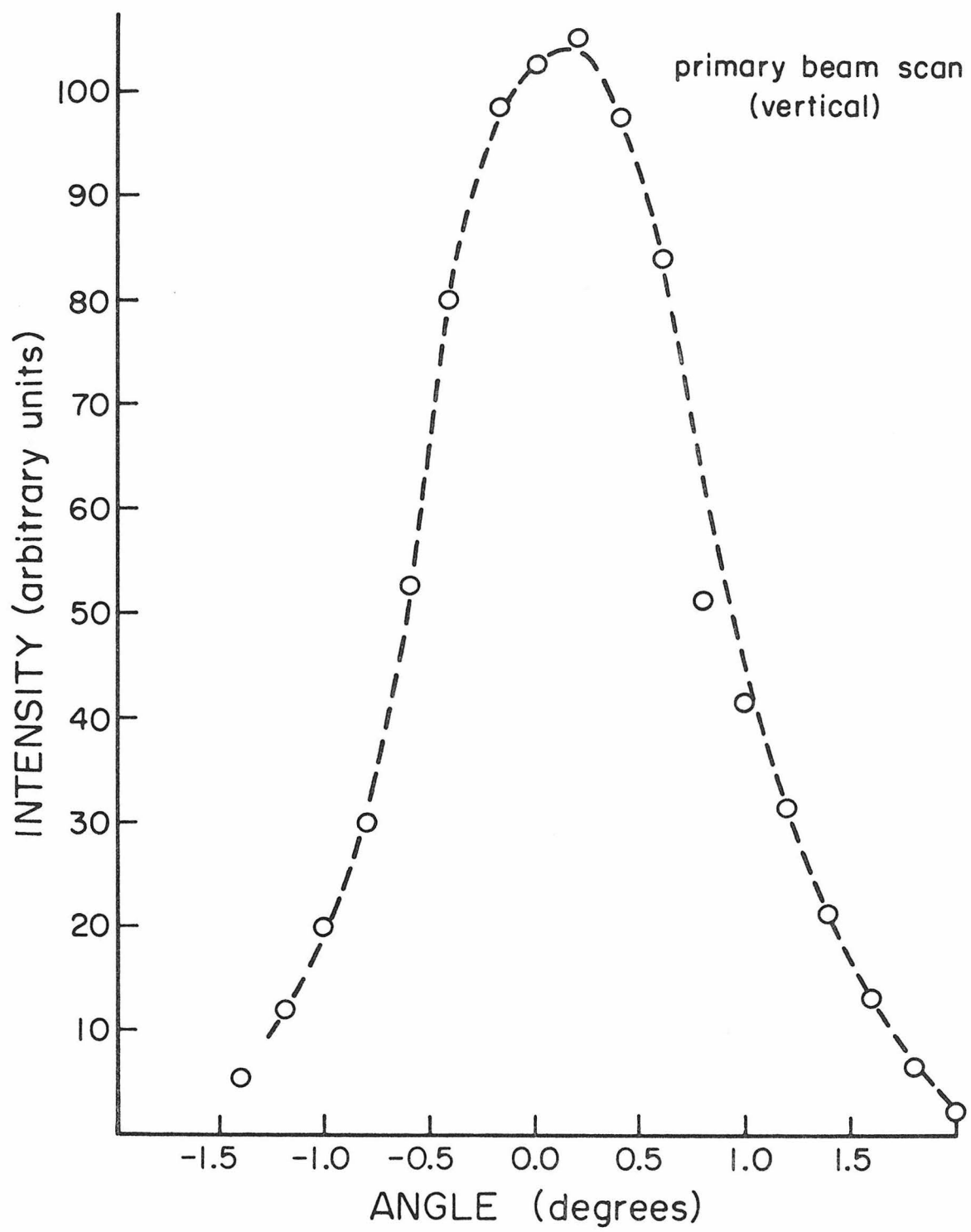


Figure 4.5

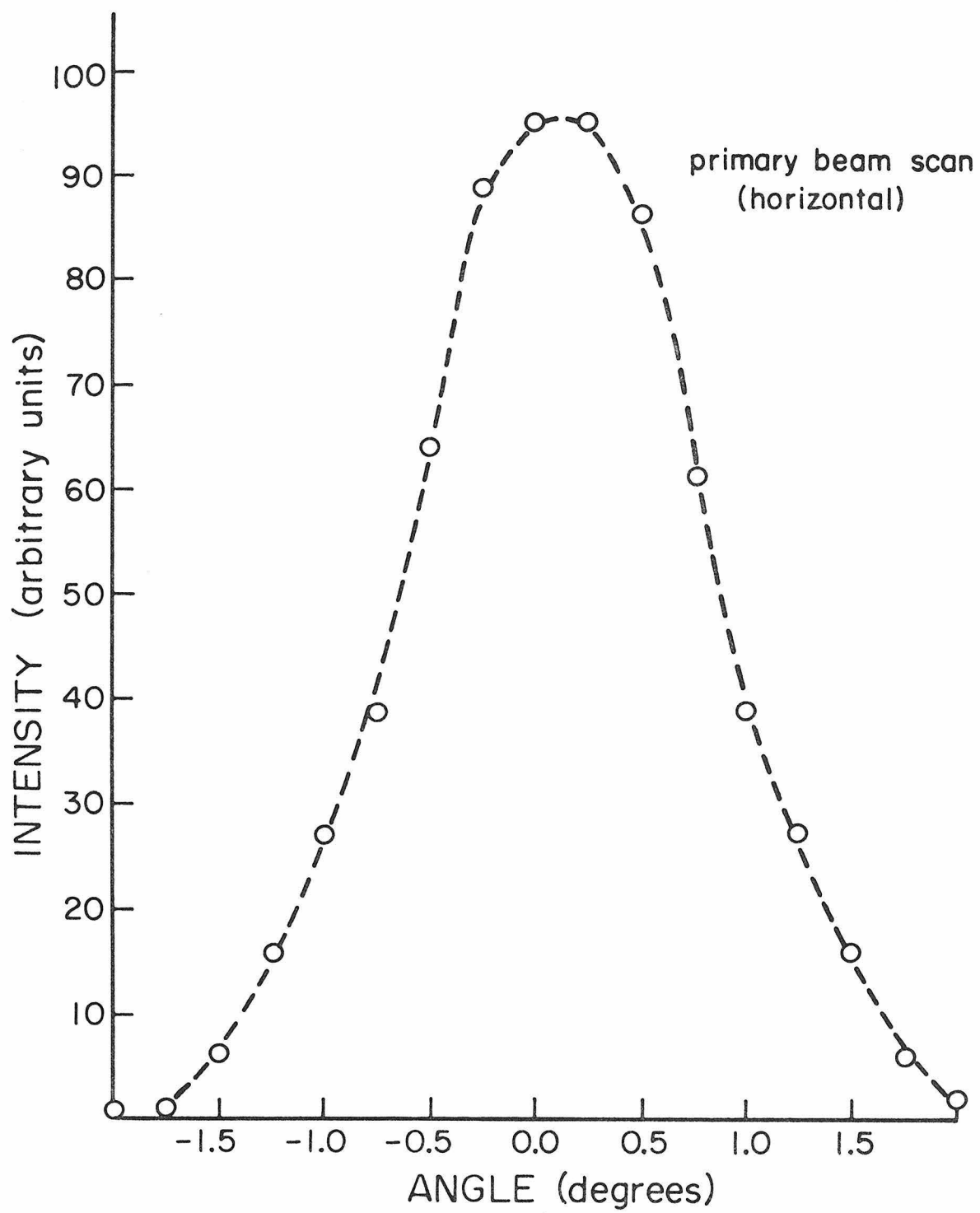


Figure 4.6

Although it appears that a great sacrifice in the quality of scattering data is introduced by use of this array with its large velocity and angle spreads (and corresponding large averaging effects which "average out" the structure in the differential cross sections), judicious selection of the secondary gas can avoid these problems. It must be remembered that the contribution of each beam to the total relative energy when the two beams are perpendicular is given by:

$$E_{\text{rel}} = \frac{1}{2} \mu v_{\text{rel}}^2 = \frac{1}{2} \mu (v_1^2 + v_2^2) = \frac{1}{2} m_1 v_1^2 \left(\frac{m_2}{m_1 + m_2} \right) + \frac{1}{2} m_2 v_2^2 \left(\frac{m_1}{m_1 + m_2} \right)$$

$$\text{where } E_{\text{rel}} = \text{total relative energy} \quad (4.16)$$

$$\mu = \text{reduced mass}$$

$$v_{\text{rel}} = \text{relative velocity}$$

$$v_1 = \text{velocity of primary beam}$$

$$v_2 = \text{velocity of secondary beam}$$

It is readily seen that the contribution of each beam to the relative energy can be considered to be approximately inversely proportional to its molecular weight if one of the two beams is much lighter. Since in practice the primary beam is chosen as H_2 , D_2 , or He and since the secondary is chosen to be a much heavier gas, the primary beam greatly dominates in its contribution to the relative energy. Thus a large variation in the secondary is only a small effect in the scattering system.

Extensive characterization of the secondary beam was performed for a large number of different gases, including NH_3 , CO , CH_4 , O_2 ,

NO, CO₂, and H₂O. Velocity distributions of all these beams were taken by replacing the nozzle-skimmer in the primary system with the multichannel array. All distributions, independent of the gas, were found to be described by a Mach number of 1.45 with a specific heat ratio of 1.64. For each beam tested, the angular distribution was taken as a function of pressure. Figure 4.7 gives a typical angular distribution at an arbitrary pressure; notice that the distribution is highly symmetrical. The attenuation of the primary beam as a function of secondary gas plenum pressure was also measured, Figure 4.8a gives these results for a NH₃ secondary beam. Figure 4.8b gives the angular divergence with plenum pressure for both a NH₃ and an O₂ secondary beam; observe the difference in angular distributions.

The purity of the secondary beam is critical, since impurities will produce a different scattering cross section. This contrasts with the primary beam whose gas is mass filtered prior to detection and thus need not be pure. As a consequence it was normal practice to check the secondary beam with the mass spectrometer/detector. This check first investigated possible contamination of the feed lines, especially with air leaks. Second, the check investigated the possible formation of dimers when such condensibles as H₂O and NH₃ were used. It was expected that such dimers would not be dissociated in the ionizer because of previously published work with H₂O dimers.¹¹ Since no dimers were detected and since the characteristic behavior of the secondary was not observed to change, the conclusion was made that dimers were not significant in any of our experiments.

Since the goal using the secondary gas was to maximize scattering intensity, i.e., attenuation of the primary beam at the scattering center, plenum pressures in the secondary were maximized. The criterion for maximum pressure was the main chamber pressure which was maintained below 2×10^{-6} torr to avoid possible secondary collisions.

4.1.4 Detector System

An extranuclear 324-9 quadrupole mass spectrometer in a double-differentially-pumped chamber is the most essential part of the crossed beam apparatus. Scattered particles traverse a distance of 80 mm from the scattering center to the entrance hole, 1.6 mm in diameter. A second, collimating hole is located between the two chambers and is also 1.6 mm in diameter. These sizes were selected to maximize detector resolution but still scan the entire scattering volume defined by the two intersecting beam FWHM profiles. Having passed through the first differential chamber pumped by a 5l/sec Vac Ion, scattered particles successively pass through a high-efficiency electron impact ionizer, a series of electrostatic focussing lens, and a 23 cm long Paul quadrupole mass spectrometer. The ionizer is a regular filament array which provides a maximum ionization efficiency of $\sim 0.5\%$, i.e., at best only 5 out of 1000 scattered primary atoms (molecules) can be detected. It should be strongly noted here that, while extremely reliable, the mass spectrometer system is complex. Great care must be taken to insure that the system is properly tuned since tuning can be made on "side bands" rather than on the primary

Figure 4.7: Angular Intensity Distribution of NH_3 Secondary Beam.

Figure 4.8a: Attenuation of Primary Beam as Function of Secondary Gas Plenum Pressure.

Figure 4.8b: Full-Width-at-Half-Maximum (FWHM) Angular Distribution as Function of Secondary Gas Plenum Pressure.

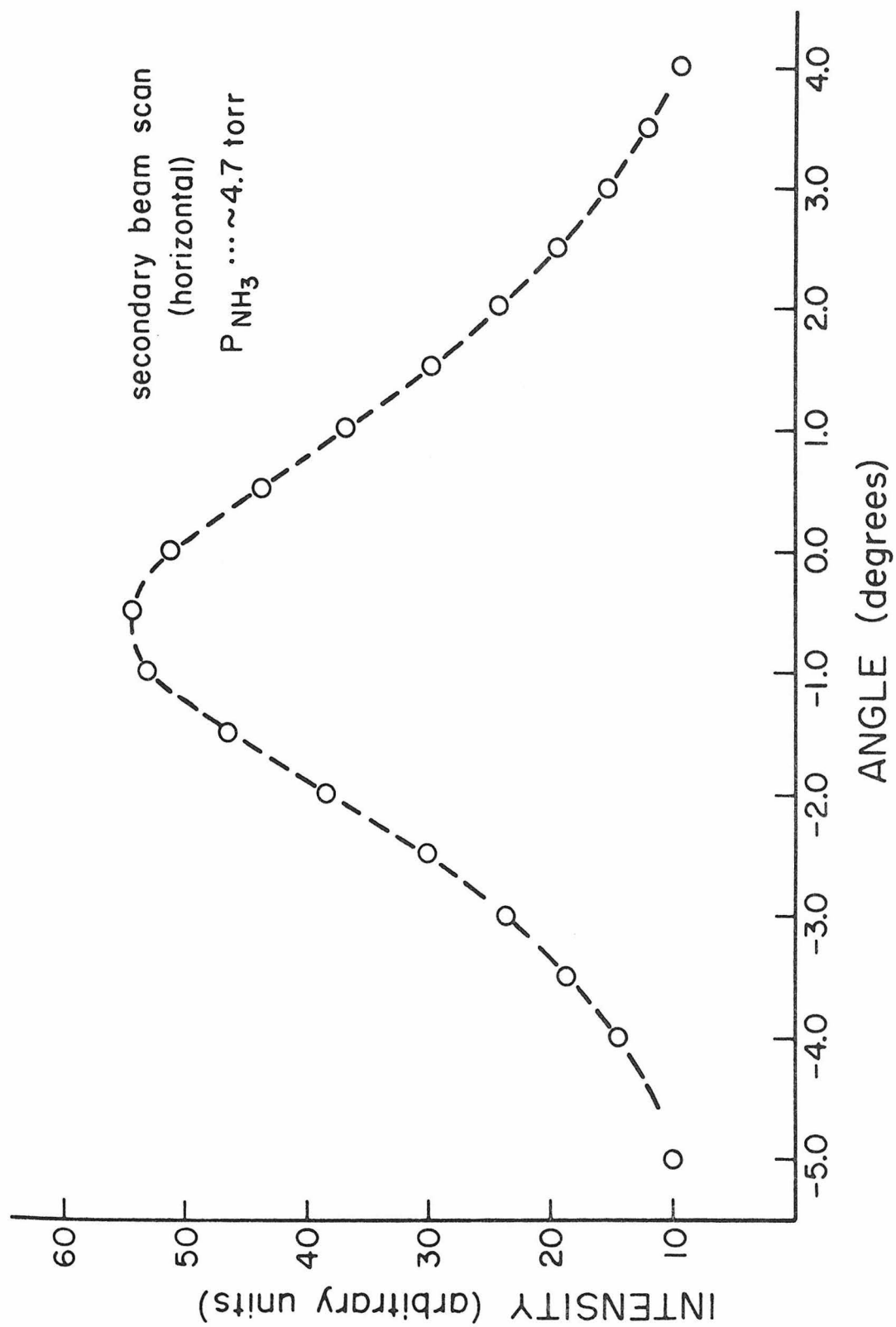


Figure 4.7

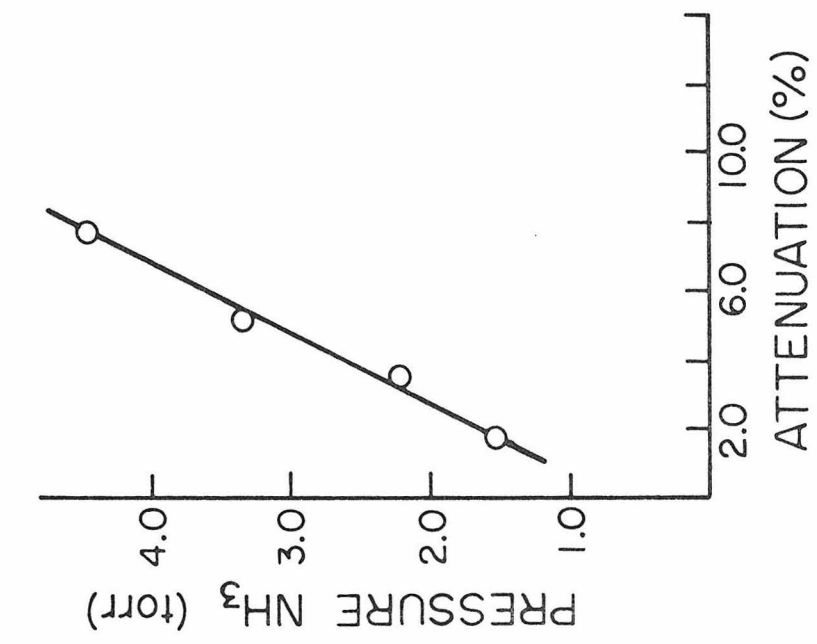


Figure 4.8a

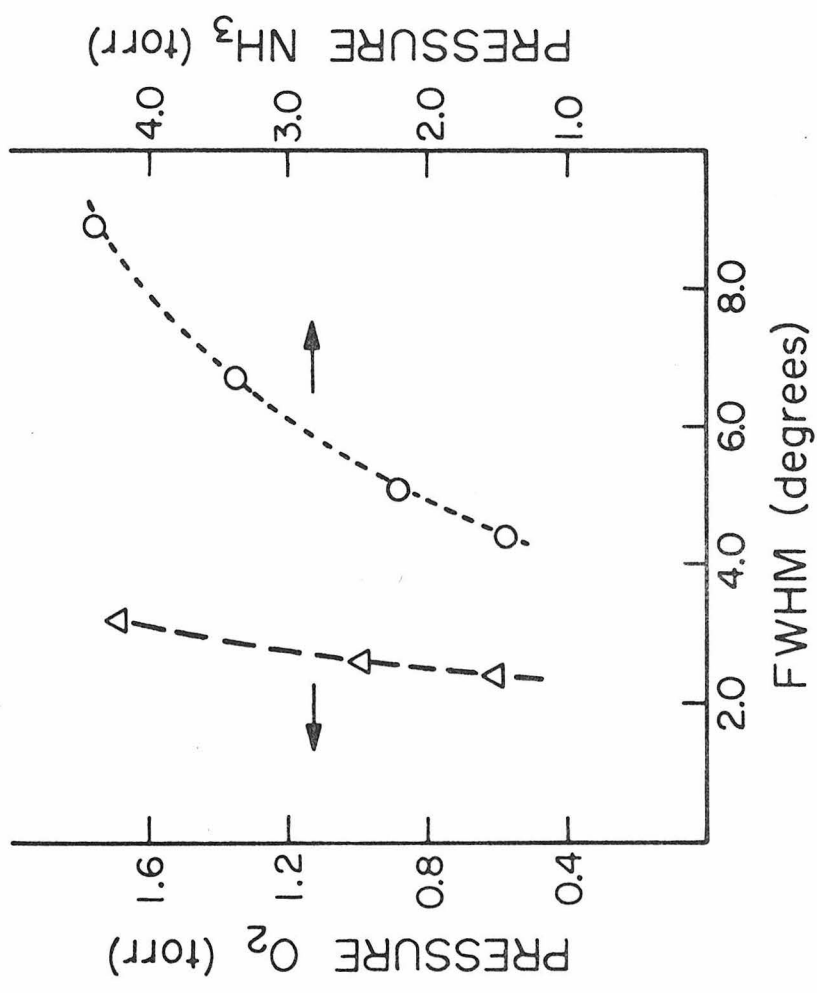


Figure 4.8b

band. These bands are relatively weak and their use requires much longer counting times since signal-to-noise ratios are proportional to the ratio of the signal divided by square root of the sum of the signal plus twice the noise.¹² It is seen that maximizing detection is always of benefit because of the linear to square root relationship -- this relation is also the reason that the signal-to-noise increases as the square root of the counting (integration) time since the time linearly increase both signal and noise while the ratio still holds.

Having passed through the mass spectrometer, the selected ions are detected by a 14-stage CuBe multiplier which has a nominal gain of 10^5 . The current produced by the last dynode of the multiplier is coupled to a bakeable four-stage preamplifier located within the mass spectrometer housing. The signal is further amplified outside the bell jar by a tuned preamplifier followed by a Princeton Applied Research HR-8 phase sensitive lock-in amplifier. The lock-in output was then sampled 60 times as second by a Scientific Control Corporation (SCC) 4700 computer which controlled the experiment during data-taking, alternately counting with the secondary beam at the scattering center and then completely out. (See appendices I and II for further discussion.)

Typical scattered beam intensities are on the order of 10^5 particles/cm³, which corresponds to a partial pressure of 10^{-11} torr, or less. Since the ionizer is not selective in its operation, it becomes necessary to minimize the background gas. Modulation of the primary beams with AC detection/filtering does not sufficiently improve signal-to-noise ratios although an improvement of three orders of magnitude

is seen. Consequently lowering the background pressure is a major goal in the experiment. The obvious approach is to put large, effective pumps on the two differential chambers of the mass spectrometer housing. While this appears initially as a simple solution, two facts must be considered. First, at very low pressures, "dirty" systems function as tremendously large reservoirs for outgassing -- pumping may only have minor effects. Second, because the mass spectrometer housing is mounted on a movable quadrant arm, distinct limitations exist for both the size and weight of any pump added to the system.

In an effort to overcome the problems of weight and size, a liquid helium cryopump was designed and built by the previous research team on this apparatus. Unfortunately, they were never able to define its operation. After some modifications to the pump which included replacement of glass-kovar sections on the cryopump neck with thin metal tubing (see Figure 4.9) and the installation of cryogenic sensors, the pump was found to hold helium and to work well if the system was adequately baked out (see Section 4.2.2). During experiments it is found that pressures in the ionization region are lowered between a factor of 2 to 10 with corresponding increases occurring in the signal-to-noise ratio. Figure 4.10 gives a vivid illustration of the improvement attained with the use of the cryopump. The top mass spectra were taken at 4×10^{-9} torr without using the cryopump; the bottom mass spectra were taken using the cryopump when the total pressure was lowered to 4×10^{-10} torr (based on uncalibrated ionization

gauge readings. It is readily obvious that the partial pressures of all gases including even H_2 , D_2 , and He are significantly reduced.

Figure 4.10 vividly demonstrates the drop where the mass spectra in the bottom is multiplied by five and is still smaller in intensity.

Figure 4.11 demonstrates the pumping capability of the cryopump.

After the helium has all evaporated, the cryopump begins to warm and outgas. The bottom left spectra was taken during the outgassing of helium (numerous checks confirmed helium was cryopumped); the bottom right spectra were taken during the outgassing of hydrogen. In both cases it is obvious that significant pumping had occurred.

(See Appendix IV for further discussion of cryopump.)

Two other smaller pumps were added to the mass spectrometer housing to replace the titanium sublimator and ORB-ION pump which were used by earlier researchers. A 5ℓ/sec Vac Ion pump was put on the first differential chamber and a 25ℓ/sec Vac Ion was put on the second chamber. Although these are continuously operating pumps and although the 5ℓ/sec Vac Ion does provide differential pumping in the first chamber, the major role of the Vac Ions is the continual maintenance of a high vacuum in the mass spectrometer chamber, even when the bell jar is raised for system repairs. Previously, a vacuum could not be maintained, necessitating a new bakeout/pumping sequence. With the Vac Ions, the vacuum during bell jar openings was maintained at 1×10^{-7} torr or lower (generally $\sim 2 \times 10^{-8}$ torr). This results in no "dirtying" of the system and allows the vacuum to return to its former baseline easily within a day after the bell jar has been again evacuated.

Figure 4.9: Liquid Helium Cryopump.

Figure 4.10: Mass Spectra Taken at 4×10^{-9} Torr (top) Without Use of Cryopump; Mass Spectra Taken at 4×10^{-10} Torr (bottom) With Use of Cryopump.

Figure 4.11: Mass Spectra of Background Gas in Detector With Cryopump Working (Top); Outgassing of Helium from Cryopump (bottom left); Outgassing of Hydrogen from Cryopump (bottom right).

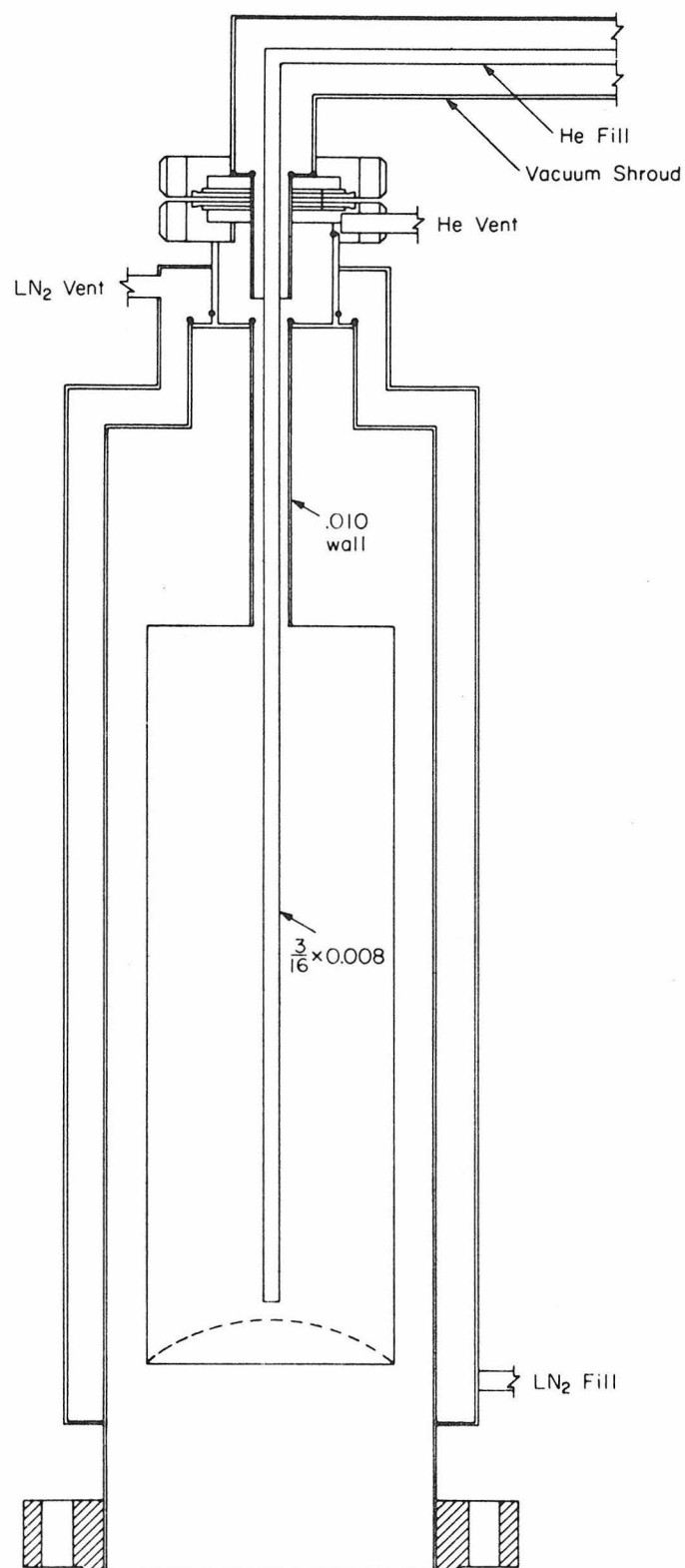


Figure 4.9

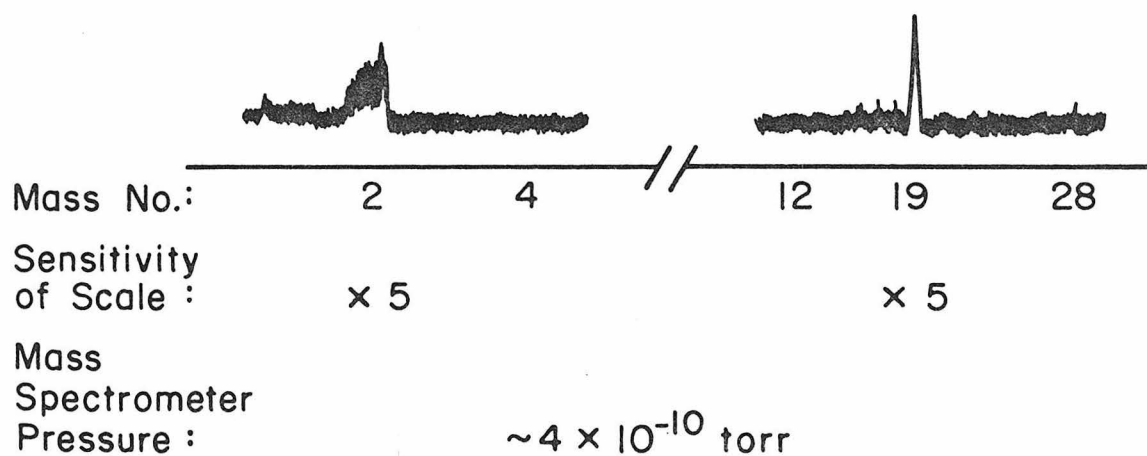
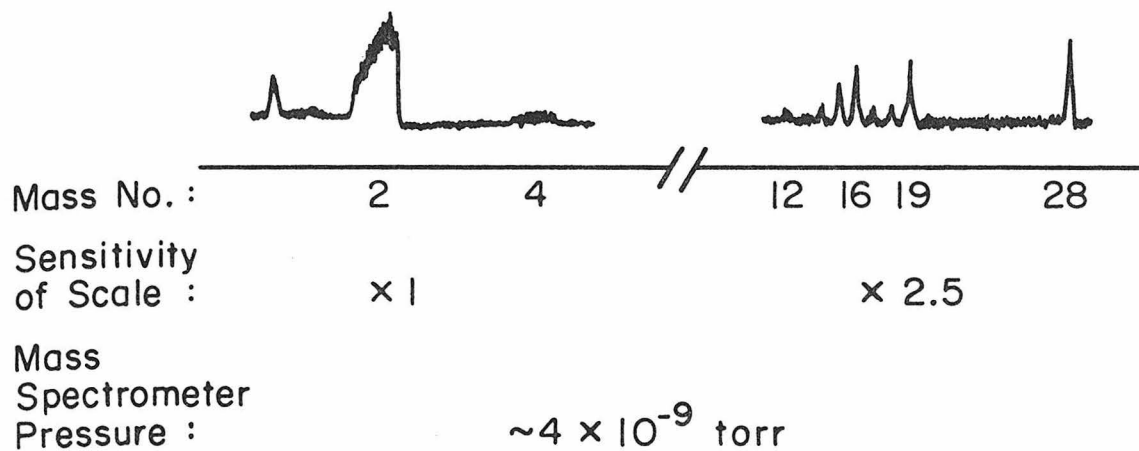


Figure 4.10

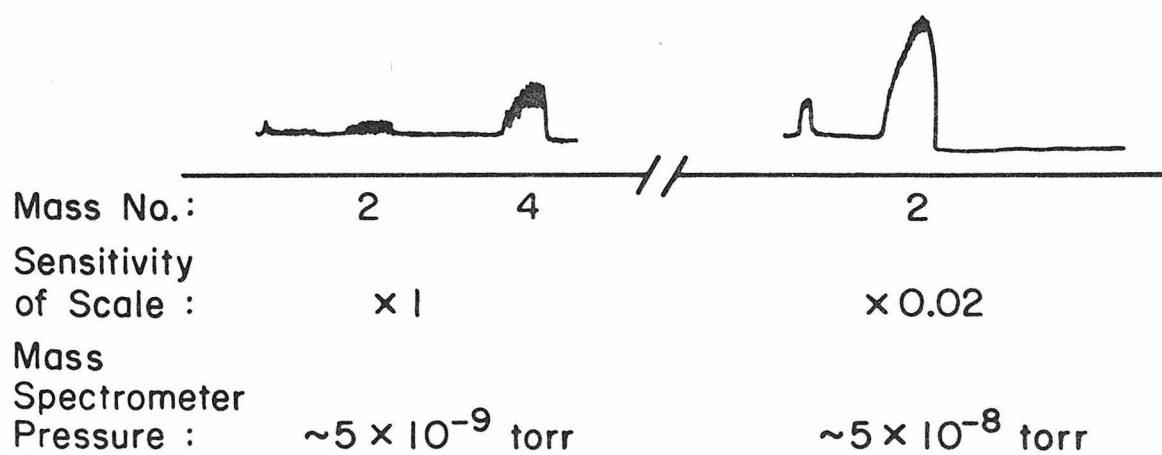
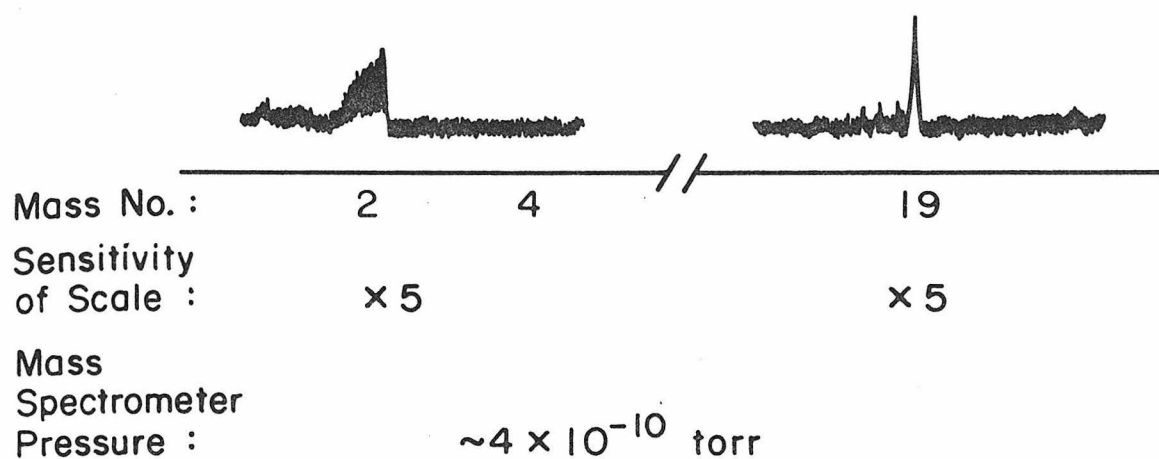


Figure 4.11

4.2 Experimental Procedures

In the previous discussion in this chapter, optimization and characterization of individual components of the crossed molecular beam scattering apparatus was presented. In the remaining portion of this chapter, discussion centers on the experimental procedures found necessary to obtain high quality data. Three specific areas will be addressed: (1) alignment of the beams and the detector, critical for accurate and precise data; (2) bakeout of the mass spectrometer chamber, necessary for adequate signal-to-noise ratios; and (3) data acquisition and processing.

4.2.1 Alignment

Because of the complexity of the apparatus and because of the experimentally-determined sensitivity of the data reduction to exact angular position, extreme care was taken to insure accurate alignment and accurate, reproducible determination of angular position. It is imperative that the beams cross at a known angle, that the beams intersect at the scattering center, and that the detector move exactly about the scattering center with its angular position accurately defined. Figure 4.12 provides a schematic for the optical alignment procedure. A precision optical level is used to align the detector (mass spectrometer) with a reference determined by the front face of the primary oven. Two plumbs are hung from the oven face; a machined pin of exactly the proper height above the main chamber (scattering chamber) floor is placed in line with the plumb wires. Simultaneously the 90°

reference and the scattering center are now defined. The detector is first aligned with these references; and, if necessary, collimator holes on the first and second differential chambers are moved. Then the detector is swung 90° in-plane where the primary beam nozzle, skimmer, and beam collimator are aligned with the scattering center (determined by the machined pin) and the detector.

To insure the validity of the procedure described, a number of actions were taken. First, four supporting posts equally spaced were placed under the outer rim of the bell jar--this eliminated the observed small positional shifts of the entire apparatus and guaranteed that alignment was in one plane, critical to use of the optical scope. Second, both the quadrant arm and the mass spectrometer were aligned with the reference--this eliminates any possible skew in scanning out-of-plane. Third, distortions in the movement of the mass spectrometer about the scattering center were examined for both in-plane and out-of-plane configuration scans. A machined ball was placed around the scattering center over the machined pin, and distortions were mechanically measured as the mass spectrometer was rotated about the scattering center. Distortions were found to be negligible, perhaps 0.10° maximum at the full range of movement and much less at the lower angles where data were primarily taken. Fourth, the accuracy and reproducibility of angular measurements were calibrated absolutely. A precision machinist's scale was placed on the machined outer diameter of the bell jar while an indicator to read this scale was attached to the detector. A full set of angular

readings were then made and calibration of the output of each transmitting synchro with the scale reading was made. It was found that the reproducibility of the synchro readouts was within $\pm 0.015^\circ$ and the accuracy was within $\pm 0.025^\circ$. As a result of these procedures, confidence exists that the alignment of components is free of significant error.

Final determination of the scattering center is made by experimentally fitting the first observed minima on both the positive and negative sides of the scattering center to optimize the symmetry of the two structures. Figure 4.13 illustrates how this trial and error, iterative process (actually done with a computer program) is used to determine the actual scattering center. It should be emphasized that the corrections given are not absolute corrections from the mechanical alignment; during the alignment it is recognized that small corrections will be necessary, and consequently the zero of the synchro is only grossly set with no concern for a finely set zero. Since complete symmetry exists in the Out-Of-Plane configuration about the scattering center, the function $I(\theta) \cdot \sin \theta \cdot \theta^{\frac{4}{3}}$ is directly used in the matching process because of its sensitivity. For the In-Plane configuration, the intensity is factored with the proper transformations so that the same fit procedure can be used. It is felt that the experimental determination of the scattering center contains a maximum error of 0.1° because of the small changes observed in the fitting procedure and because of the small errors seen in the optical alignment when compared against precise mechanical scales.

Figure 4.12: Optical Alignment Schematic.

Figure 4.13: Scattering Center Determination Through Symmetry of Positive and Negative Scattering Data.

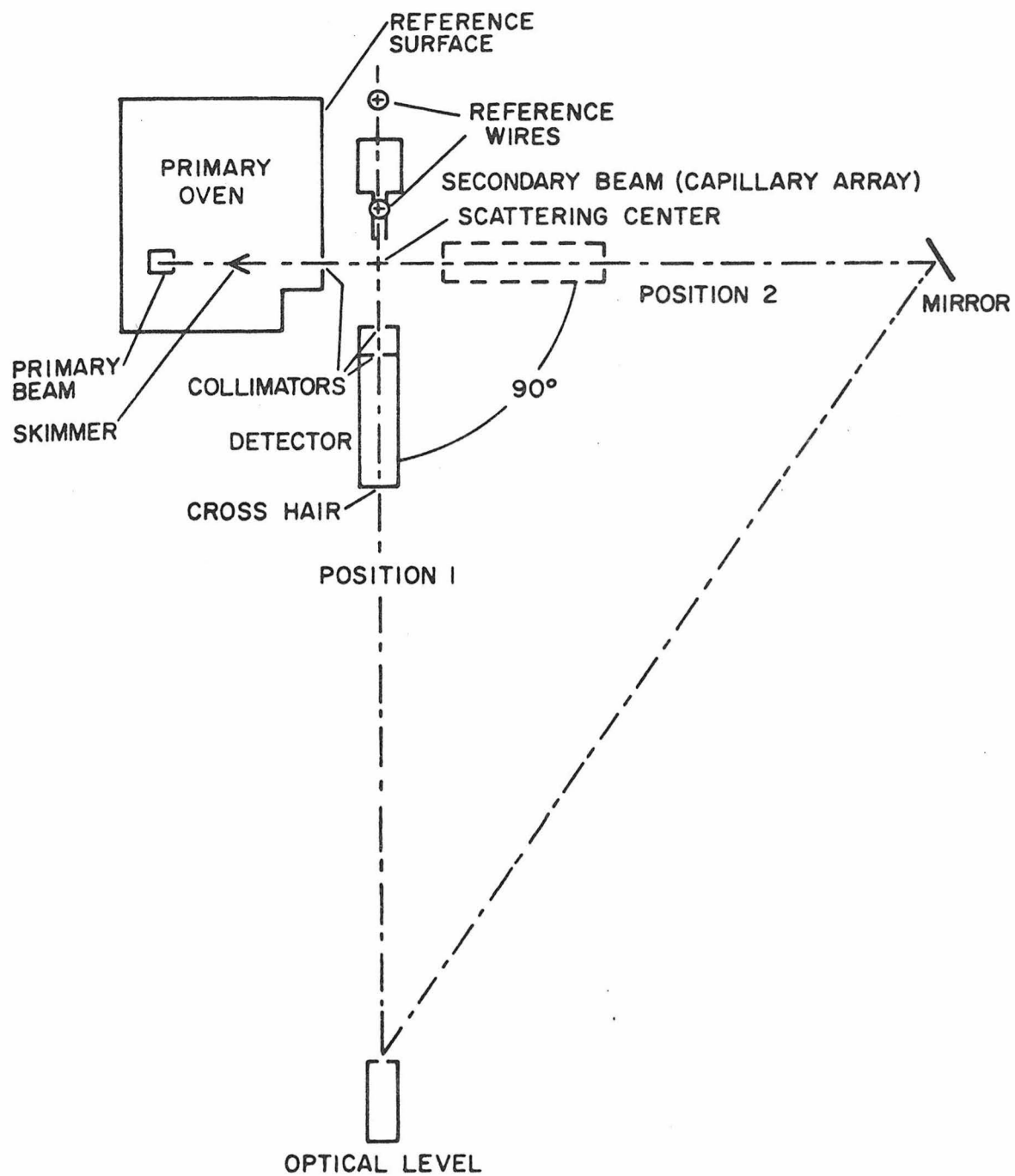


Figure 4.12

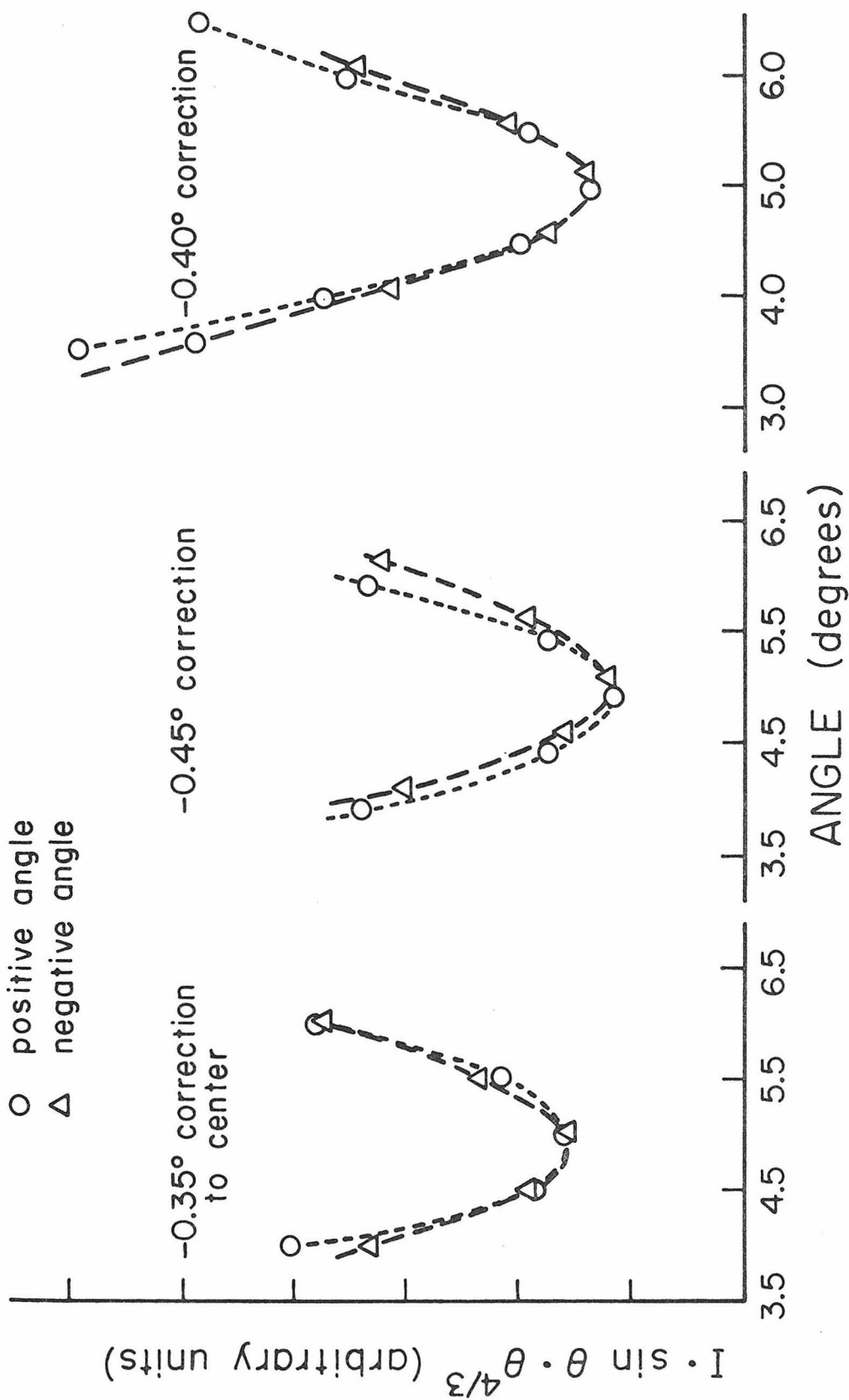


Figure 4.13

4.2.2 Bakeout

After the mass spectrometer chamber has been opened and if the inside components have been touched, pressures in the chamber will remain in the 10^{-8} torr regime even after days of pumping. This has two effects: (1) background is so high that the mass spectrometer can not be operated at full sensitivity and (2) the high background drives the signal-to-noise ratio to even lower values. The decreased sensitivity and high background result in intolerably low signal-to-noise ratios which would require literally hours of counting (integration) times. To overcome the large background pressures which result from both contamination on the interior chamber surfaces and from outgassing of the interior components themselves, the chamber and its components are baked at the highest temperatures compatible with the hardware. This results in elimination of volatile (relatively speaking) components from the contaminated surfaces and of trapped gases near the component surfaces. All the contaminants and gases obviously cannot be removed, but the very large majority can. With a long, forty hour bakeout with maximum temperatures exceeding 200°C , it was found that a previously "filthy" system could have a baseline pressure of 2×10^{-9} torr or less.

Initially the high speed oil pumps may or may not be used. The bakeout valve,¹ a relatively large valve opening the mass spectrometer second chamber to the main chamber, is opened and then power is gradually applied to the heating tapes external on the mass spectrometer housing. Gradually the temperature of the entire mass

spectrometer/detector/housing is allowed to increase until after approximately twelve (12) hours, the temperature is uniformly $210^{\circ} \pm 10^{\circ}\text{C}$ -- magnitude of the temperature is limited by O-ring and Vac-Ion pump compatibility design restrictions for temperature. The high-speed oil diffusion pumps are in use and pressures are continually monitored. Slowly the pressure in the mass spectrometer chamber begins to fall. After an appropriate time, power to the heating tapes is cut and the hardware begins to cool with outgassing decreasing. Toward the end of the cooling time, all the ionization gauges, the mass spectrometer ionizer, and the Vac-Ion pumps are all outgassed. When the bakeout valve and the front mass spectrometer gate valve can be closed without a major pressure surge and when also the Vac-Ion pumps can be reasonably operated (10^{-7} torr regime), the bakeout is essentially finished. A few days further wait is required to insure that all components are cool and no undue thermal stresses are induced by liquid nitrogen cooling. Additionally, pumping of the abnormally high outgassing continues, i.e., reduction of background gases is still made. As mentioned earlier, the liquid helium cryopump can be used after the bakeout is complete and pressures in the 10^{-10} torr regime are observed. The mass spectrometer can be operated at full sensitivity with a relatively low background, resulting in an optimized signal-to-noise ratio.

4.2.3 Data Acquisition and Processing

Generally, the crossed molecular beam apparatus is ready for operation approximately a week after a long bakeout. This allows time

for cooling the apparatus and allows checkout of the liquid helium cryopump. Operation of the beams and detector electronics is always initiated a few hours ahead of the actual process of taking data, since this allows the systems time to stabilize. Compensation for drift in the scattered signals either due to slow variations of the beams of the detector and its electronics is continually made. During the experiment the signal at a chosen reference angle (nominally 5°) is continually monitored, at least after every other data point is taken. The data points are then normalized against the variation in the reference signal which is found generally to be within $\pm 5\%$ of the baseline. The primary beam is modulated with a chopper at 160 Hz, and the detected signal is taken both with the secondary beam in the scattering plane and with it out. This permits subtraction of the background modulated signal, as well as the "white noise" background seen by the detector. It should be emphasized that the detected signal is assumed to have a phase-shifted 160 Hz component and that the process described is an A.C. counting (integration) one. With suitable amplification, filtering, and processing, the A. C. component of the signal can be obtained with an increase in the signal-to-noise ratio of over three orders of magnitude. The difference in the A.C. signals with the secondary beam in and with it out is the net signal, i.e., the data point at the set angle. (See Appendix I for a detailed analysis of the acquisition and processing procedures, including examination of its linearity.) The process of obtaining a signal with the secondary beam in and then out is generally repeated three times for a data point and generally three or four data points are taken at an

angle. Specifics were determined by the observed reproducibility of the difference in signals and the data points. Counting (integration) times were characteristically on the order of a total of ten (10) minutes at low angles and of a total of ninety (90) minutes at the higher angles investigated.

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This applies, of course, to our AC counting, not DC counting where signal-to-noise is proportional to the ratio of signal to the square root of the sum of signal plus background. AC counting introduces another noise term in the summed divisor.

CHAPTER 5

Central-Field Intermolecular Potentials
for $\text{H}_2(\text{D}_2)$ -Ar from Low-Energy Crossed
Molecular Beam Differential Elastic Scattering

Central-field intermolecular potentials for $H_2(D_2)$ -Ar from low-energy crossed molecular beam differential elastic scattering^{a)}

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Abstract: Differential elastic scattering cross sections (DCS) for the systems $H_2 + Ar$ and $D_2 + Ar$ have been measured in a crossed molecular beam apparatus. Potentials were obtained from this data, assuming different mathematical forms which included the Lennard-Jones (12-6), Lennard-Jones (n-6), Klein-Hanley (n-8-6), the double Lennard-Jones, the Morse-spline-van der Waals, the Morse-Morse-spline-van der Waals, and the Simmons-Parr-Finlan-Dunham potentials. For each form, the van der Waals well minimum position (r_m) and depth (ϵ) for the H_2 and the D_2 systems agreed with each other within experimental accuracy, as did the well shapes. Furthermore, the fits are all of good

a) This work was supported in part by contract (EY-76-S-03-767) from the Department of Energy. Report Code: CALT-767P4-167.

b) Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

c) Contribution No. 5875.

quality, and the differences among the r_m and ϵ from the several forms are also within experimental error. These potentials are in good agreement with those obtained from DCS measurements made elsewhere and from the measurement of other properties. Anisotropy in the potential for this system, in the region of the van der Waals minimum, seems to be small.

I. Introduction

Over the past few years considerable work has been done to elucidate the nature of interatomic potentials between symmetric and nonsymmetric noble gas pairs.¹⁻³ In addition, work has been done to determine the intermolecular potentials between $\text{H}_2(\text{D}_2)$ and other molecules ($\text{N}_2, \text{O}_2, \text{NH}_3, \text{CO}, \text{CH}_4$).^{4, 5} Only recently has a characterization of the He-Ar rare gas pair been made which is parameterization-independent.⁶

A logical extension of this work is the investigation of the $\text{H}_2(\text{D}_2)$ - Ar system. This represents only a small step away from noble gas pairs. Previous atom-molecule and molecule-molecule scattering experiments have been successfully analyzed in terms of central-field interaction potentials.⁷ In addition, a wealth of spectroscopic data on the $\text{H}_2(\text{D}_2)$ - Ar van der Waals molecule exists.⁸⁻¹⁵ LeRoy and van Kranendonk¹¹ have analyzed the $\text{H}_2(\text{D}_2)$ - Ar spectra of McKellar and Welsh^{8, 9} using a Lennard-Jones n-6 (LJ n-6) form¹⁶ to obtain anisotropic intermolecular potentials. Dunker and Gordon¹⁵ have also analyzed the same spectroscopic data using a Morse-spline-van der Waals form to obtain anisotropic intermolecular potentials. This allows a direct comparison between a potential obtained from DCS measurements by assuming a central-field form with the potential obtained from spectroscopic experiments.

We report in the present paper thermal energy differential cross-section measurements (DCS) for the $\text{H}_2(\text{D}_2)$ - Ar system. In Section II we give a short description of the experimental methods used. In Section III the results of the DCS measurements are presented, as well as the central-field potentials resulting from them. The nature of these potentials are discussed in Section IV and a summary and conclusions are given in Section V.

II. Experimental

The apparatus used in the present experiments has been described previously.^{3,4} It consists essentially of a vacuum chamber into which are injected two beams at an intersection angle of 90° . A quadruple mass spectrometric detector with an electron impact ion source is used to detect the scattering signal. It is criogenically pumped and can move in or out of the plane of the incident beams. Characteristics of the optimized primary D_2 beam were a velocity distribution with a full-width-at-half-maximum (FWHM) of $\sim 11\%$, a Mach number of 17.5, and a 1.0° FWHM angular spread. The optimized primary H_2 beam had a velocity distribution with a FWHM of $\sim 10\%$, a Mach number of 20, and a 1.0° FWHM angular spread also. The secondary beam had a characteristic Mach number of 1.5. It was formed by expanding argon through a glass capillary array with holes 2μ in diameter whose cross section represents 50% of the total cross sectional area of the array. The plenum pressure behind the array was about 3 torr and resulted in a secondary beam angular divergence of 3.0° (FWHM). The main chamber pressures were approximately 2×10^{-6} torr when both beams were on, ensuring that only single collision phenomena were observed. Detailed conditions of the experiment are given in Table I.

Data were reduced using techniques described previously³ and assuming a central-field potential. The justification for

this assumption is discussed in Section IV.A. For some of the data reduction, the overall angular resolution was considered as a fitting parameter. For the D_2 - Ar system, the value of the fitted angular resolution parameter was found to be essentially independent of the mathematical forms assumed for the potential. Similar results were obtained for the H_2 + Ar system. Values of the angular resolution parameter were 1.4_5° and 1.7° for the D_2 + Ar and the H_2 + Ar systems, respectively. For the experimental conditions used, the most probable relative collision energies were 72.4 meV and 68.3 meV and deBroglie wavelengths were 0.56 Å and 0.74 Å for the D_2 + Ar and H_2 + Ar systems, respectively.

Because of the experimentally-demonstrated sensitivity of the data reduction to the absolute values of the scattering angles,³ extreme care was taken to insure an accurate alignment of the detector and an accurate measurement of its angular position. It is also imperative that the angle between the beams be well known and that the detector move exactly about the scattering center. Figure 1 provides a schematic diagram of the optical alignment procedure. A precision optical level is used to align the detector (mass spectrometer) horizontally and make it parallel to reference planar surface defined by the front face of a milled square flange of the primary beam oven. Two plumbs are hung at an accurately measured distance from that surface;

a machined pin of exactly the proper height above the main chamber floor is placed in line with the plumbs. The 90° reference direction (with which the secondary beam is later aligned) and the scattering center (tip of the pin) are thereby defined. The detector is first aligned with this reference line and, if necessary, the position of the collimators on its first and second differential chambers are adjusted. The detector is then swung in the horizontal (in-plane) by 90° (see below); and the primary beam nozzle, skimmer, and collimator are aligned with the scattering center (defined by the machined pin tip) and the detector.

The scattering angle measurements were accurately calibrated as follows. A precision machinist's scale (accurate to ± 0.00002 m) was snugly attached to the machined outer diameter of the scattering chamber (1.27 m diameter) while an indicator to read positions on this scale was attached to the detector. A full set of angular readings were then taken, and used to calibrate the output of each of the transmitting synchros (used for the angular measurements). It was found that the reproducibility of the synchro readouts was $\pm 0.015^\circ$ and their absolute accuracy $\pm 0.025^\circ$. The zeros of the in-plane (detector in plane of beams) and the out-of-plane (detector and primary beam in a plane perpendicular to the plane of beams) scattering angles were determined by symmetry considerations of the scattering pattern, as described previously.³ They are accurate to $\pm 0.03^\circ$.

Because of the procedures described, it is felt that this apparatus is free of any significant artifact which would affect either the absolute angular position of the detector or the alignment of the primary beam, the secondary beam, the detector, or the scattering center. Linearity of the data processing electronics was extensively checked using known test signals. Linearity within $\pm 1.0\%$ for all test conditions was observed. Furthermore, two electron multipliers at the output of the mass spectrometer were used: a 14 dynode Cu - Be one and a Spiraltron (continuous dynode) one (SEM). The first was used as a DC current measuring device and the second as a pulse counter. The output of the two were proportional to one another within 2%. The Cu - Be dynode multiplier was used throughout the present experiments.

III. Results and Data Reduction

In order to check the self-consistency of the apparatus, data were taken for the $D_2 + Ar$ system in the in-plane and out-of-plane configurations and in both directions for each configuration. Because of the physical limitations inside the scattering chamber, scans in the negative out-of-plane configuration (i.e., below the plane of the beams) can be made only out to 12° . Consequently scans in all four configurations were made out only to $\sim 12^\circ$ to allow equally weighted comparisons of the reduced data.

Figures 2 and 3 show the experimental results.¹⁷ For out-of-plane scattering angles, θ_{lab}^o , above (below) the plane of the beams are by convention positive (negative). For in-plane scattering, laboratory scattering angles, θ_{lab}^i , towards (away from) the secondary beam are positive (negative). The positive and negative out-of-plane results should be superimposable because of the symmetry with respect to the plane of the beams. The positive and negative in-plane results are expected to be slightly different because of the different kinematic transformations from center-of-mass to laboratory coordinates corresponding to positive and negative in-plane laboratory scattering angles.³

The solid curves in these figures represent central-field fits to the experimental data using a Lennard-Jones 12-6 (LJ 12-6) potential.¹⁶ A more sophisticated potential such as the five parameter Simons-Parr-Finlan-Dunham (SPFD) potential^{18,19}

was not used because the limited angular range in these self-consistency checks do not warrant the use of potential forms with 4 or 5 adjustable parameters. It turns out, as shown later, that even over a wider angular range, the LJ 12-6 potential provides nearly as good a representation of the data as does the SPFD one. This reinforces the reasonability of using the LJ 12-6 form in the self-consistency checks.

In each of the two in-plane and two out-of-plane configurations, measurements were taken at about 20 different angular positions; (see Table II). The potential parameters for the fits to the data for these four configurations are given in Table II and are shown in Figs. 2 and 3. Agreement between them is essentially within experimental error, thus indicating the self-consistency of the apparatus and the lack of kinematic bias in the data. In spite of this agreement, the fit in the positive out-of-plane configuration is significantly better than any of the other fits, as indicated by the value of the goodness-of-fit parameter $\frac{\Delta \alpha}{\alpha}$.^{3,6} These differences between the results of the in-plane and the out-of-plane configurations are consistent with those observed in the He + Ar system.³ We consider the positive out-of-plane measurements to be more accurate than the others.

More extensive data were taken with D₂ as the primary scattering gas out to ~ 22° in the positive out-of-plane configuration at 43 different angular positions. In addition, data were taken

with H_2 as the primary out to $\sim 14^\circ$. The experimental DCS's were fitted by weighted least-squares optimization of the parameters of the intermolecular potentials described below. These potentials are written in the reduced form

$$f(\rho) = \frac{V(r)}{\epsilon}, \quad \rho = \frac{r}{r_m},$$

where r_m is the radius of the attractive minimum and ϵ is its depth. The zero of the potential, occurring at $r = \sigma$, may be related to r_m and the potential shape $f(\rho)$. The potential shapes considered are:

a) Lennard-Jones 12-6 (LJ 12-6)¹⁶

$$f(\rho) = \rho^{-12} - 2\rho^{-6} \quad (1)$$

b) Lennard-Jones n-6 (LJ n-6)¹⁶

$$f(\rho) = \frac{6}{n-6} \left\{ \rho^{-n} - \frac{n}{6} \rho^{-6} \right\} \quad (2)$$

c) Klein-Hanley n-8-6 (n-8-6)²⁰

$$f(\rho) = \frac{\rho^{-n}}{n-8} (8-2c_6) - c_6 \rho^{-6} - \frac{\rho^{-8}}{n-8} (6c_6 + n - nc_6) \quad (3)$$

d) Double Lennard-Jones (DLJ)²⁰

$$\left. \begin{aligned} f(\rho) &= \frac{m}{n_1-m} \left\{ \rho^{-n_1} - \frac{n_1}{m} \rho^{-m} \right\} & \text{for } \rho < 1 \\ f(\rho) &= \frac{6}{n_2-6} \left\{ \rho^{-n_2} - \frac{n_2}{6} \rho^{-6} \right\} & \text{for } \rho \geq 1 \end{aligned} \right\} \quad (4)$$

e) Morse-Spline-van der Waals (MSV)²¹ and M²SV⁶.

The MSV potential used is

$$\left. \begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } \rho \leq \rho_1 \\ f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{(2i+4)} && \text{for } \rho \geq \rho_2 \end{aligned} \right\} (5)$$

The s_i ($i = 1, 2, 3, 4$) are cubic spline coefficients, which are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 . The first spline point is taken as the inflection point of the Morse curve, $\rho_1 = 1 + \beta^{-1} \ln 2$. The second spline point may be treated as a fitted parameter but was held fixed at $\rho_2 = 1.6$. The remaining shape parameters are β , governing the shape of the repulsive and well regions, and the dispersion series coefficients. We have also modified this potential (MSV) by using a second Morse function for $r < \sigma$, joined smoothly to the first at $r = \sigma$. This M²SV potential has the additional parameter β^1 and differs from the one above by having

$$\left. \begin{aligned} f(\rho) &= \frac{1}{\omega} e^{(\beta^1 - \rho\beta\omega)} [e^{(\beta^1 - \rho\beta\omega)} - 2] && \text{for } \rho < 1 - \beta^{-1} \ln 2 \\ \text{and} \\ f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } 1 - \beta^1 \ln 2 \leq \rho \leq \rho_1 \end{aligned} \right\} (6)$$

where

$$\omega \equiv \frac{\beta^1 - \ln 2}{\beta - \ln 2}$$

f) Simons-Parr-Finlan-Dunham (SPFD)^{17,18}

$$\left. \begin{aligned} f(\rho) &= b_0 \lambda^2 \left(1 + \sum_{i=1}^N b_i \lambda^i \right) - 1 & \text{for } \rho < \rho_f \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} & \text{for } \rho \geq \rho_f \end{aligned} \right\} \quad (7)$$

where $\lambda = 1 - \frac{1}{\rho}$ and we usually set $N = 3$.

Smoothness conditions at $\rho = \rho_f$ are used to fix the highest-order coefficients b_N and b_{N-1} . ρ_f may be treated as a variable but is fitted at $\rho_f = 1.6$; the b_i ($i = 1, 2, 3, 4, N-2$) determine the shape of the potential; the dispersion series constants are also independent parameters. Since the SPFD potential often shows spurious maxima or oscillations below $\rho = 0.65$, an exponentially repulsive wall, i.e., $f(\rho) = Ae^{-b\rho}$, is joined to the potential at $\rho = 0.7$ (A and b are fixed by smoothness conditions).

The number of parameters which are being varied in these potentials range from two to five. For the LJ 12-6 potential, only two parameters are varied: r_m and ϵ ; for the LJ n-6, three parameters are varied: n , r_m , and ϵ where n is the repulsive exponent; for the n-8-6, four parameters are varied: n , c_6 ,

r_m , and ϵ where n and c_6 are shape parameters; for the DLJ, five parameters are varied: n_1 , m , and n_2 , r_m , and ϵ where r_m and ϵ are shape parameters; for the MSV, four parameters are varied: β , c_6 , r_m , and ϵ where β and c_6 are shape parameters; for the M^2SV , five parameters are varied: β^1 , β , c_6 , r_m , and ϵ where β^1 , β , and c_6 are shape parameters; and finally for the SPFD potential, five parameters are also varied: b_0 , b_1 , c_6 , r_m , and ϵ where b_0 , b_1 and c_6 are shape parameters. Previous studies⁶ have shown that two and three parameter potentials are not satisfactory in representing the actual intermolecular potential. Additionally, it has been shown that many potential forms which have more than two parameters have a high correlation between parameters leading to less flexibility and capability of representing the intermolecular potential than apparent to initial examination. Among such potentials is the DLJ which has been shown to have a correlation of n , and m with r_m and ϵ and also of n_1 and m . This results in a potential which only has three effective parameters, not five. It follows that great care must be taken in fitting scattering with various potential forms. Potentials which have the necessary flexibility, such as the SPFD and M^2SV , should be used.^{3,6} A word of caution should be given here that such potentials with five free parameters require more data for fitting than two or three parameter potentials, i.e., more degrees of freedom require more information in order to be defined. (This is illustrated below where the $H_2 + Ar$ system

can not fit using the SPFD potential while the $D_2 + Ar$ system, which has considerably more scattering data, can be fit.)

Fits to the various potential forms are shown in Figure 4 for the $H_2 + Ar$ system and in Figure 5 for the $D_2 + Ar$ system. The corresponding potentials are shown in Figures 6 through 9 with the parameters for these potentials given in Table III. It may immediately be observed that the potentials for the $H_2 + Ar$ and the $D_2 + Ar$ systems agree within experimental error (about $0.04 \text{ \AA}$ in r_m and 10% in ϵ^7). This not only provides further substantiation of the internal consistency of the apparatus but also provides an indication of the reasonability of the central-field assumption since the corresponding de Broglie wavelengths differ by 32%.

IV. Discussion

A. Effects of Anisotropy

As mentioned in Section II, the optimized fits to the DCS data were based on the assumption that the interaction potential between $\text{H}_2(\text{D}_2)$ and Ar was central. Our DCS experiments are sensitive to the value of the potential over the intermolecular distance range of about 3.1 Å to 6.9 Å (see Section IV.B), whereas the H_2 bond length is 0.74 Å and its electron density contour at about 1.7 Å from its center is already nearly spherical.²³ Therefore, the $\text{H}_2(\text{D}_2)$ molecule is expected to behave as a structureless particle (i.e., a spherical atom) in thermal scattering with Ar. This central-field assumption is supported by several facts. First, our fits to the DCS data based on such an assumption were independent of the molecular isotope of the primary scattering gas. According to the Born-Oppenheimer approximation, which is valid for the present case, all isotopes of a given system have the same intermolecular potential function. However, if anisotropy effects such as quenching or shifting of the extrema were important, their magnitude would be expected to be sensitive to the relative momentum, or de Broglie wavelength, of the colliding molecule and atom. These effects would then result in different central-field potential fits for the two isotopes; but, as noted, the central-field potentials for $\text{H}_2 + \text{Ar}$ and $\text{D}_2 + \text{Ar}$ agree within experimental error. Second, the work of Kuppermann et al.^{4a} on

$\text{H}_2(\text{D}_2 + \text{NH}_3, \text{SF}_6)$ systems further substantiates our assumption. Not only were different isotopes used but also different primary beam temperatures were used to vary the relative momentum of the colliding molecules. The potential fits at the different de Broglie wavelengths were in agreement with each other within experimental error showing, therefore, no major effects of anisotropy. Since these systems are more anisotropic than $\text{H}_2(\text{D}_2) - \text{Ar}$, it can be reasonably assumed that $\text{H}_2(\text{D}_2) - \text{Ar}$ is essentially free of anisotropy effects. Third, recent work done on $\text{He} + \text{N}_2, \text{O}_2, \text{CO}$ and NO in this laboratory²⁴ has shown that central-field potentials are indistinguishable, within experimental error from the spherical averages of the corresponding anisotropic potentials for interactions which are too weak to significantly distort the DCS scattering patterns from those expected from central-field interactions. Fourth, Jacobs and Reuss²⁵ investigated the influence of the anisotropic part of the $\text{H}_2 - \text{Kr}$ intermolecular potential on the DCS_g by performing exact quantum calculations of the latter. Various sets of anisotropy parameters were assumed for a relative velocity of 2600 m/s corresponding to thermal scattering. They concluded that the use of an intermolecular potential that included realistic angle-dependent terms would not change the values of ϵ and r_m obtained from a fit of DCS cross section measurements using central-fields. Fifth, Wagner and McKoy,²⁶ for a collision energy of 172 meV (about 2.5 times greater than ours) found no significant quenching or shifting of

extrema in the total differential cross section when they compared solutions of the Schroedinger equation for H_2 - Ar scattering using the breathing sphere approximation with more accurate ones involving the fully anisotropic intermolecular potential. Sixth, other experiments indicate or show that the effects of anisotropy are within the error of our experiments. Total cross section experiments,^{5,27} total cross section experiments with state selected beams,²⁸⁻³⁰ and van der Waals spectroscopy experiments^{11,13-15} all support this statement (see E and F below).

B. The Intermolecular Potential

In earlier work done in this laboratory,⁶ the range of sensitivity for the He + Ar intermolecular potential to the DCS in the scattering angle interval of 1.5° to 20° was determined with the help of computer simulation experiments to have a lower limit of $2.8 \text{ \AA}$ and an upper limit of $6.5 \text{ \AA}$ at a collision energy of 64 meV. This range is considerably larger than that determined by classical considerations, $2.9 \text{ \AA} - 4.8 \text{ \AA}$. For our D_2 + Ar system, the classical range of the intermolecular potential is approximately $3.2 \text{ \AA} - 5.2 \text{ \AA}$. The de Broglie wavelengths of these He + Ar and the D_2 + Ar systems are almost the same. The corresponding A and β parameters are 35, 34 and 37, 121, respectively. Since a value greater than 300 for β is recognized as beginning the transition regime from quantum behavior towards classical behavior, the He + Ar and D_2 + Ar systems can be considered as

strongly quantum in behavior (also the $\text{H}_2 + \text{Ar}$ which has a lower β value than $\text{D}_2 + \text{Ar}$).³² Consequently, the $\text{D}_2 + \text{Ar}$ system is expected to display nonclassical behavior in a manner similar to that of $\text{He} + \text{Ar}$, i.e., the range of sensitivity for the inter-molecular potential to scattering data will be larger than the classically determined range. Based on the assumption that quantum effects for the $\text{He} + \text{Ar}$ and the $\text{D}_2 + \text{Ar}$ systems are very similar (which may not be completely true), we estimate the range of sensitivity to be 3.1 Å to 6.9 Å.

For the LJ 12, 6 and for the LJ n-6 potentials, the attractive part of the potential is not determined by a separate parameter. However, the other potentials used (DLJ if coupling is ignored, n-8-6, MSV, $M^2\text{SV}$, and SPFD) do contain the flexibility necessary to fit the long-range attractive part of the potential essentially independently of the well or short-range regime. We normally prefer to concentrate our fitting efforts on the more flexible MSV, $M^2\text{SV}$, and SPFD forms.

Since the c_6 term in our fits accounts for all terms of the multipole expansion ($c_8 = c_{10} = 0$) over the range of distances to which the DCS measurements are sensitive, the fitted c_6 coefficient for the MSV, $M^2\text{SV}$ and SPFD potentials may be significantly larger than the true c_6 coefficient. Langhoff and Karplus³³ give a value of $16.9 \pm 0.5 \text{ eVÅ}^6$ as the bounded estimate of the c_6 dispersion coefficient derived from Padé approximants used with optical dispersion data for $\text{?} + \text{Ar}$; Dalgarno³⁴ gives

a semiempirical estimate of $16.7 \text{ eV } \text{\AA}^6$; and Bernstein and Muckerman³⁵ suggest the value $17.3 \text{ eV } \text{\AA}^6$ from a review of experimental data. Our average fitted c_6 value from the last four lines of Table III is about $35 \text{ eV } \text{\AA}^6$.

The similarity of the fits using different central-field potential forms is surprising, since previous experiments^{3,24,36} and analyses⁶ have shown significant differences between fitted potentials for the He - Ar system and for various He-molecule systems. Some of these differences have been pronounced. For the He - Ar system well depth differences up to 25% are found for different mathematical forms, and significant differences in the steepness of the repulsive wall are also found.³ These effects are much less pronounced when comparing the various potential fits for the D₂ - Ar and H₂ - Ar data. Previous analyses⁶ showing the inherent bias for the LJ 12-6, LJ n-6, and other simple potential forms not having the flexibility of an SPFD potential were based on the assumption that the true intermolecular potential had a form which could be significantly different from any of the more simple, fewer parameter, potential forms, as seems to be the case for the He + Ar system.³ For the H₂(D₂) + Ar system, however, our results indicate that the correct intermolecular potential has a form which can be closely duplicated by relatively simple potentials over the range of distances to which the DCS measurements are sensitive. Part of the reason for this behavior may be the fact that the well depth for this system is much greater

than for the He + Ar one and the experiment is consequently less sensitive to the repulsive wall. This makes the flexibility for independently fitting the repulsive wall and attractive well region of the potential, displayed by the SPFD and M^2SV forms, and so essential for the He + Ar case, much less necessary in the present situation. The appropriateness of the LJ 12-6 form in fitting the data is the basis of our use of it for making the four-quadrant consistency checks described in Section III.

C. Comparison with Other Results

Differential Cross Section (DCS)

In Table IV, we give a comparison between our results and those of others. Our LJ 12-6 parameters agree within experimental error with those obtained by Rulis *et al.*³⁷ Their potential supercedes earlier published work done in the same laboratory by Bickes *et al.*³⁸ (third entry of Table IV). Their new experiments were run at a lower relative collision energy which is more sensitive to the well, and the cross section data were measured with greater precision. The velocity distribution of the primary H_2 was closely investigated and accurately determined because of the sensitivity of the position and amplitude of the interference oscillations in the DCS to the relative collision energy and its spread.^{4a} This is in agreement with our experience. We find that high quality fits to the experimental data can only be

obtained when the velocity distribution and angular spreads of both beams are characterized, when an accurate alignment of both beams has been made, when the location of the zero of the scattering angle scale has been accurately determined (to within 0.03°), and when the angular scale has been accurately calibrated.

Integral Cross Sections

The results of Helbing et al.²⁷ and of Butz et al.⁵ given in Table IV were both obtained from integral cross section measurements in which velocity-selected beams of H_2 or D_2 at thermal energies were attenuated by Ar gas contained in a scattering chamber. These measurements are sensitive to the intermediate attractive part and the van der Waals minimum part of the potential. The potential parameters obtained from these experiments tend to be model-dependent; furthermore, individual values of r_m and ϵ are recognized to have relatively large uncertainties while the ϵr_m products are much more precise.^{4a,27} Whereas their values of ϵ can be considered to be in agreement with ours for $H_2 + Ar$, their r_m is significantly below ours and that of Rulis et al. Moerkerken et al.²⁸ have also made integral cross section measurements with beams of state-selected H_2 molecules to determine the magnitude of the anisotropic part of the intermolecular potential. They assumed a potential of the form

$$V = c_n r^{-n} [1 + q_n P_2(\cos\theta)] - c_6 r^{-6} [1 + q_6 P_2(\cos\theta)] = V_0 + V_2 P_2(\cos\theta) \quad (8)$$

with $c_n = [6/(n-6)] \epsilon r_m^n$ and $c_6 = [n/(n-6)] \epsilon r_m^6$ to fit the data, where r has the same meaning as in the present paper and θ is the angle between the H_2 internuclear vector and the position vector of Ar with respect to the center of mass of H_2 . They set $m = 12$ and considered q_6 and q_{12} to be adjustable anisotropy parameters varied to fit the data. They were able only to fit their results by using for the central-field part of their potential a value of the ϵr_m product 4% greater than that of Helbing et al.²⁷ In a later publication the same authors²⁹ report fits to improved data (with the signal-to-noise ratio of the state-selected beam intensity measurement increased by a factor of 3.5) which uses for the central-field part of the potential the parameters r_m and ϵ (an LJ 12-6 potential) given by LeRoy and Van Kranendonk.¹¹

In still a later paper from the same laboratory, Zandee et al.³⁰ report results of new measurements which they again fit using the potential form of Eq. (8) and the ϵr_m value of LeRoy and Van Kranendonk.¹¹ From Eq. (8) one obtains for the position $r_{m,a}$ and the depth ϵ_a of the anisotropic part $V_2(r)$ of the potential the expressions³⁹

$$r_{m,a} = r_m \left(\frac{q_n}{q_6} \right)^{\frac{1}{6}} ; \quad \epsilon_a = \epsilon \frac{q_6^2}{q_n}$$

Zandee et al.³⁰ obtain the values 0.21 for q_{12} and 0.15 for q_6 from which they set $\epsilon_a = 0.11 \epsilon$ and $r_{m,a} = 1.06 r_m$. These values permit an assignment of the magnitude of the anisotropy in the $H_2(D_2) + Ar$ potential. At $r = r_m$, V_2/V varies from 0.08 to -0.05 as θ varies from 0 to π . This is within the 10% error in our experimental determination of the intermolecular potential at $r = r_m$ from DCS data,⁷ a further justification of our assumption of the validity of the central-field approximation in analyzing our data.

van der Waals Molecule Spectroscopy

McKellar and Welsh^{8,9} have made detailed, extensive measurements of the infrared spectra associated with the weakly bound van der Waals molecules $H_2 - Ar$ and $D_2 - Ar$. Additionally, McKellar¹⁰ has made subsequent measurements on the spectrum of $HD - Ar$. When $HW(D_2, HD)$ comes into close contact with Ar , an electric dipole moment is induced in the system by intermolecular interactions. This gives rise to infrared vibration absorption spectra having a fine structure due to transitions between rotational levels of the van der Waals complex formed between the hydrogen molecule and the argon atom. Let us denote by $\underline{J}$ the "internal" angular momentum of the H_2 around its own center of mass and by $\underline{L}$ the relative orbital angular momentum of the H_2, Ar pair around the center of mass of the whole system. Total angular momentum is $\underline{j} = \underline{J} + \underline{L}$. If the $H_2 + Ar$ interaction

were completely isotropic, $\tilde{J}$ and $\tilde{L}$ would each be a constant of the motion. If, however, the interaction contains even a weak anisotropic term, only j remains a constant of motion. The rotational $\tilde{L}$ levels for $\tilde{J} \neq 0$ are split and shifted. Hence, for a given $\tilde{J}$ and $\tilde{L}$, different j states exist. This is indeed the case for the $H_2(D_2)$ - Ar complex.

The spectra for the $H_2(D_2, HD)$ - Ar van der Waals complexes have been analyzed by a number of groups. Le Roy and Van Kranendonk¹¹ have done this for the H_2 - Ar and D_2 - Ar systems employing a LJ n-6 anisotropic potential. Using a nonlinear least squares fitting procedure, they obtained the corresponding intermolecular potential parameters. Since the n exponent was found to be optimized at 12, the potential reduced to a Lennard-Jones 12-6 with anisotropic components and components due to the vibration of H_2 . The ratio of the anisotropic well depth to the isotropic well depth (with stretching parameter accounted in both terms) was 0.076; and the ratio of well minima radii was 1.16. Again, the magnitude of this anisotropic contribution to the intermolecular potential is less than the errors involved in determining this potential from thermal DCS data using a central-field assumption. Our results for ϵ agree with those of LeRoy and Van Kranendonk¹¹ within our experimental error, whereas our r_m is slightly larger than theirs (see Table IV). The overall agreement between our LJ 12-6 potential and the central part of theirs is within our experimental error, as indicated in

Fig. 10. This agreement is very satisfying, in view of the very different nature of the corresponding experiments. Kreek and LeRoy¹³ later tried to fit the experimental spectra of HD - Ar in which the shift in the diatomic center of mass was accounted for. Using the H₂ - Ar and D₂ - Ar potential parameters yielded a potential for HD - Ar from which a predicted spectra were obtained which disagreed strongly with the observed ones. The authors attributed these discrepancies to the strong sensitivity of the precise shape of the intermolecular potential in the narrow range $\sigma \leq r \leq r_m$ for the spectra of the HD - Ar complex but not for the spectra of the H₂ - Ar or D₂ - Ar complex. LeRoy et al.¹⁴ repeated the analysis of the H₂ - Ar and the D₂ - Ar spectra with a different potential form that is a generalization of the Buckingham-Corner potential and in which the c_6 constant is held fixed at the theoretical value of Langhoff et al.⁴⁰ Again, for the HD - Ar spectra the fit was poor and, in fact, no better than with the LJ 12-6 potential. Dunker and Gordon¹⁵ also analyzed the H₂ - Ar spectra but dealt with P and r branches as well as with N and T branches and, furthermore, employed a Morse-spline-van der Waals parametric form of the intermolecular potential. The central-field part of the potential determined in this manner is similar to the one obtained by LeRoy and Van Kranendonk having, however, a slightly larger well depth and a slightly larger well radius. In addition, the magnitude of the intermediate and long range parts of the isotropic potential were smaller. The size

of the anisotropic part of the potential was about the same. Again, the latter is smaller than the error of our fits to the present DCS data and this confirms the conclusion that there is agreement between these spectroscopic results and our DCS results.

V. Summary and Conclusions

Effects of the anisotropy of the potential on the DCS data for the $\text{H}_2(\text{D}_2) + \text{Ar}$ are discussed and shown to be unimportant, permitting the use of central-field forms in obtaining intermolecular potentials from this data. Potential fits assuming a variety of mathematical forms, including some very flexible ones, were obtained. They indicate that, for this system, the relatively simple central-field Lennard-Jones 12-6 potential describes the intermolecular potential surprisingly well. Our potentials agree well with those obtained in other laboratories by a variety of techniques.

TABLE I. Beam operating conditions

Characteristic	Primary Beam		Secondary Beam
	H ₂	D ₂	Ar
Beam gas	H ₂	D ₂	Ar
Inlet pressure/torr	500	500	3.2
Inlet temperature/°K	298	298	298
Angular diversence (FWHM ^a /deg)	1.0	1.0	1.0
Most probable velocity/ (Km/sec)	2.48	1.76	0.50
Relative velocity spread (FWHM ^a , $\Delta v/v$)	0.10	0.11	0.75
Mach number	20	18	1.5

^a Full width at half-maximum.

TABLE II. $D_2 + Ar$ central-field Lennard-Jones 12-6 potential parameters for fits to the data of the four quadrant scans^a

Configuration	$r_m (\text{\AA})^b$	$\sigma (\text{\AA})^c$	$\epsilon (\text{meV})^d$	$\Delta\alpha / \alpha (\%)^e$
Positive angle/ In-Plane ^f	3.61 ± 0.11	3.22 ± 0.10	8.0 ± 0.9	4.2
Negative angle/ In-Plane ^f	3.60 ± 0.06	3.21 ± 0.05	7.7 ± 0.5	2.6
Positive angle/ Out-of-Plane ^g	3.61 ± 0.03	3.22 ± 0.03	6.9 ± 0.3	1.6
Negative angle/ Out-of-Plane ^g	3.59 ± 0.08	3.20 ± 0.07	7.6 ± 0.8	2.9

^a deBroglie wavelength $\lambda = 0.56 \text{ \AA}$. Errors indicated are for 95% confidence limits.

^b Intermolecular distance for the minimum of the van der Waals well.

^c Intermolecular distance at which the interatomic potential vanishes.

^d van der Waals well depth.

^e This is a quality of fit statistical index described in detail in references 3 and 7.

^f Data taken at 20 different angular positions.

^g Data taken at 21 different angular positions.

TABLE III. Intermolecular potential fits to the experimental DC'S's for D₂ + Ar and H₂ + Ar.

Potential Type ^a	Primary Beam ^{b,c}	r_m (Å)	σ (Å)	ϵ (meV)	Shape Parameters ^d	c_6 (eV·Å) ^e	χ^2 ^{f,g}	$\Delta\alpha_{0.95}/\alpha(\%)$ ^h
LJ 12-6	D ₂	3.61	3.22	6.90		30.7	36.2	1.38
LJ 12-6	H ₂	3.61		6.40		28.5		1.64
LJ n-6	D ₂	3.62	3.20	6.97	$n = 11.11$	35.1	28.8	1.24
LJ n-6	H ₂	3.62		6.40	$n = 11.44$	30.1		1.69
n-8-6	D ₂	3.62	3.20	6.98	$n = 11.01, c_6 = 2.34$	36.6	28.7	1.23
n-8-6	H ₂	3.62		6.30	$n = 10.85, c_1 = 2.35$	33.3		1.89
DLJ	D ₂	3.64	3.20	6.91	$n_1 = 11.1, n_2 = 14.8$ $m = 3.45$	34.9	28.2	1.27
DLJ	H ₂	3.62		6.55	$n_1 = 12.3, n_2 = 16.5$ $m = 3.98$	28.7		1.80
MSV	D ₂	3.64	3.18	7.03	$\beta = 5.47$	36.5	29.2	1.27
MSV	H ₂							
M ² SV	D ₂	3.65	3.21	7.12	$\beta = 5.69, \beta^1 = 12.6$	35.8	27.8	1.26
SPFD	D ₂	3.62	3.21	7.14	$b_0 = 35.2, b_1 = -4.63$ $c_6 = 2.13$	34.2	26.8	1.24

^a Defined in Eqs. (1) through (7) of the text.^b For D₂ primary beam: de Broglie wavelength $\lambda = 0.56$ Å and relative collision energy = 72.4 meV.^c For H₂ primary beam: de Broglie wavelength $\lambda = 0.74$ Å and relative collision energy = 68.3 meV.^d Symbols have same meaning as in Eqs. (2) through (7) of text. The MSV and M²SV potentials also have $\rho_2 = 1.60$; the SPFD potential has $\rho_f = 1.60$ and $N = 3$.^e c_6 dispersion constant.^f Scattering measurements for D₂ + Ar normalized to 500. at 4.69°. Number of experimental points = 42.^g Scattering measurements for H₂ + Ar normalized to at . Number of experimental points = .^h Quality-of-fit parameter. See references 3 and 6 for details.

TABLE IV. Potential Parameters for $H_2(D_2)$ - Ar.

System	Type of Measurement ^a	Potential Type ^b	r_m (Å) ^c	ϵ (meV)	Shape Parameters	$\epsilon \cdot r_m$ (meV·Å) ^c	Reference
$D_2 + Ar$	DCS	LJ 12-6	$3.61 \pm .02$	$6.90 \pm .29$		24.9 ± 1.2	this work
$H_2 + Ar$	DCS	LJ 12-6	$3.61 \pm .04$	$6.40 \pm .36$		23.1 ± 1.5	this work
$H_2 + Ar$	DCS	LJ 12-6	$3.44 \pm .05$	$7.84 \pm .29$		27.0	ref. 38
$H_2 + Ar$	DCS	LJ 12-6	$3.56 \pm .04$	$6.92 \pm .43$		24.6	ref. 37
$H_2 + Ar$	Q	LJ 12-6	3.34	6.30		$21.0 \pm .8$	ref. 27
$D_2 + Ar$	Q	LJ 12-6	3.32	6.05		$20.1 \pm .8$	ref. 27
$H_2 + Ar$	Q	LJ 12-6	3.33	6.37		21.2	ref. 5b
$H_2 + Ar$	QS	LJ 12-6				21.8	ref. 28
$H_2 + Ar$	QS	LJ 12-6	3.56^d	6.46^d		23.0	ref. 29
$H_2 + Ar$	QS	LJ 12-6	3.56^d	6.46^d		23.0	ref. 30
$H_2(D_2) + Ar$	S	LJ 12-6	3.56	6.46		23.0	ref. 11
$H_2(D_2) + Ar$	S	LJ 12-6	3.56	6.45		23.0	ref. 14
$H_2 + Ar$	S	MSV	3.59	6.70	$\beta = 6.92$	24.0	ref. 15
$H_2 + Ar$	DCS	MSV					this work
$D_2 + Ar$	DCS	MSV	3.64	7.03	$\beta = 5.47$	25.6	this work

^a DCS - differential cross section, Q - integral cross section, QS - integral cross section with state-selected beam, S - spectroscopy.

^b Defined in Eqs. (1) through (7) of the text.

^c Error bars represent precision-of-fit.

^d Parameters of ref. 11 assumed.

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Figure Captions

Figure 1. Schematic for alignment of apparatus.

Figure 2. Laboratory differential cross sections $I(\theta)^{17}$ for out-of-plane scattering of $D_2 + Ar$ as a function of the out-of-plane laboratory scattering angle θ_{lab}^0 . Points with error bars are the experimental measurements of $I(\theta) \cdot \sin\theta$ vs the scattering angle θ . The upper (lower) curve is the DCS calculated from the best-fit central-field Lennard-Jones 12-6 potential for scattering in the configuration above (below) the plane of the beams. The upper curve is shifted upwards (by a factor of 10) with respect to the lower curve points for clarity of display.

Figure 3. Laboratory differential cross sections $I(\theta)^{17}$ for in-plane scattering of $D_2 + Ar$ as a function of the in-plane laboratory scattering angle θ_{lab}^i . Points with error bars are the experimental measurements of $I(\theta) \cdot \sin\theta$ vs the scattering angle θ . The upper (lower) curve is the DCS calculated from the best-fit central-field for scattering in the configuration towards (away from) the direction of the secondary beam. The upper curve is shifted upwards (by a factor of 10) with respect to the lower curve for clarity of display. The two curves are not supposed to be exactly superimposable because of the slightly different kinematic transformations from the center-of-mass to the laboratory system for each of the two modes of scanning.

Figure 4. Laboratory differential cross sections¹⁷ for out-of-plane scattering of H_2 by Ar. Curves are DCS's calculated using potentials extracted from the data. Uppermost curve (a) is fit using LJ 12-6 potential; next curve shifted down (b) is fit using LJ n-6 potential; curve below (c) is fit using n-8-6 potential; lowest curve (d) is fit using DLJ potential.

Figure 5. Laboratory differential cross sections¹⁷ for out-of-plane scattering of D_2 by Ar. Curves are DCS's calculated using potentials extracted from the data. Uppermost curve (a) is fit using LJ 12-6 potential; next curve (b) is fit using LJ n-6 potential; curve below (c) is fit using n-8-6 potential; curve after (d) is fit using DLJ potential; curve next to bottom (e) is fit using MSV potential; bottom curve (f) is fit using SPFD potential.

Figure 6. Spherically symmetric intermolecular potentials for $H_2 + Ar$ as a function of intermolecular distance. Solid line: LJ 12-6 potential; dotted line: n-8-6 potential; dashed line: DLJ. Error bar on the LJ 12-6 potential represents accuracy with which it has been determined (based on results of ref. 7), $\pm 15\%$ of the potential energy at the attractive minimum, $\pm 0.05 \text{ \AA}$ in the position of the repulsive wall at $\sim 0.0 \text{ meV}$.

Figure 7. Spherically symmetric intermolecular potentials for $D_2 + Ar$ as a function of intermolecular distance. Symbols same as in Figure 6 except that dashed line represents SPFD potential

fit. Error bar on the LJ 12-6 potential represents accuracy with which it has been determined (based on results of ref. 7), $\pm 10\%$ of the potential energy at the attractive minimum, $\pm 0.04 \text{ \AA}$ in the position of the repulsive wall at $\sim 0.0 \text{ meV}$. (SPFD and n-8-6 potentials are very similar). Solid line: SPFD potential.

Figure 8. Spherically symmetric intermolecular potentials for $\text{D}_2 + \text{Ar}$ as a function of intermolecular distance. Solid line: SPFD potential; dashed line: M^2SV potential.

Figure 9. Spherically symmetric intermolecular potentials for $\text{H}_2 + \text{Ar}$ and $\text{D}_2 + \text{Ar}$ as a function of intermolecular distance. Solid line: LJ 12-6 potential fit to $\text{D}_2 + \text{Ar}$ data; dotted line: SPFD potential fit to $\text{D}_2 + \text{Ar}$ data; dashed line: LJ 12-6 potential fit to $\text{H}_2 + \text{Ar}$ data.

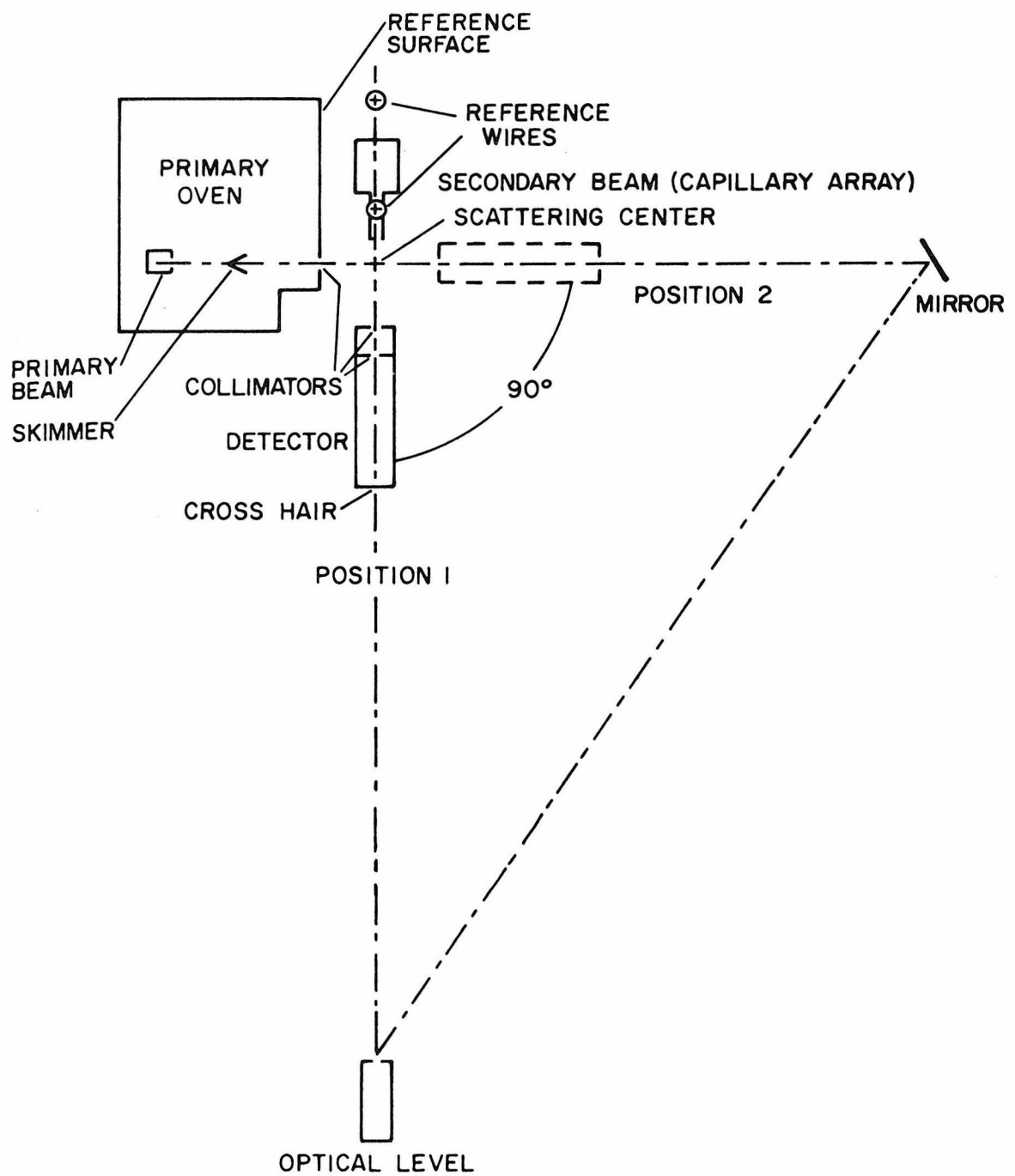


Figure 1.

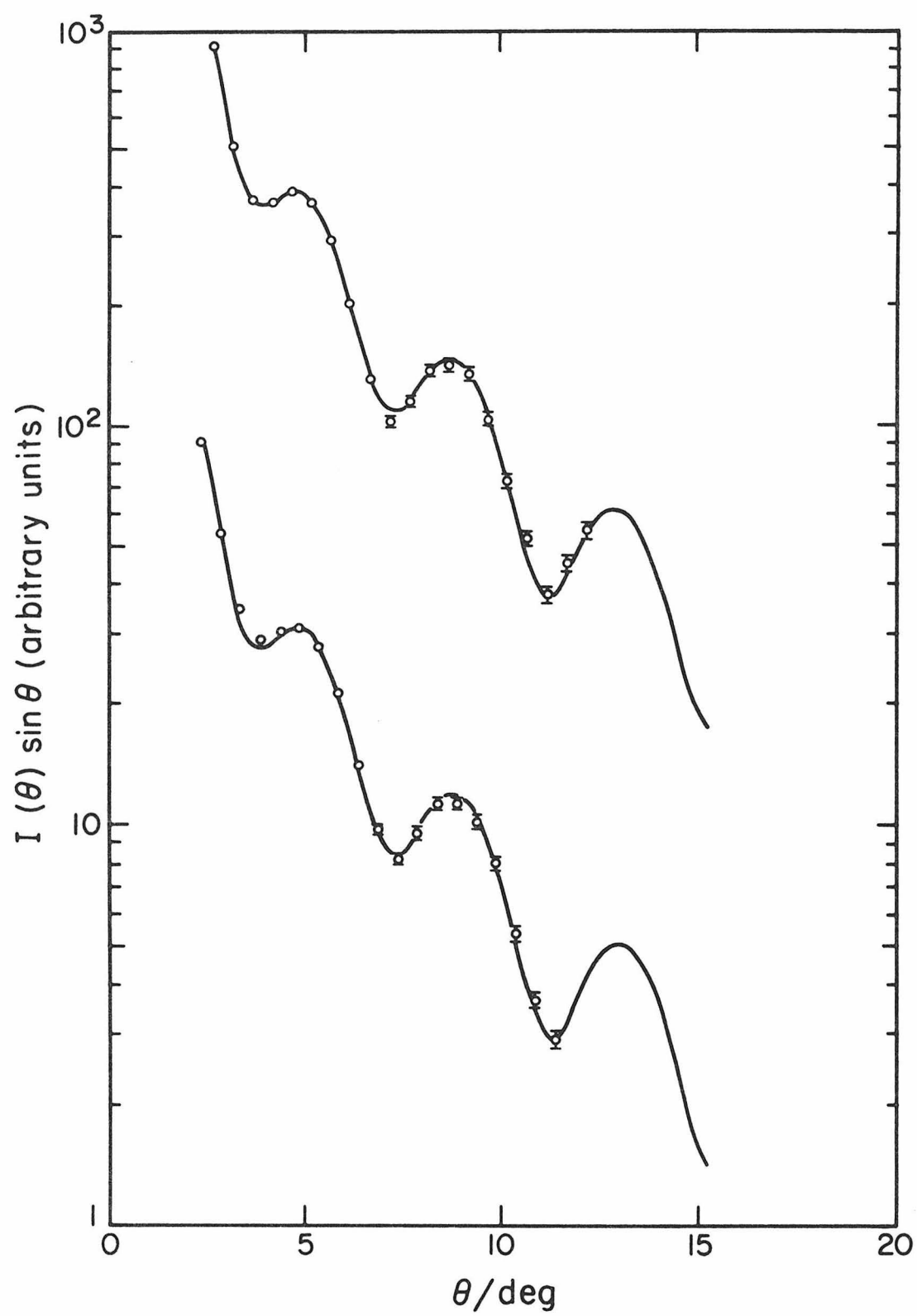


Figure 2.

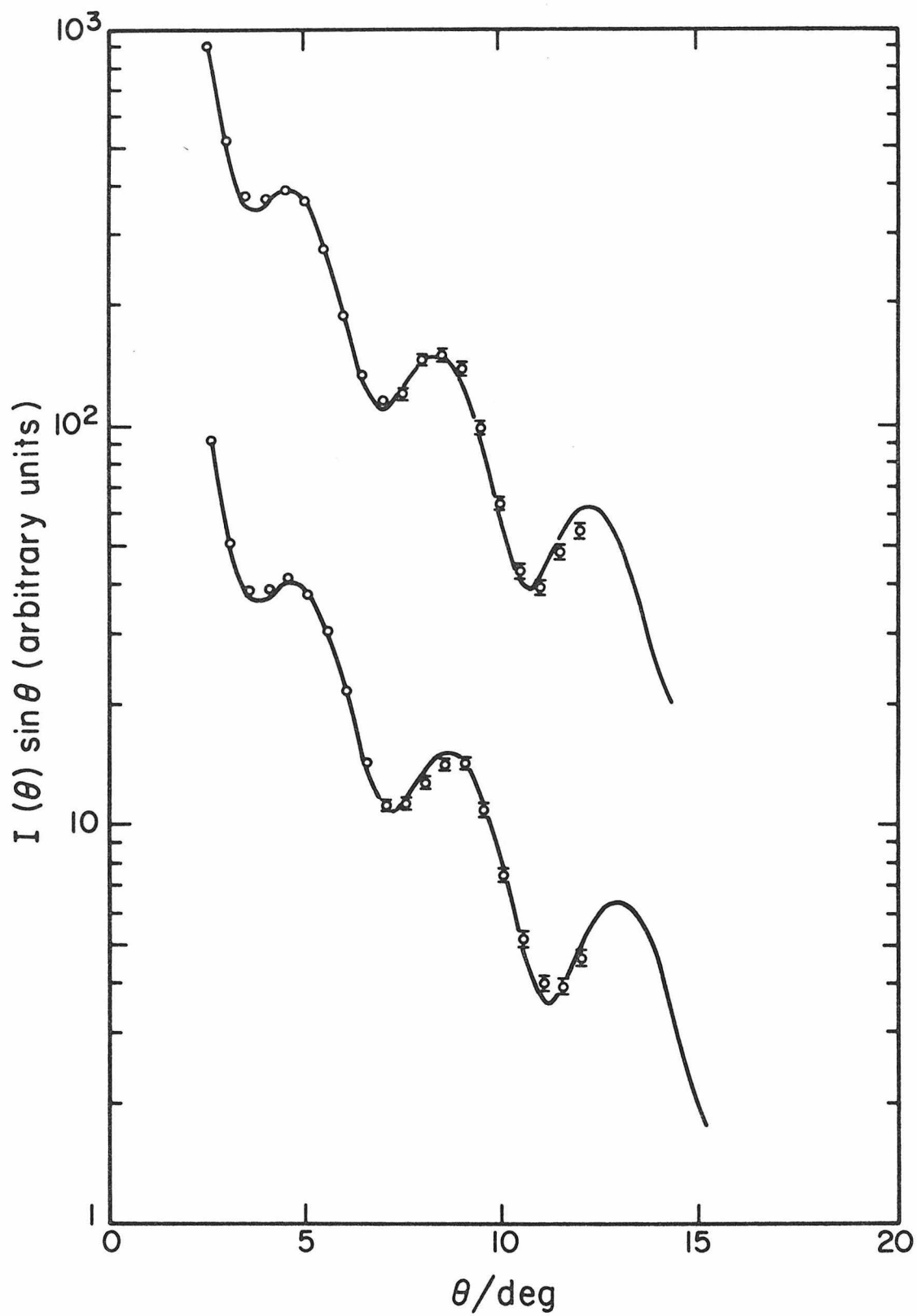


Figure 3.

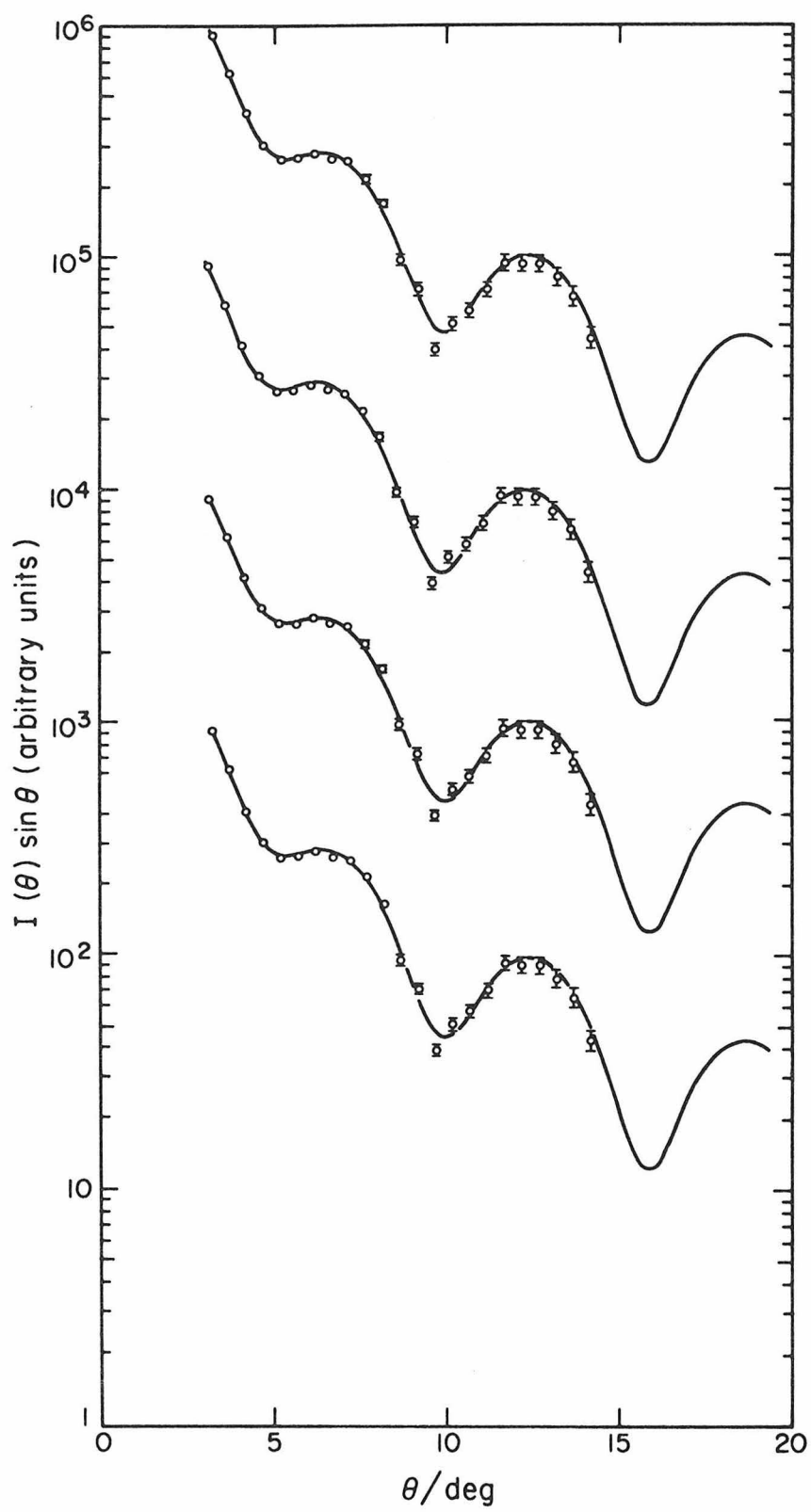


Figure 4.

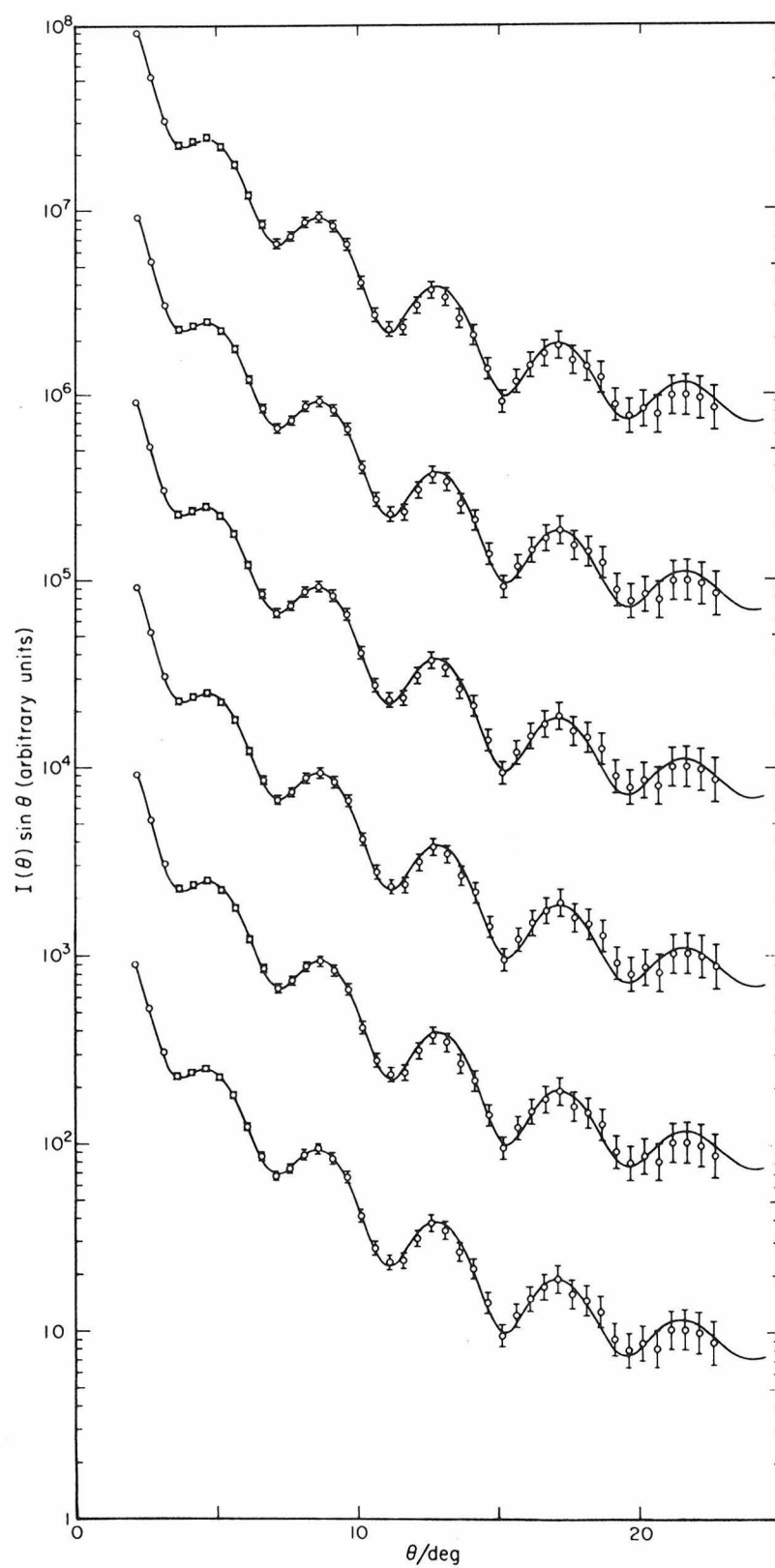


Figure 5.

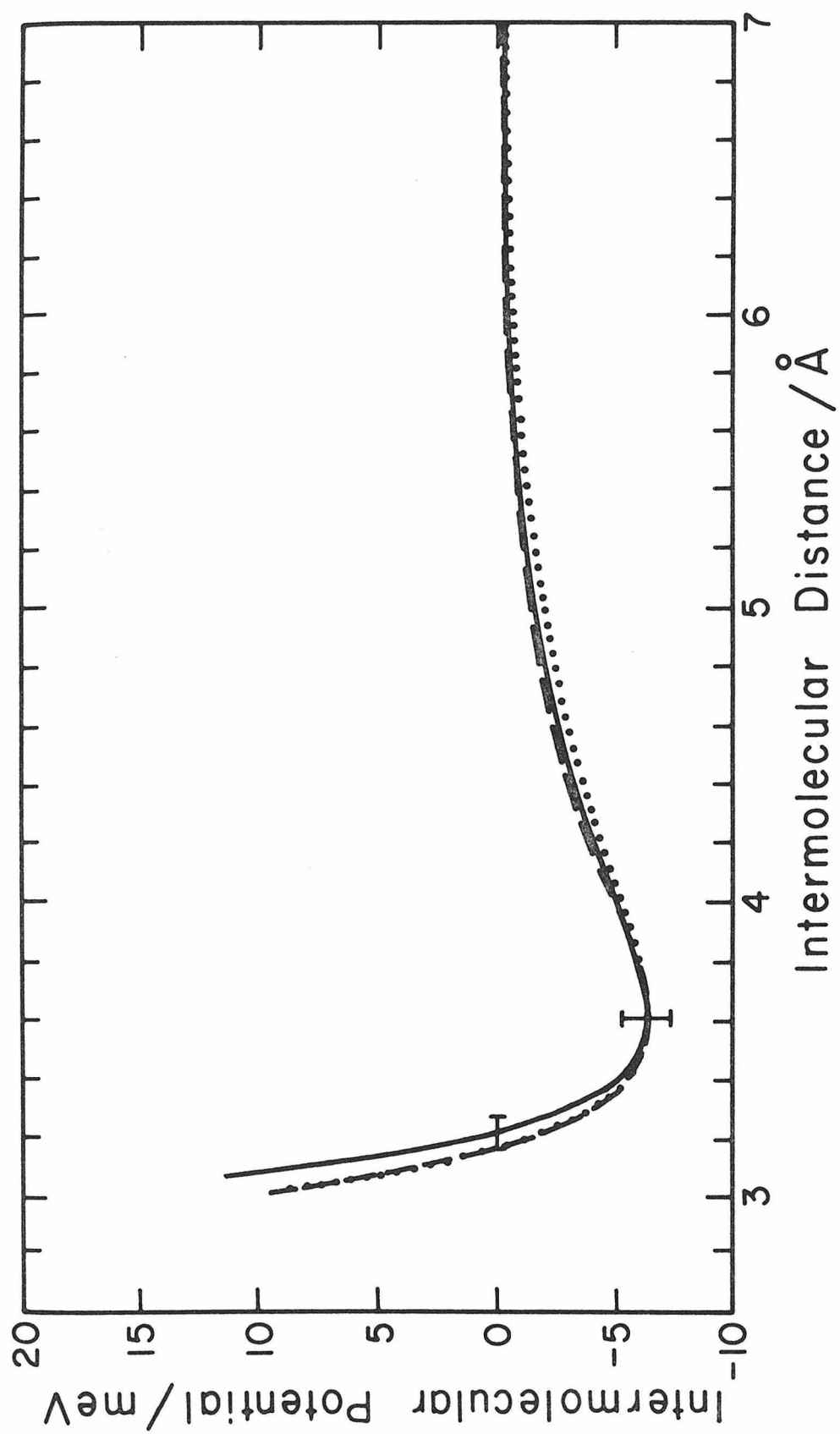


Figure 6.

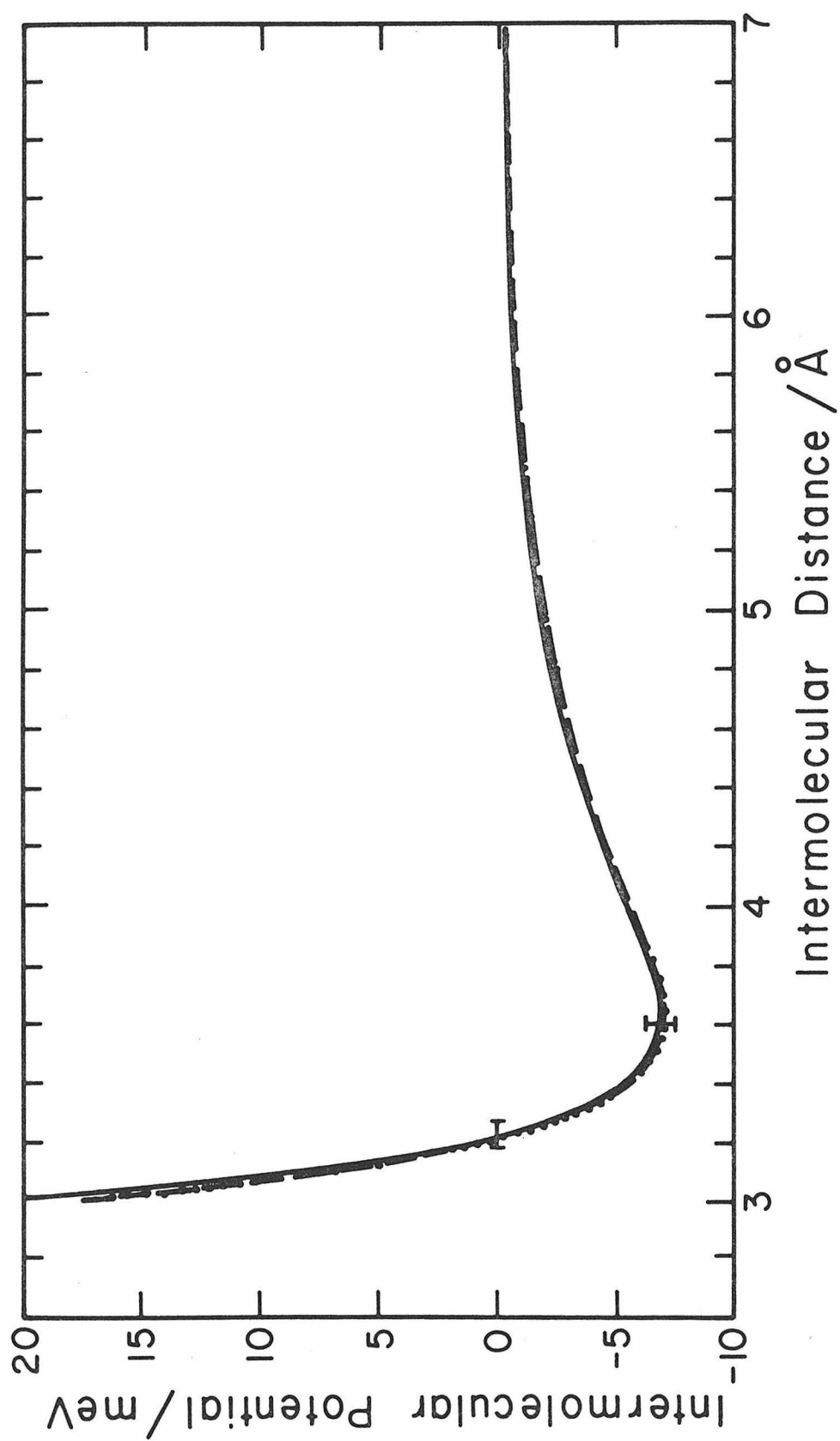


Figure 7.

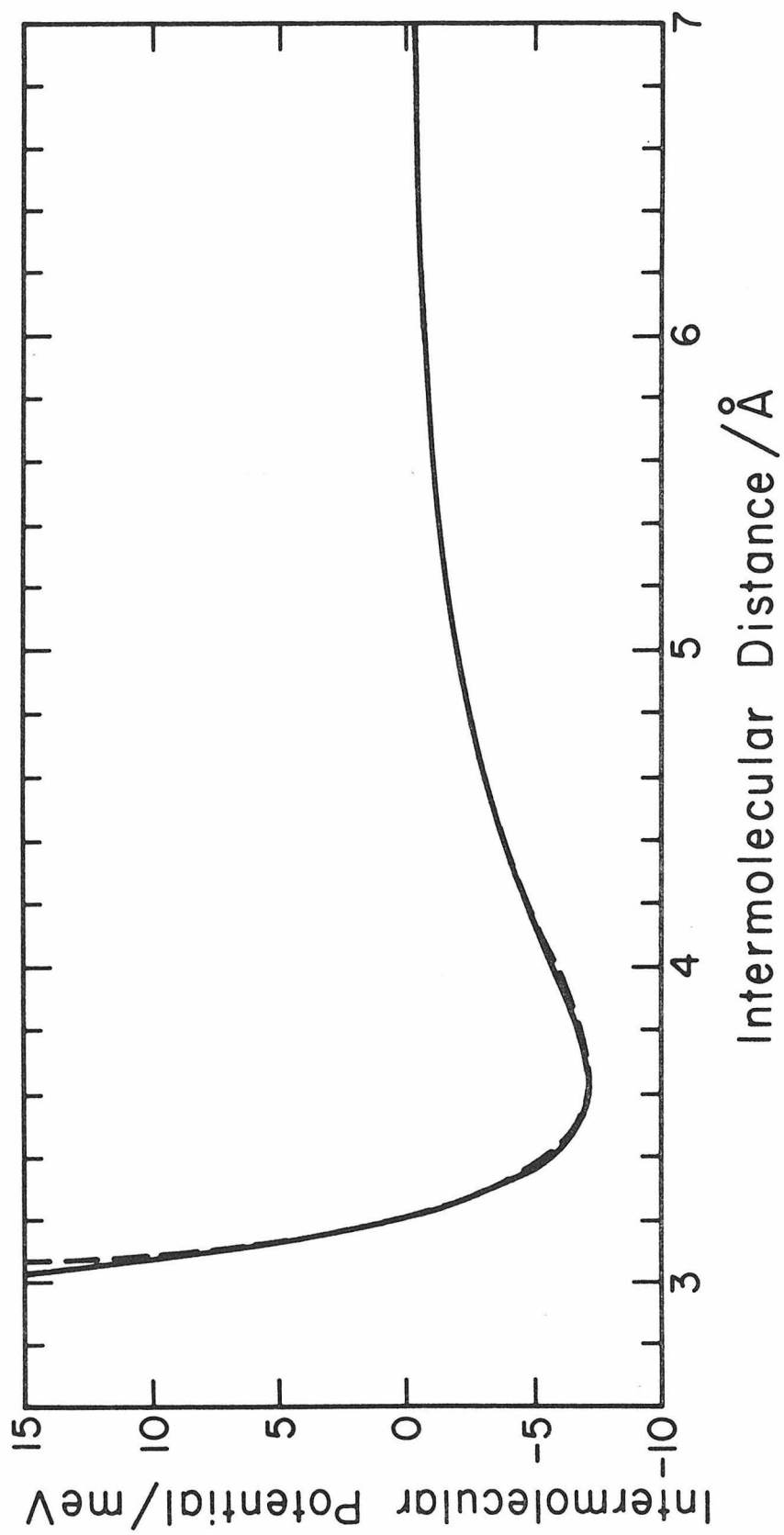


Figure 8.

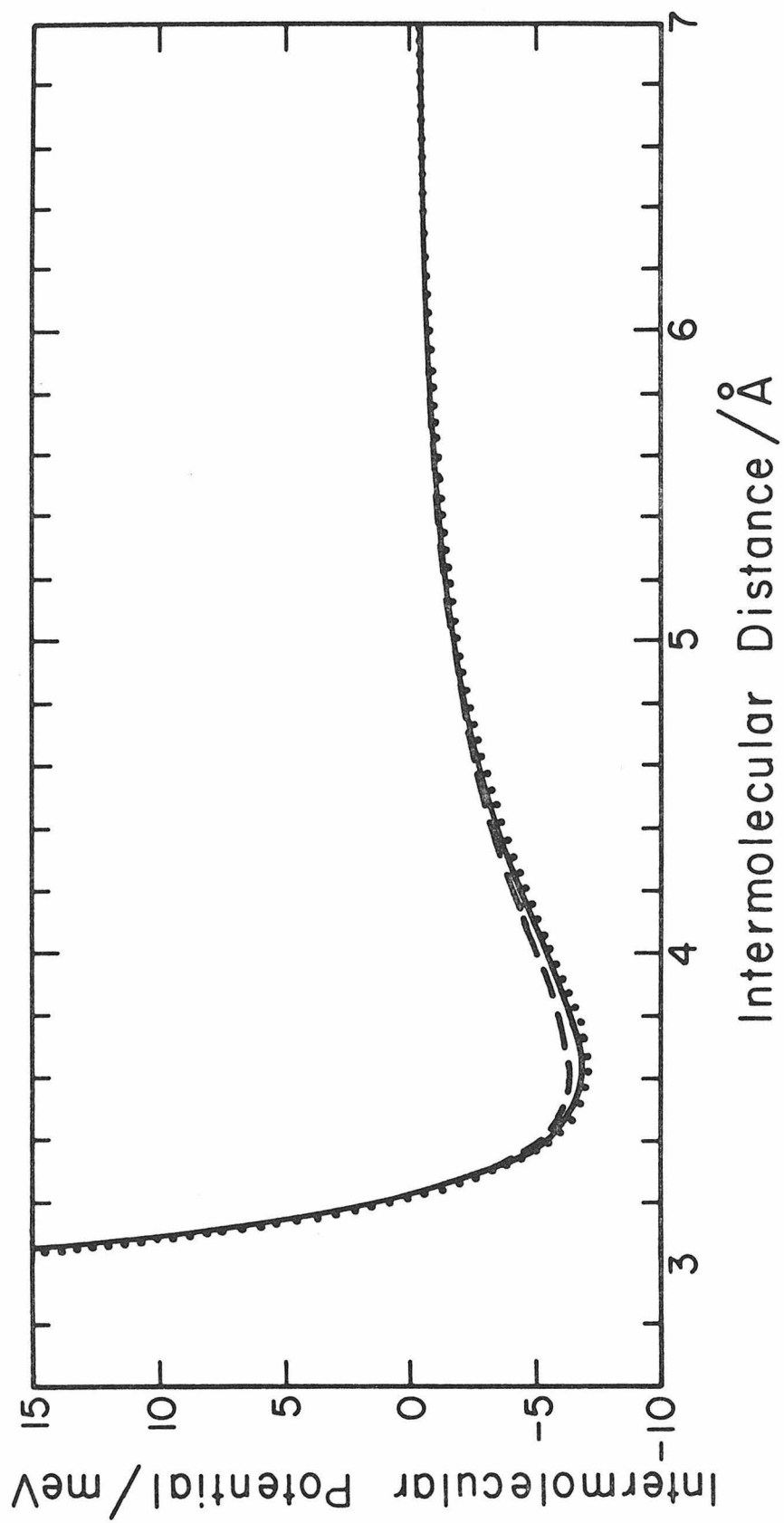


Figure 9.

CHAPTER 6

Spherically Symmetric Intermolecular
Potentials for He + CH₄, NH₃, H₂O, SF₆

Scattering of thermal He beams by crossed atomic and molecular
beams. IV. Spherically symmetric intermolecular potentials for
He + CH₄, NH₃, H₂O, SF₆.^{a)}

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ABSTRACT

Differential scattering cross sections are measured for He + CH₄, NH₃, H₂O, and SF₆, using the crossed molecular beams technique. These data, which are sensitive to the van der Waals attractive minima and adjacent regions of the intermolecular potential, are interpreted in terms of central-field models. No evidence is found for quenching of the observed diffraction oscillations. The interactions of the isoelectronic hydrides CH₄, NH₃, H₂O with He are found to have decreasing van der Waals radii in this sequence, and their attractive wells all have similar depths. However, the He + SF₆ attractive well is found to be anomalously deep, and provides a counter-example to the supposition that only the polarizability of the least polarizable of the interacting partners (atoms or molecules)

^{a)}This work was supported in part by a Contract (EY-76-S-03-767) from the Department of Energy. Report Code: CALT-767P4-175.

^{b)}Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

^{c)}Contribution No. 5798.

correlates with the van der Waals well depth. Simple combination rules for predicting unlike-pair potential parameters from the corresponding like-pair ones are tested and found inadequate.

I. INTRODUCTION

In recent years, a considerable amount of work has been done, both experimentally¹ and theoretically,² to improve our knowledge of interatomic potentials for van der Waals interactions.³ Molecular beam elastic scattering experiments yield information about these weakly attractive potentials at a level of detail inaccessible to many other techniques, especially for highly quantum systems.^{3c, 4, 5} Potentials for such systems are now well characterized, enabling experimental data of many different kinds to be correlated and accurately described.^{4, 6, 7} However, relatively little is known about atom-molecule or molecule-molecule van der Waals potentials, especially with regard to their orientation dependence.⁸⁻¹¹

In the present paper we analyze experimental measurements of the differential cross sections (DCS) for the highly quantum systems $\text{He} + \text{CH}_4$, NH_3 , H_2O , and SF_6 , using room-temperature crossed beams. The first three molecules represent an isoelectronic series, progressing from non-polar CH_4 to the highly polar NH_3 and H_2O . The $\text{He} + \text{SF}_6$ system is an example of the interaction between an atom and a highly symmetric large molecule. In this sense, the $\text{He} + \text{CH}_4$, NH_3 , and H_2O interactions span an interesting transition from a highly symmetric molecule to ones having rather asymmetric nuclear arrangements.

In Sec. II we briefly describe the apparatus used to measure DCS's, and the data reduction procedures used to analyze them. The DCS measurements, and the intermolecular potentials extracted from them, are presented in Sec. III. The importance of

anisotropic contributions (or lack thereof) to the measured potentials is discussed in Sec. IV, where we also compare our results with those of different experiments. Systematic trends in the potentials for the systems of this study are discussed. Finally, we summarize our findings in Sec. V.

II. EXPERIMENTAL AND DATA REDUCTION

The crossed molecular beam apparatus used in this investigation has been described previously,^{4, 8c, 12} and only its major components are discussed here. The modulated He primary beam comes from a room-temperature nozzle source, and is angularly well collimated in two stages of differential pumping. Secondary beams of the various gases studied emerge from a glass capillary array, directly into the scattering chamber, and are intense but only slightly supersonic. This beam source may be tilted upwards, thus uncrossing the beams and allowing measurements of the modulated primary beam scattered by background gas. Beam operating characteristics are summarized in Table I. We note that the secondary beam velocity distributions are best described by a Mach number of 1.5 and an "effective" specific heat ratio of 1.64,¹³ indicating only very slight cooling of internal states; thus the rotational temperature is presumably close to the ambient one (298 K).

A doubly-differentially pumped quadrupole mass spectrometer, scanning out-of-plane angles (with the in-plane scattering angle set to zero), is used to detect scattered He atoms. Angular spacings between the observed diffraction oscillations are slightly greater for this selection of scattering geometry than for the in-plane scanning geometry that the apparatus also permits. The out-of-plane geometry also allows a more straightforward verification of the symmetry for scattering on both sides of the primary beam, since coordinate frame transformations are not required for this purpose. This symmetry is exploited,

as in previous work, to yield scattering angle measurements accurate to within $\sim 0.03^\circ$.⁴ A 14-stage Cu-Be dynode multiplier is used for ion detection in the analogue mode. Its output is processed by several stages of preamplification, followed by phase-sensitive lock-in amplification, with the reference of the lock-in synchronized with the primary beam chopper. The output of the lock-in amplifier is digitized for sampling and averaging by a laboratory minicomputer, which also performs background signal subtraction by uncrossing the beams and remeasuring the modulated signal. With liquid-helium cryopumping in the ionizer region of the mass spectrometer, background pressures of $\lesssim 5 \times 10^{-10}$ torr were realized for these experiments. For the He + CH₄, NH₃, and H₂O experiments, total integration times at each scattering angle, representing data accumulated over several days' experimentation, ranged from ~ 2 min near 3° , to ~ 20 min at the widest angles. Corresponding signal-to-noise ratios were about 40 and 6, respectively. Because of its larger scattering cross section, the same signal-to-noise ratios could be attained for the He + SF₆ experiment with only $\sim \frac{2}{3}$ of the total integration times used for the hydride scattering partners.

Maintaining the scattering chamber pressure below $\sim 3 \times 10^{-6}$ torr, and keeping the primary beam attenuation due to scattering by the secondary beam at $\lesssim 5\%$, ensures that the single-collision conditions essential for DCS measurements prevail. Rapid cryopumping of NH₃ and H₂O on liquid-nitrogen cooled surfaces in the scattering chamber allowed the use of somewhat higher secondary beam pressures for these gases, which however, increased these beams' angular divergences somewhat (see Table I). Periodic mass spectro-

metric checks of the secondary beams revealed their high purity for all the scattering experiments. In particular, a careful check was made for dimers of the particularly condensable NH_3 and H_2O beams. No dimerization was detected down to the estimated sensitivity limit of $\sim 10^{-7}$ relative to the monomer, despite the integrity of (for example) H_2O ionic polymers as produced by electron-impact ionization.¹⁴

Scattered primary beam signals were measured between $\sim 2.8^\circ$ and $\sim 18^\circ$ (for CH_4 , NH_3 and H_2O) or 15.3° (for SF_6) above the plane of the beams, at a most probable relative collision energy of ~ 63 meV (for CH_4 , NH_3 and H_2O) or 64.1 meV (for SF_6). The corresponding de Broglie wavelengths are ~ 0.64 Å for the first three systems and 0.58 Å for the latter one. Measurements were also made for out-of-plane scattering below the plane of the beams, in order to locate accurately the zero position of the scattering scale (see above). Long-term drifts in beam intensities and detection efficiency were compensated for by periodic measurements of the scattering signal at a reference angle near 5° . The experimentally measured DCS's are shown in Fig. 1 for $\text{He} + \text{CH}_4$, $\text{He} + \text{NH}_3$ and $\text{He} + \text{H}_2\text{O}$, and in Fig. 2 for $\text{He} + \text{SF}_6$.¹⁵

The data reduction procedure used to obtain the fits shown in Figs. 1 and 2 has been described previously.⁴ It consists of a standard weighted nonlinear least-squares optimization of the parameters¹⁶ of mathematical functions chosen to represent the intermolecular potential, as discussed in Sec. III. As in previous work, appropriate velocity and angle averaging is included in the DCS

calculations. The overall apparatus relative velocity resolution is $\sim 15\%$ FWHM for He + CH₄, NH₃, H₂O, and $\sim 11\%$ FWHM for He + SF₆; the overall apparatus angular resolution is 1.9° FWHM.⁴

The least-squares parameter optimization minimizes the functional

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2. \quad (1)$$

As in our earlier studies, we define a goodness-of-fit statistical index more suitable than χ^2 for describing the quality of the fits to the DCS by

$$\Delta\alpha_{0.95}/\alpha = 1/\alpha \cdot t_{0.05}(n-k) \left[\frac{\chi^2}{(n-k) \cdot \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}}. \quad (2)$$

In these equations, I_i and σ_i are the measured (arbitrarily normalized) and calculated (absolute) cross sections¹⁵ at each of n scattering angles, respectively, with the normalized weights g_i . For n data points and k parameters, $t_{0.05}(n-k)$ is the appropriate Student t -distribution statistic for a 95% confidence level of the scaling factor α .¹⁷ We point out that the $\Delta\alpha_{0.95}/\alpha$ statistical index is independent of the arbitrary normalization used in the experiment. Furthermore, it is statistically adjusted for the number of data points and fitted parameters, which should allow a more straightforward comparison between different potential forms, and between scattering results from different laboratories.

III. DATA ANALYSIS AND INTERMOLECULAR POTENTIALS

The experimental DCS's measured as described in Sec. II and displayed in Figs. 1 and 2 were fitted by a least-squares procedure, using the intermolecular potential forms described below. These are written in the reduced form,

$$f(\rho) = \frac{V(r)}{\epsilon} , \quad \rho = \frac{r}{r_m} , \quad (3)$$

where r_m is the radius of the attractive minimum and ϵ is its depth. The zero of the potential, occurring at $r = \sigma$, is related to r_m and the potential shape $f(\rho)$, and is not an independent parameter. The intermolecular distance r is usually regarded as the separation between the He atom and the molecular center-of-mass. For the anisotropic interactions considered in the present study, alternate choices for the origin of r , such as the molecular center-of-charge, could also be considered. Among the mathematical shape functions $f(\rho)$ used in the present study is the familiar LJ12-6 potential, in order to allow a comparison with the results of integral scattering measurements for He + CH₄,¹⁸ and of other DCS results for He + NH₃ and He + H₂O.¹⁹ More flexible parametric forms for $f(\rho)$ are however, required to accurately describe the weak van der Waals interactions being studied.^{12, 20} One such potential function is the Morse-spline-van der Waals (MSV) parameterization,²¹ given by

$$\left. \begin{aligned}
 f(\rho) &= e^{\beta(1-\rho)} \left[e^{\beta(1-\rho)} - 2 \right] && \text{for } \rho < \rho_1 \\
 f(\rho) &= (\rho_2 - \rho)[s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1)[s_2(\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\
 f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho > \rho_2
 \end{aligned} \right\} \quad (4)$$

The cubic spline coefficients s_i ($i = 1$ through 4) are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 with the first one being chosen as the inflection point of the Morse function, $\rho_1 = 1 + \beta^{-1} \ln 2$.

It has recently been shown that, for room-temperature DCS measurements of the type being considered in the present study, up to five independent potential parameters may be determined.²⁰ For these parameters to be statistically independent of each other, and hence physically meaningful, the mathematical form of the potential in which they are used must be appropriately flexible. For the experiments considered herein, the shape of the attractive minimum region, to which the DCS data are highly sensitive, must be adjustable independently of the adjacent regions. In particular, for systems with a collision energy relative to ϵ of ~ 30 (however, see also Sec. IV), the DCS data are somewhat sensitive to the weakly repulsive wall (up to $V \simeq 8$ meV), requiring a parametric form that decouples this region from the attractive well.²⁰ Consequently, we also analyze the data using a modification of the MSV potential, having a second Morse function joined smoothly to the first at $r = \sigma$. In the resulting M^2SV potential,²² the additional Morse parameter β' is used exclusively to

describe the shape of the repulsive wall. Another parameterization that successfully decouples the attractive minimum region from adjacent regions of the potential is the third-order Simons-Parr-Finlan Dunham (SPFD) potential,²³ and is given by

$$\left. \begin{aligned} f(\rho) &= b_0 \lambda^2 \left(1 + \sum_{i=1}^3 b_i \lambda^i \right) - 1 && \text{for } \lambda = 1 - 1/\rho \text{ and } \rho < \rho_f \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_f \end{aligned} \right\} \quad (5)$$

The two highest-order SPFD coefficients b_2 and b_3 are fixed by smoothness conditions²⁴ at the value of $\rho_f = 1.6$.^{4, 20}

Although some of the dispersion coefficients have been calculated for the interactions of the three lighter molecular partners with He,^{25, 26} we felt it best to fit this region of the potential empirically, for reasons discussed below. By fixing $c_8 = c_{10} = 0$ in Eqs. (4) and (5), we obtain "effective" dispersion constants C'_6 for each interaction pair. We expect these C'_6 ($= \epsilon r_m c_6$) to be somewhat greater than the corresponding correct C_6 constants, because of our neglect of higher-order contributions. This neglect may have a substantial effect on the long-range part of the potential, especially for interactions of He with the highly polar molecules NH_3 and H_2O . These should have large r^{-7} contributions to the dispersion energy, which have been estimated as $\sim 30\%$ of the r^{-6} component (at $\rho = 1.6$), even for the nonpolar $\text{He} + \text{CH}_4$ interaction.²⁶ However, the sensitivity of the present DCS data to the intermolecular potential is restricted to reduced distances $\rho \lesssim 1.7$, since very low-angle scattering data are lacking.²⁰ Because we use

the dispersion expansion only for $\rho \gtrsim 1.6$, the $C'_6 r^{-6}$ representation should provide a reasonable approximation to that part of the long-range potential which affects our DCS scattering measurements. For these reasons, the C_6 parameter is permitted to vary in these fits instead of being fixed at its theoretical value. The MSV potential thus has four adjustable parameters (r_m , ϵ , β , and c_6), while the M^2SV and SPFD potentials each have five (r_m , ϵ , β , β' , and c_6 ; r_m , ϵ , b_0 , b_1 , and c_6 , respectively).

A prerequisite for Eq. (3), together with the reduced potential forms of Eqs. (4) and (5), to provide an accurate description of the intermolecular interactions of the systems considered in the present paper, is that anisotropic contributions to the potential must be small over the intermolecular distance range to which the DCS data are sensitive. Although this central-field assumption may not be made a priori for the analysis of atom-molecule scattering experiments,¹⁰ we nevertheless base our extraction of intermolecular potentials on it. This procedure is justified in the following discussion (Sec. IV).

IV. DISCUSSION

The van der Waals interactions for the atom-molecule systems considered here are anisotropic. As such, the central-field potentials generically represented by Eq. (3) provide at best an approximate description of these interactions. Consequently, the first problem to be addressed is the validity of the central-field assumption.

Even if this assumption were invalid within the range of intermolecular distances sampled, Eq. (3) could still be expected to provide an "effective" description of processes which occur on a time scale much slower than molecular rotations. Any such process would sample only the spherical average of the anisotropic potentials for sufficiently weak interactions. Such processes do not, however, include the present scattering experiments. Typical rotation frequencies of the molecules in the secondary beams used in the present studies are $\sim 10^{12}$ Hz for the hydrides and $\sim 5 \times 10^{10}$ Hz for SF_6 . Under the present experimental conditions, the collision interaction time (to traverse $\sim 8 \text{ \AA}$) is $\sim 5 \times 10^{-13}$ sec, corresponding to only about half a revolution during the collision for the hydride molecules, whereas the SF_6 molecule remains essentially motionless. The inversion frequency of NH_3 is ~ 50 times slower than its rotation frequency, and therefore does not contribute to averaging of the interaction.

Interpretations of scattering results for anisotropic interactions have been based for some time on semiclassical calculations.²⁷ However, this theory is inappropriate for the highly quantum systems studied herein. As an example of the differences between semiclassical

and quantal scattering, we note that the present DCS's exhibit strong undulations well beyond the classical rainbow angle (at $\sim 4^\circ$ for these systems); semiclassical oscillations should not appear on the dark (wide-angle) side of the rainbow^{8c,28} unless the effect of complex trajectories is included.²⁹ In the present study, we predicate our analysis on a recent empirical, quantitative validation of the central-field assumption for highly quantum systems that are only weakly anisotropic.¹⁰ In that study (Paper III of this series), it was found that the DCS's for He + N₂, O₂, CO, and NO showed little evidence for quenching of the observed rapid quantum oscillations that is expected for anisotropic potentials both semi-classically²⁷ and quantum mechanically,³⁰ and that has recently been observed for scattering in highly anisotropic systems (e.g., He + CO₂).¹¹ This lack of quenching is equally evident for other H₂, D₂, and He collisions with weakly anisotropic molecules.⁸ Moreover, the results of Paper III showed that the spherical averages of the anisotropic potentials extracted from an infinite-order sudden approximation^{30a} analysis of the DCS data presented there were indistinguishable, within experimental error, from the potentials obtained by accurate central-field analyses of those data. This is true despite a van der Waals attractive minimum distance that was found to be up to 20% greater for linear configurations than for perpendicular ones. From this it was concluded that a central-field analysis does indeed yield the spherically symmetric component of the interaction potential. This conclusion is valid for weakly anisotropic systems showing little evidence (according to the quantitative criteria given in Paper III) for quenching of the rapid oscillatory

structure characteristic of central-field elastic scattering of highly quantum systems. This had previously been supposed for molecular scattering.⁸ Unfortunately, a quantitative validation of this result for the present polyatomic systems would be difficult, because too many parameters would be needed to adequately model the corresponding potentials (e.g., two angular degrees of freedom, strong polar effects, etc.). Consequently, we may apply only the qualitative aspects of the conclusions enumerated above to the present study. We first discuss the results for the hydride partners, and treat the $\text{He} + \text{SF}_6$ interaction somewhat separately later in this section.

A. $\text{He} + \text{CH}_4$, NH_3 , and H_2O interactions

Potential parameters obtained from central-field analyses of the $\text{He} + \text{CH}_4$, NH_3 , and H_2O DCS's are presented in Table II. As in previous work, it may immediately be seen that the five-parameter M^2SV and SPFD potentials are better able to fit the DCS data for these three systems than is the MSV model, even when the use of one additional parameter in the former potentials is statistically accounted for⁴ (see $\Delta\alpha_{0.95}/\alpha$ column of Table II). Again as in previous work, the well position parameters are largely model-independent ($\pm 0.06 \text{ \AA}$ for r_m and $\pm 0.01 \text{ \AA}$ for σ); however, ϵ values obtained by using the MSV potential model are consistently $\sim 20\%$ greater than for the M^2SV or SPFD potentials. Despite the different mathematical parameterizations of the latter two potentials, they both have the appropriate flexibility (see also Sec. III) to allow ϵ to be determined with an accuracy of about $\pm 10\%$;²⁰ indeed the M^2SV and SPFD values of ϵ for the $\text{He} + \text{CH}_4$, NH_3 , and H_2O systems are different by only $\sim 2\%$. We also display in Table II

the integral cross sections Q at a relative collision energy of 64 meV, calculated for these three systems using the partial wave expansion. Because of the consistently greater well depths of the MSV potentials, their Q are about 10% larger than those of the corresponding M^2SV or SPFD potentials.

The quality of even the five-parameter fits to the He + CH₄, NH₃, and H₂O experimental DCS's unfortunately is not quite as good as could be hoped for ("good" fits furnish $\Delta\alpha_{0.95}/\alpha \lesssim 2.2\%$ ²⁰). By comparing the calculated DCS's to the experimental ones, as in Fig. 1, we see however, that there is no evidence for quenching of the oscillations in the experimental DCS relative to those calculated using central-field potentials. If anything, the experimental DCS's have slightly greater oscillatory amplitudes than do the calculated ones (cf. the first and second minima of He + CH₄, and the first and second maxima of He + H₂O). In any case, all three systems yield ϵ and r_m values that are very close to those of other atomic^{7,12,31} and molecular^{10,19} interactions with He. Since there is thus no evidence for significant anisotropic contributions to the measured DCS's, we conclude¹⁰ that the central-field analysis yields the spherically symmetric component of the intermolecular potential, for the range of reduced distances probed in these experiments ($0.8 \lesssim \rho \lesssim 1.7$).

The He + CH₄ interaction potential has previously been studied by (arbitrarily normalized) integral scattering cross section measurements Q , as a function of the collision velocity v .¹⁸ An LJ12-6 analysis of these data yielded a value of $\epsilon \cdot r_m$ as a measure for the "area" of the attractive well. As an indication of the consistency between those $Q(v)$ measurements and the present DCS results, we display in Table III values of $\epsilon \cdot r_m$ for He + CH₄ as determined from both these experiments (within the LJ12-6 parameterization). The agreement is seen to be quite satisfactory; we also present $\epsilon \cdot r_m$ values for our more accurate five-parameter potentials. In addition, we compare

in Table III our fitted "effective" C'_6 dispersion coefficients (Sec. III) with those obtained theoretically.^{25, 26} The experimentally determined coefficients for He + CH₄, NH₃, and H₂O are seen to be ~ 70% greater than for the corresponding calculated ones. Although this discrepancy is rather large, it is not unexpected, and is caused primarily by our neglect of higher-order contributions to the dispersion interaction (Sec. III).

Finally, we compare in Table III r_m and ϵ parameters obtained from LJ12-6 analyses of the present DCS results, and those of another laboratory.¹⁹ All these experiments were performed at about the same relative collision energy (60 ± 4 meV), and for about the same range of scattering angles (2° or 3° to $\sim 18^\circ$). Data reduction using the same potential form should allow a fairly direct comparison between these results, although we caution that the LJ12-6 parameterization is too rigid to yield accurate intermolecular potentials for the interactions being considered. We see that the He + H₂O results agree well, but that the σ (or r_m) parameters for He + NH₃ differ substantially. A similar discrepancy also exists for H₂ + NH₃ scattering, where again the Waterloo results¹⁹ yielded a significantly smaller σ (or r_m) parameter than obtained in this laboratory.^{8c} We have conducted very extensive self-consistency checks of our measurements⁴ comparable to those of the Waterloo group.¹⁹ We have also established the compatibility of our in-plane and out-of-plane measurements (the latter geometry is kinematically identical to the out-of-plane scattering geometry used by the Waterloo group). Nevertheless, the experimental (H₂, He) + NH₃ scattering data of the two laboratories still appear to be somewhat inconsistent. That the discrepancy appears

only for scattering of NH_3 , but not for the $\text{He} + \text{H}_2\text{O}$ or $\text{He} + \text{Ar}$ systems,^{4,12} indicates that the cause may lie in the secondary beam composition. We have already eliminated the possibility of NH_3 beam impurities, particularly with respect to dimerization by highly sensitive mass spectrometric checks (Sec. II). To compare the quality of the fit to the data, we may renormalize (see footnote e of Table II) the scattering intensity of the present DCS results (fit to the LJ12-6 potential) to those obtained previously.¹⁹ We find a goodness-of-fit statistic of $\chi^2 = 17.9$ [Eq. (1)], even with four data points more than the Waterloo experiment, which yielded a corresponding value of $\chi^2 = 38.3$. The difficulty in the fit to the latter experiment is evident for scattering angles beyond $\sim 10^\circ$, where the experimental DCS is systematically higher than the calculated one.¹⁹ It is possible that the above differences are caused more by the rigidity of the LJ12-6 potential form than by inconsistencies between the data; more flexible potential forms are needed to attain appropriate descriptions of DCS scattering results²⁰ from the two laboratories (such as the M^2SV and SPFD potentials used in this study).

In the above comparison between the present results and potentials obtained previously, we have ignored bulk property data. This is because the latter are usually sensitive only to interactions more repulsive than those sensitively probed by the present thermal scattering experiments.⁴ Moreover, the effect of potential anisotropies on bulk properties has not yet been investigated to a sufficient extent.^{30a}

We now discuss systematic trends among the accurate five-parameter potentials extracted from the present $\text{He} + \text{CH}_4$, NH_3 , and

H₂O DCS data. The SPFD potentials for these systems are displayed in Fig. 3; the M²SV potentials are indistinguishable from the former within experimental error and are not plotted. Two features are clearly apparent from a comparison of these curves. Most evident is that the repulsive walls for the three systems are displaced to smaller intermolecular separations in the order CH₄ > NH₃ > H₂O. This trend is correlated with the H...H non-bonded distance, and thus to the molecular size. We also notice that continuing in this isoelectronic series, the He + Ne interaction has $\sigma = 2.73 \text{ \AA}$,³¹ 0.28 Å less than for the He + H₂O potential (Table II); accurate He + HF data are not yet available.^{33,34} Thus, it appears that although H atoms are ineffective in promoting anisotropies in the interaction of He with CH₄, NH₃, and H₂O, they do increase the apparent size of these molecules. It may be that the lone-pair electrons of NH₃ and H₂O contribute to the apparent isotropicity of the interactions of these molecules with He, despite their rather asymmetric nuclear arrangements.

The second trend displayed by the potentials of Fig. 3 is evident in their long-range regions. We see that the strength of the attractive potential for $r \gtrsim 4 \text{ \AA}$ falls in the sequence CH₄ $\approx$ NH₃ > H₂O. This is also reflected by the calculated C₆ constants (see Table III).²⁵ The calculated long-range potential is dominated by induced dipole-induced dipole, rather than by dipole-induced dipole, dispersion forces. The former accounts for 90% of the He + NH₃ C₆ coefficient and 80% of the He + H₂O one.³² The permanent dipole moments of NH₃ and H₂O thus do not substantially affect their long-range interactions with He, as is also reflected by the experimental potentials of Fig. 3.

B. The He + SF₆ interaction

We discuss this system separately from the He + CH₄, NH₃, and H₂O ones primarily because of the much larger well depth for He + SF₆, as is evident from the potential parameters presented in Table II. We note that this well depth is more than twice that for most other molecular interactions with He,^{10,19} having the important consequence of reducing the collision energy from ~ 30 ϵ to ~ 13 ϵ . (For a system with a well depth of $\epsilon \simeq 2$ meV, the latter value corresponds to a collision energy of ~ 25 meV.) Consequently, we expect the He + SF₆ DCS to be more sensitive to the long-range region of the intermolecular potential than are those of the other systems considered here. Computer simulation calculations²⁰ (with which the He + CH₄, NH₃, and H₂O systems were compared) lead us to expect our He + SF₆ potential to have somewhat better than 20% accuracy for reduced distances ρ between about 1.4 and 1.6. Those simulations also indicate that our determination of the He + SF₆ well depth should still be accurate to $\sim 10\%$. Furthermore, the He + SF₆ DCS should be rather insensitive to the repulsive wall, and so the M²SV and SPFD potential forms should effectively have about the same flexibility as does the MSV potential. This effect has been shown to occur for low collision energy (~ 9 ϵ) interactions in highly quantum systems.²⁰ Indeed, the MSV potential parameters displayed in Table II show no bias towards a larger well depth than is obtained from the M²SV and SPFD analyses, and no improvement in fitting quality is seen. The corresponding integral cross sections also show no bias (see Sec. IV.A). It may be more appropriate to introduce greater flexibility into the long-range region by using a dispersion term of higher order than C₆. We also note that the He + SF₆ potential predictably has

a rather large range parameter r_m . The He + SF₆ potential extracted from the present DCS results is displayed in Fig. 4.

Among the systems investigated here, the He + SF₆ DCS gives the best potential fit (Table II): there is again no evidence in that fit for quenching of the rapid quantum oscillatory structure (Fig. 2). We conclude that the present He + SF₆ data are insensitive to anisotropic components of the potential, which probably only become evident for repulsive interactions. The large ϵ observed for this system may be due to interactions with the F atoms. It would be interesting to conduct a scattering study of He + CF₄ to elucidate the nature of such interactions. It is also possible that the d-orbital of the S atom plays a role in governing the nature of the van der Waals attractive interactions. Note however, that the spherically symmetric H₂(D₂) + SF₆ van der Waals interaction has about the same ϵ as do the H₂(D₂) + NH₃ and H₂ + CH₄ interactions.^{8c} The He + SF₆ potential thus provides a clear counter-example of previous empirical observations that it is primarily the least polarizable partner that is responsible for the magnitude of the van der Waals well depth.³¹

The effect of the large r_m and ϵ parameters on He + SF₆ scattering is apparent from the fact that the DCS of Fig. 2 is significantly different from those of Fig. 1. The residual rainbow at $\sim 4^\circ$ is more evident than in the He + CH₄, NH₃, and H₂O DCS's while the amplitude of the rapid quantum oscillations is comparably diminished. We also see a closer spacing of these oscillations, expected from their reciprocal relationship to the reduced collision wavenumber, which in turn is directly proportional to r_m .²⁸

C. Combination Rule Predictions

Historically, the incentive for the extensive development of combination rules—only some of which are based soundly upon theoretical or experimental considerations^{32, 35}—may in part be attributed to difficulties in the bulk sample measurements of unlike-pair properties. The validity of such rules is predicated upon the existence of a single reduced form or "universal function" for the interaction pairs being considered. The existence of such a universal function is related to the "law of corresponding states" for the equation of state of real gases.³² Together with values for the distance and energy scaling parameters (σ or r_m and ϵ , respectively) appropriate for each of these interactions, the corresponding potential energy functions would then be predictable. However, the concept of such universal functions has been shown to be inappropriate for potentials determined accurately by other means;^{3d, 20} the validity of various combination rules for predicting potential parameters for unlike-pair interactions from the constituent like-pair ones has been discussed extensively for atom-atom potentials.^{3d, 4, 7, 31, 36}

Combination rules for describing interactions in molecular systems ignore anisotropic contributions to the interaction potential and consider only their spherically symmetric components. As discussed earlier, this approximation is valid for the present atom-molecule systems for the range of intermolecular distances sampled by our experiments, but the validity of the central-field assumption for the constituent like-pair molecule-molecule interactions is uncertain. Moreover, experimental determinations of homomolecular interaction potentials have yielded widely different values for the potential parameters.³⁷

As a quantitative indication of the difficulties encountered in using combination rules to accurately predict potential parameters for unlike-pair interactions, we compare in Table IV the present experimental determinations of σ and ϵ to the results of several commonly used simple combination rules. The like-pair potential parameters are based on a variety of potential energy functional forms. It may easily be seen that the predictions for σ are consistently too low, even when [for $(\text{NH}_3)_2$ and $(\text{H}_2\text{O})_2$] the wide range of like-pair experimental results are considered. Similarly, the predictions for ϵ are consistently too high (except for $\text{He} + \text{SF}_6$). The failure of the combination rules is in all cases beyond the experimental error of $\pm 1\%$ in our determination of σ , and $\pm 10\%$ in ϵ .²⁰ The use of combination rules should therefore be restricted to those interactions for which accurate potentials are unavailable, and must not be considered reliable.^{3a}

V. SUMMARY AND CONCLUSIONS

Van der Waals potentials for the interactions of He atoms with molecules of CH_4 , NH_3 , H_2O , and SF_6 have been extracted from differential cross sections (DCS), as measured by the crossed-beams technique. For systems showing only weak anisotropies, a suitable central-field analysis yields the spherically symmetric component of the interaction potential.¹⁰ The present DCS's show no evidence of quenching, which has been predicted,³⁰ and observed,¹¹ for molecular scattering in highly anisotropic quantum systems. Hence we conclude that the central-field potentials extracted from the data are good representations for the spherically symmetric components of the He + CH_4 , NH_3 , H_2O , and SF_6 interactions, and that anisotropic components are small for the attractive, and even weakly repulsive, regions of their potentials.

We find a simple correlation between molecular size and the van der Waals radii of the He + CH_4 , NH_3 , and H_2O interactions, which fall in the sequence $\text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O}$. This sequence may be extended to the isoelectronic He + Ne interaction,³¹ whose size is even less than that of He + H_2O . We find no substantial effect of the large dipole moments of NH_3 and H_2O upon the long-range attractive potential. The He + SF_6 potential is found to violate the usual supposition³¹ that only the least polarizable of the interacting atoms (or molecules) are correlated with the van der Waals well depth.

Simple combination rules for predicting values of the well depth ϵ and interaction distance σ [$V(\sigma)=0$] of unlike pairs from the corresponding like-pair potential parameters are tested and found inadequate.

TABLE I. Beam operating conditions

Characteristic	Primary beam	Secondary beams			
Beam gas	He	CH ₄	NH ₃	H ₂ O	SF ₆
Inlet pressure/torr	1300	2.9	4.8	4.1	3.9
Inlet temperature/K	298	298	298	298	298
Angular FWHM ^a /deg.	1	4	6	6	3
Most probable velocity/(km/sec)	1.757	0.792	0.769	0.747	0.262
Velocity FWHM, ^a $\Delta v/v$	0.10	0.75	0.75	0.75	0.75
Mach number ¹³	18	1.5	1.5	1.5	1.5

^aFull width at half-maximum.

TABLE II. Central-field intermolecular potentials fit to the experimental DCS's.

System ^a	potential type ^b	$r_m/\text{\AA}$	$\sigma/\text{\AA}$	ϵ/meV	shape parameters ^c	$Q^d/\text{\AA}^2$	$\chi^2 e, f$	$\Delta\sigma_{0.95}/\sigma^f$ (%)
He + CH ₄ (30)	MSV	3.86	3.41	2.42	$\beta = 6.01; c_6 = 2.20$	95	340 (4)	2.73
	M ² SV	3.90	3.40	2.06	$\beta = 5.43; \beta' = 10.2; c_6 = 1.92$	88	270 (5)	2.46
	SPFD	3.80	3.40	2.00	$b_0 = 36.2; b_1 = -5.96; c_6 = 2.10$	86	250 (5)	2.39
He + NH ₃ (31)	MSV	3.76	3.29	2.48	$\beta = 5.54; c_6 = 2.23$	91	200 (4)	2.13
	M ² SV	3.82	3.28	2.03	$\beta = 4.94; \beta' = 9.57; c_6 = 1.86$	83	140 (5)	1.83
	SPFD	3.73	3.28	2.08	$b_0 = 27.5; b_1 = -4.98; c_6 = 2.19$	84	150 (5)	1.89
He + H ₂ O (30)	MSV	3.46	3.03	2.71	$\beta = 5.54; c_6 = 2.40$	80	210 (4)	2.53
	M ² SV	3.50	3.01	2.31	$\beta = 5.02; \beta' = 10.6; c_6 = 2.01$	73	160 (5)	2.24
	SPFD	3.38	3.01	2.27	$b_0 = 31.4; b_1 = -6.15; c_6 = 2.30$	71	150 (5)	2.16
He + SF ₆ (26)	MSV	4.24	3.75	4.68	$\beta = 6.10; c_6 = 1.25$	220	100 (4)	1.46
	M ² SV	4.23	3.76	4.68	$\beta = 6.15; \beta' = 5.07; c_6 = 1.29$	220	90 (5)	1.43
	SPFD	4.23	3.77	4.79	$b_0 = 39.8; b_1 = -4.62; c_6 = 1.31$	220	90 (5)	1.46

^aExperimental conditions given in Table I; the number of experimental data points is given in parentheses.

^bDefined in Eqs. (3-5).

^cSymbols have the same meanings as in Eqs. (3-5) of the text. The MSV and M²SV potentials also have $\rho_s = 1.60$; the SPFD potential similarly has $\rho_f = 1.60$. The dispersion constant C'_6 is obtained from the fitted reduced dispersion coefficient c_6 , where $C'_6 = \epsilon r_m^6 c_6$. The prime denotes an effective dispersion coefficient, obtained by neglecting contributions from higher-order multipole terms.

^dIntegral cross sections at a relative collision energy of 63 meV (for He + CH₄, NH₃, H₂O) or 64 meV (for He + SF₆) calculated from the partial wave expansion and the potentials given.

^eScattering intensity normalized to 500 at $\theta = 4.8^\circ$ (which differs from the arbitrary normalizations used in Figs. 1 and 2).

^fThe number of parameters varied is given in parentheses.

^gSee Eqs. (1) and (2).

TABLE III. Potential parameters obtained from DCS results, integral cross section measurements, and calculated dispersion coefficients.

Potential quantity	system				error	Method of determination	Ref.
	He + CH ₄	He + NH ₃	He + H ₂ O	He + SF ₆			
$\epsilon \cdot r_m / (\text{meV} \cdot \text{\AA})$	9.0	-	-	-	0.6	$Q(v)^a$	18
	8.9	9.0	9.3	23	-	DCS ^a	this work
	7.8	7.8	7.9	20	0.2	DCS ^b	this work
$C_6 / (\text{eV} \cdot \text{\AA}^6)$	7.9	6.6	4.8	-	-	calculated ^c	25
	8.9	-	-	-	-	calculated ^c	26
	6.6	5.6	4.5	22	-	calculated ^d	d
$C'_6 / (\text{eV} \cdot \text{\AA}^6)$	13	12	8	35	2	DCS ^e	this work
$\sigma^f / \text{\AA}$	-	3.09	2.98	-	0.06	DCS ^a	19
	3.40	3.28	3.02	3.75	0.03	DCS ^a	this work
ϵ / meV	-	2.2	2.5	-	0.3	DCS ^a	19
	2.3	2.5	2.7	5.6	-	DCS ^a	this work

^aUsing the LJ12-6 potential.

^bUsing the M²SV and SPFD potentials; the error reflects the discrepancies among the $\epsilon \cdot r_m$ products for these potential forms.

^cSpherically symmetric contributions to C_6 .

^dFrom the approximate formulae of Ref. 32 in terms of static polarizabilities, ionization energies and dipole moments.

^eUsing the M²SV and SPFD potentials, and neglecting contributions of higher order than C_6 to the dispersion interaction. The error reflects the $\pm 20\%$ or poorer accuracy with which the "attractive tail" portion of the potential ($r \gtrsim 5 \text{\AA}$) is determined²⁰ for the He + CH₄, NH₃, H₂O systems. See Sec. IVB for a discussion of the corresponding error in C'_6 for He + SF₆.

^fFor the LJ12-6 potential, $\sigma = 2^{-1/6} r_m$.

TABLE IV. Potential parameters from simple combination rules compared with experiment.

System ^a	$\sigma_{ij}/\text{\AA}$	$\sigma_{ij}^b/\text{\AA}$	$\sigma_{ij}^c/\text{\AA}$	ϵ_{ij}/meV	$\epsilon_{ij}^d/\text{meV}$	$\epsilon_{ij}^e/\text{meV}$	$\epsilon_{ij}^f/\text{meV}$
He + CH ₄ ^f	3.43	3.06	3.40	20	4.3	3.9	2.0
He + NH ₃ ^g	3.15	2.92	3.28	31	5.3	2.6	2.1
He + NH ₃ ^h	3.42	3.06	3.28	14	3.6	3.3	2.1
He + H ₂ O ^g	2.71	2.70	3.01	44	6.3	3.3	2.3
He + H ₂ O ^h	3.06	2.88	3.01	17	3.9	3.8	2.3
He + SF ₆ ^f	4.53	3.61	3.77	36	5.7	3.6	4.7

^a For He₂, $\sigma_{ii} = 2.69 \text{ \AA}$, $\epsilon_{ii} = 0.91 \text{ meV}$, from Ref. 1d.

^b $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$.

^c Present experiments, average of M²SV and SPFD potential fits.

^d $\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{\frac{1}{2}}$.

^e $\epsilon_{ij} = \frac{2\alpha_i \alpha_j}{\sigma_{ij}^6 (\gamma_i + \gamma_j)}$, where $\gamma_k = \frac{\alpha_k^2}{\epsilon_{kk} \sigma_{kk}^6}$ ($k = i, j$); α_k is the spherically averaged polarizability and

σ_{ij} is obtained from the combination rule of footnote b.

^f Homomolecular parameters from Ref. 38.

^g Homomolecular parameters from Ref. 39.

^h Homomolecular parameters from Ref. 40.

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FIGURE CAPTIONS

Figure 1. Laboratory differential cross sections $I(\theta)^{15}$ for out-of-plane scattering of He by CH_4 , NH_3 , and H_2O . These curves are successively shifted downwards by one decade for clarity of display. Points with error bars are the experimental measurements of $I(\theta) \cdot \sin \theta$ vs. the scattering angle θ at a relative collision energy of 63 meV. Solid curves are DCS's calculated from the best-fit central-field SPFD potentials, whose parameters are given in Table II.

Figure 2. Laboratory differential cross sections¹⁵ for out-of-plane scattering of He by SF_6 at a relative collision energy of 64 meV. Symbols are as in Fig. 1.

Figure 3. Central-field intermolecular potentials of the SPFD shape, corresponding to the He + CH_4 , NH_3 , and H_2O DCS fits of Fig. 1, as a function of the intermolecular distance (see Sec. III for a discussion of the definition of this distance). Solid curve: He + CH_4 ; dashed curve: He + NH_3 ; dotted curve: He + H_2O . The error bars on the He + CH_4 potential represent the accuracy with which it has been determined, $\pm 10\%$ of the potential energy at the attractive minimum, $\pm 0.04 \text{ \AA}$ in the position of the repulsive wall at $\sim 7.5 \text{ meV}$. The potentials are plotted over the approximate range of distances to which the experiments are sensitive.²⁰

Figure 4. Central-field intermolecular potential of the SPFD shape, corresponding to the He + SF_6 fit of Fig. 2, as a function of the inter-

molecular distance (see Sec. III for a discussion of the definition of this distance). The accuracy of this potential is discussed in Sec. IV. B. The range of validity of this potential is approximately $3.7 \text{ \AA}$ ($V \gtrsim 5 \text{ meV}$) to $7 \text{ \AA}$.

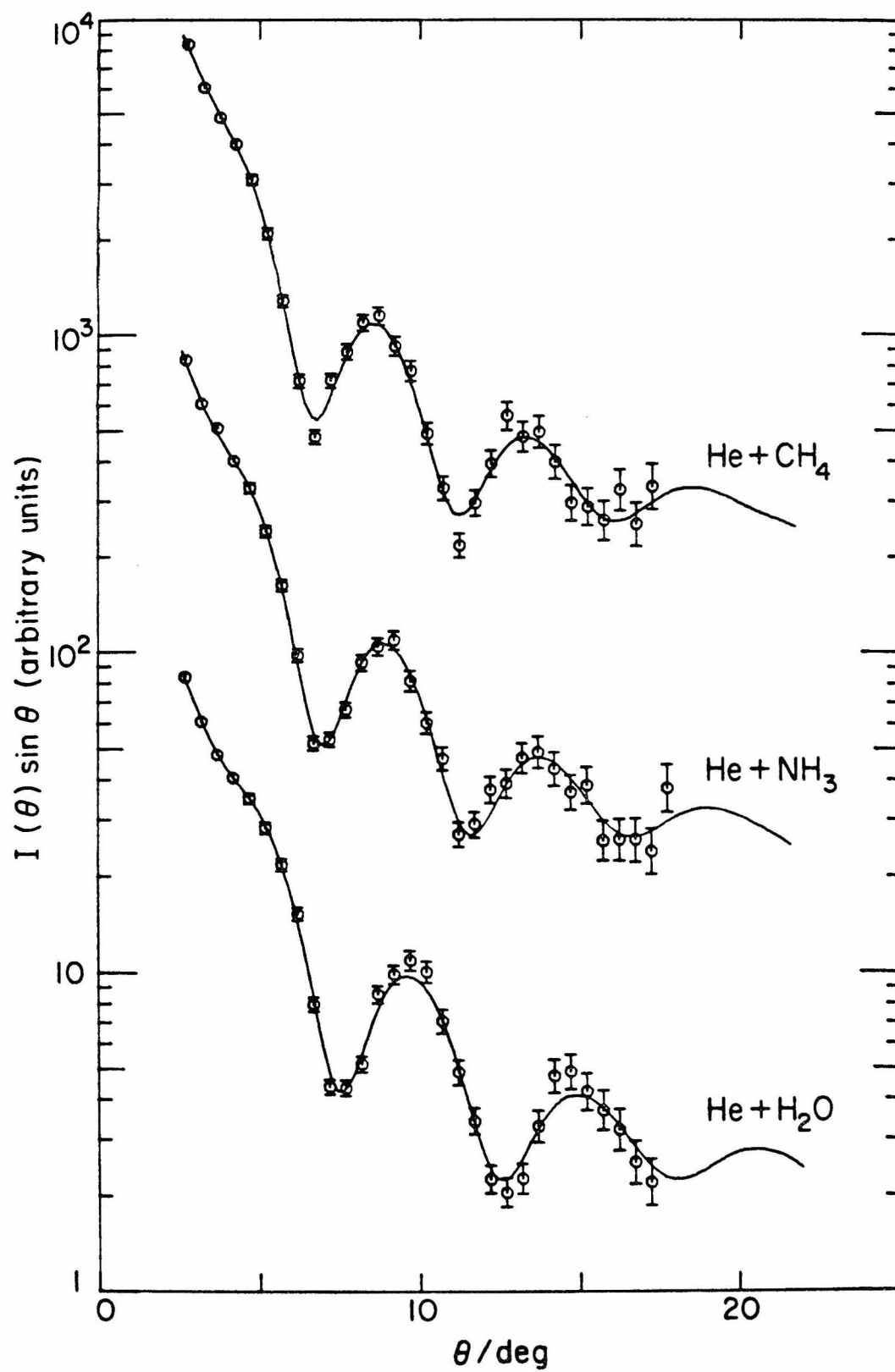


Figure 1.

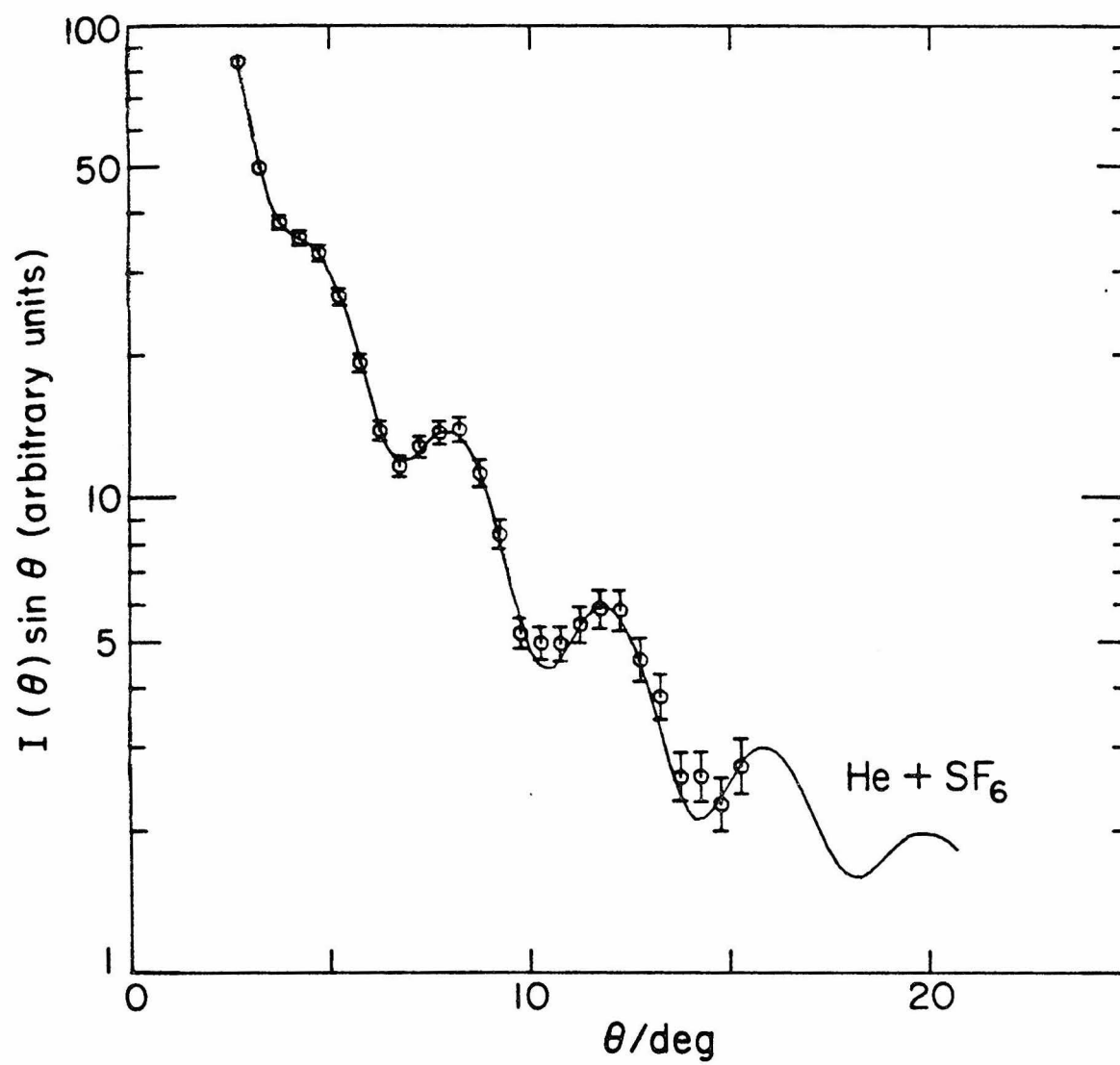


Figure 2.

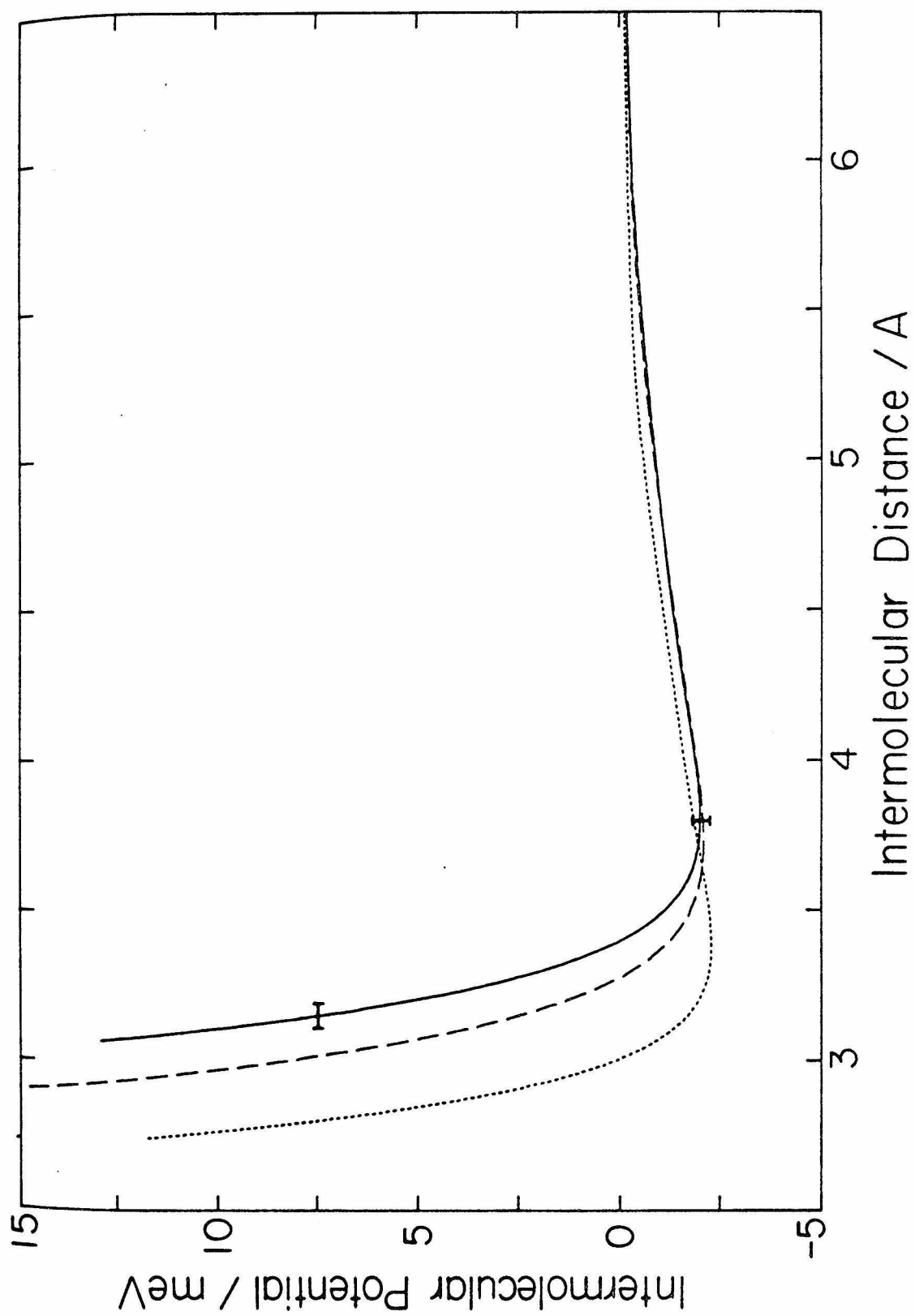


Figure 3.

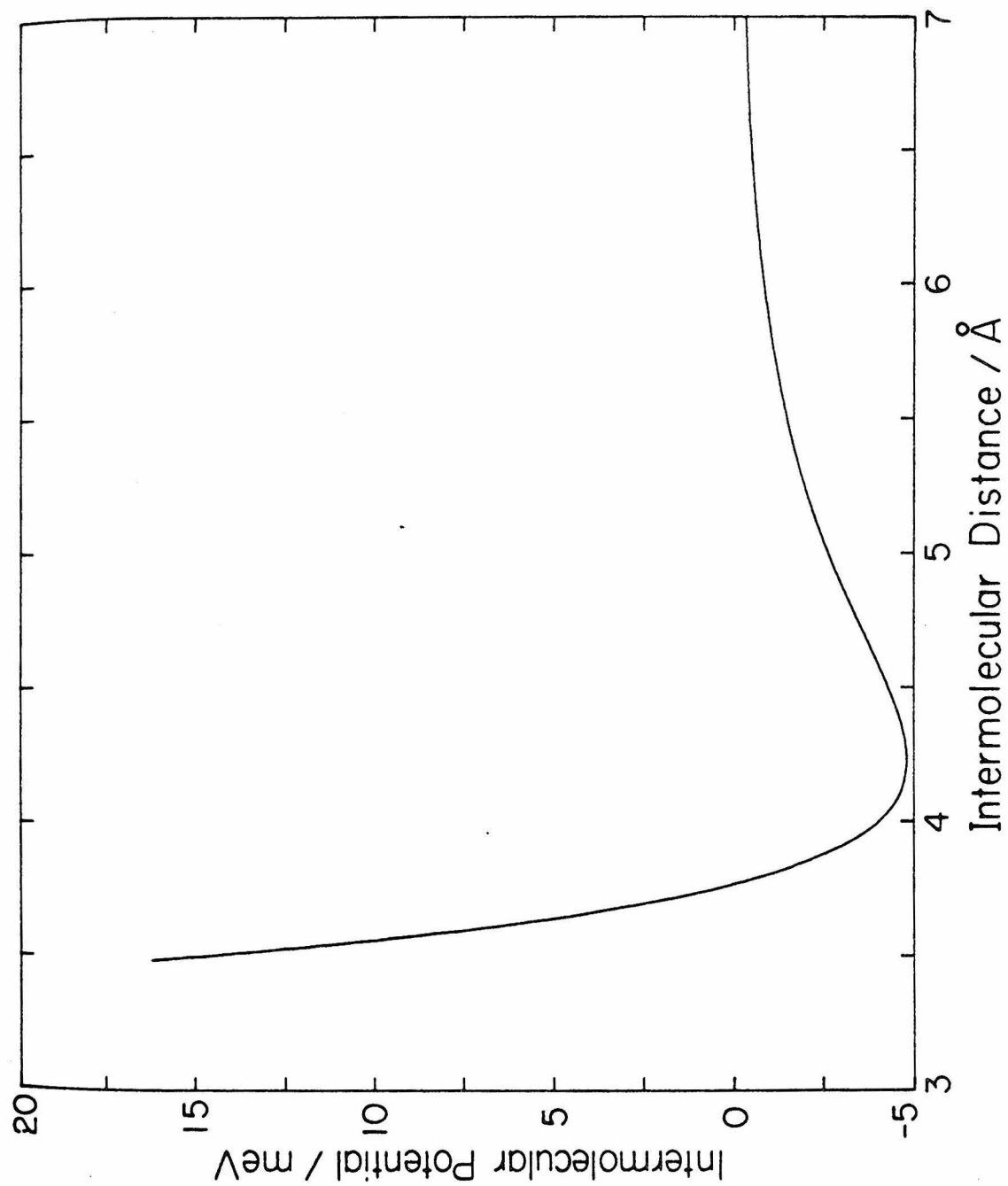


Figure 4.

CHAPTER 7

Intermolecular Potentials for $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$
and $\text{H}_2(\text{D}_2) + \text{NH}_3$ from Differential Cross Sections

Intermolecular Potentials for $H_2(D_2)+H_2O$ and $H_2(D_2)+NH_3$ from
Differential Cross Sections^{a)}

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Differential scattering cross section (DCS) are measured for $H_2(D_2) + NH_3$ and $H_2(D_2) + H_2O$ using the crossed molecular beam technique. These DCS show rapid interference oscillations, which permit the determination of the corresponding van der Waals potential, assuming that the central-field assumption is valid, i.e., that anisotropy effects are not important. Several mathematical forms for the central field interaction potential were assumed for this determination. The potentials obtained assuming the very flexible Simmons-Parr-Frulan-Dunham (SPFD) and Morse-Morse-Spline-van der Waals (M_2SV) agreed with one another within experimental error and differed

a) This work was supported in part by a contract (EY-76-S-03-767) from the Department of Energy. Report Code: CALT-767P4-175.

b) Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

c) Contribution No. .

significantly from the Lennard-Jones 12-6 potentials. Results for $\text{H}_2(\text{D}_2) + \text{NH}_3$ are found to be consistent with earlier investigations in this laboratory. As found for the $\text{He} + \text{NH}_3$ and $\text{He} + \text{H}_2\text{O}$ systems, the interactions of the isoelectronic hydrides NH_3 and H_2O with $\text{H}_2(\text{D}_2)$ are found to have decreasing van der Waals radii in correlation with molecular size. The validity of simple combination rules for the Lennard-Jones 12-6 parameters was tested and found to give crude estimates of the experimental values, at best.

I. INTRODUCTION

Over the past decade or so considerable work has been done, both experimentally¹ and theoretically,² to improve our knowledge of intermolecular (atomic) potentials for van der Waals interactions.³ Molecular beam elastic scattering experiments yield information about these weakly attractive potentials at a level of detail inaccessible to many other techniques, especially for highly quantum systems.^{3c,4,5} Only recently has a characterization of the He - Ar rare gas pair been made which is parameterization-independent.^{4,6} Furthermore, the effects of anisotropy have been found to be small in He+ diatomic-gas systems where little evidence of quenching of the diffraction oscillations has been observed.⁷ In fact, the potentials obtained by accurate central-field analysis have been seen to be indistinguishable, within experimental error, from the spherical averages of anisotropic potentials extracted from an infinite-order sudden approximation⁸ analysis of the same differential cross section (DCS) data. In further work done in this laboratory,⁹ the intermolecular potentials for He + CH₄, NH₃, H₂O, and SF₆ determined assuming central-field potentials provide a good representation of the DCS data. In addition, comparison of the H₂(D₂) + Ar potential obtained in this laboratory¹⁰ with those obtained in different laboratories using both differential cross sections¹¹ and spectroscopic analysis¹²⁻¹⁴ are in close agreement.

A logical extension of these studies is the investigation of the $\text{H}_2(\text{D}_2) + \text{NH}_3$, H_2O systems. We have previously studied the $\text{H}_2(\text{D}_2) + \text{NH}_3$ system using in-plane detection geometry.¹⁵ Results obtained subsequently at the University of Waterloo¹⁶ were in disagreement with ours; and we decided to restudy this system using, in addition, out-of-plane detection geometry. The $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$ system involves an interesting polar hydride, H_2O . Together with the previous results on $\text{He} + \text{H}_2\text{O}$, NH_3 , CH_4 , SF_6 ⁹ and $\text{H}_2(\text{D}_2) + \text{CH}_4$, SF_6 ,¹⁵ the two systems considered in the present paper complete the study of intermolecular forces in two series of molecules interacting with either He or $\text{H}_2(\text{D}_2)$.

In Section II, we briefly describe the apparatus used to measure the DCS's and then describe the experimental procedures used to obtain the DCS's. The data reduction techniques and the intermolecular potentials extracted from them are presented in Section III. In Section IV we discuss the importance (or lack thereof) of the anisotropic contributions to the intermolecular potential and compare our results with previously published ones. Trends in the data and an evaluation of the usefulness of combination rules are also presented. Finally, we summarize our findings in Section V.

II. EXPERIMENTAL METHODS

The crossed molecular beam apparatus used in this investigation has been described previously^{4,15} and only its major components are summarized here. The main features of the machine are a movable, differentially pumped quadrupole mass spectrometer detector having an electron impact ion source; a differentially pumped supersonic primary beam; and a slightly supersonic secondary beam. These components are all housed in a stainless steel 1200 liter main vacuum chamber which serves as the scattering chamber. The beams intersect each other at the point about which the detector rotates, either in the same plane as the beams (the in-plane configuration, hereafter referred to as the h, i.e., horizontal detection geometry) or in a plane perpendicular to the plane of the beams but in the same plane as the primary beam (the out-of-plane configuration, hereafter referred to as the v, i.e., vertical detection geometry). The detector chamber is mounted on a semicircular quadrant arm. This arm can be rotated about the vertical axis of symmetry of the bell jar; and the detector can be moved up or down along the arm's rim while continuously pointing at the cross point between the two beams. The scanning of laboratory scattering angles in the v geometry was done by moving it either above the plane of the beams (+v geometry) or below it (-v). In the h geometry it was moved in the plane of the beams from the primary beam

either towards the secondary beam (+h geometry) or away from it (-h geometry). The primary $\text{H}_2(\text{D}_2)$ beam comes from a room-temperature nozzle source, is angularly well-collimated in two stages of differential pumping, and is modulated at 160 Hz by a chopping system. Secondary beams of both NH_3 and H_2O emerge from a glass capillary array directly into the scattering chamber. This relatively intense beam may be tilted upwards out of the plane of the crossed beams allowing measurement of the modulated background scattering. Beam operating characteristics are listed in Table I. We note that the primary beam velocity distributions give Mach numbers of 18 for D_2 and 20 for H_2 while the "effective" specific heat ratios are 1.54 and 1.60, respectively, indicating that significant cooling of the rotational degrees of freedom occurs. The secondary beam velocity distributions are best described by a Mach number of 1.5 and an "effective" specific heat ratio of 1.64,¹⁷ indicating only a very slight cooling of the gas; thus, the rotational temperature is presumably close to the ambient one (298" K).

The quadruple mass spectrometer detector is housed in a doubly differentially pumped chamber and is used to detect scattered $\text{H}_2(\text{D}_2)$ molecules in either the in-plane or out-of-plane geometries. Angular spacings of the observed diffraction oscillations in the out-of-plane configuration are slightly greater than in the in-plane one; additionally, in the out-of-plane geometry, there is an up-down symmetry of the laboratory scattering

differential cross sections with respect to the plane of the beams, i.e., results of the +v and -v measurements should be symmetric about the plane of the beams. This symmetry is exploited to yield scattering angle measurements accurate within $\sim 0.03^\circ$.⁴ Ions are detected by a 14 stage CuBe electron multiplier whose output is amplified by a tuned preamplifier followed by a phase sensitive detector/amplifier. That output in turn is converted by an analog-to-digital converter whose output is then sampled at 60 Hz by a minicomputer. This computer samples and averages the processed signal and, by causing the secondary beam to either tilt out of or lie in the scattering plane, permits subtraction of the back-ground from the detected-signal-plus-background intensity. Test signals were used to verify the linearity of the processing electronics; linearity within $\pm 1.0\%$ was observed for all test conditions. Additionally, the output of the CuBe electron multiplier was compared with the output of a Spiraltran electron multiplier also located behind the quadrupole mass spectrometer. The output of the two were proportional to relative normalized signals within 2%.

With liquid-helium cryopumping in the ionizer region of the mass spectrometer, background pressures of $\lesssim 5 \times 10^{-10}$ torr were achieved for these experiments. Rapid cryopumping of the NH_3 and H_2O on liquid-nitrogen cooled surfaces in the scattering chamber allowed the use of secondary beams which caused $\sim 5\%$ attenuation of the primary beam due to scattering while maintaining a main chamber pressure $\leq 5 \times 10^{-7}$ torr. Periodic mass spectrometer checks of the secondary beams revealed their high purity for all the scattering experiments. Careful check was made especially for either NH_3 or H_2O dimers with no detectable evidence for formation of such dimers within

the estimated $\sim 10^{-7}$ sensitivity relative to the monomer, despite the integrity of H₂O ionic polymers as produced by electron-impact ionization.¹⁸

For the determination of intermolecular potentials, scattered primary beam signals were measured for both in-plane and out-of-plane geometries. The laboratory scattering angle range for the +v geometry was 2.5 to 18°. The total integration times for each scattering angle ranged from ~ 3 minutes near 3° to ~ 20 minutes at the widest angles. The measurements for the -v geometry were made to permit an accurate determination of the zero position of the scattering angle scale. Long-term drifts in beam intensities and detector efficiencies were compensated for by periodic measurements of the scattering signal at a reference angle of about 5°.

III. DATA REDUCTION AND INTERMOLECULAR POTENTIALS

The data reduction procedure used to obtain intermolecular potentials from the measured DCS versus scattering angle curves has been described previously.⁴ It consists of a standard weighted nonlinear least-squares optimization of the parameters of mathematical functions chosen to represent the intermolecular potential, as described below. As in previous work, the DCS calculations are appropriately velocity and angle averaged.

The least-squares parameter optimization minimizes the functional

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2 \quad (1)$$

As in our earlier studies, we define a goodness-of-fit statistical index $\Delta \alpha_{0.95} / \Delta \alpha$ more suitable than χ^2 for describing the quality of the fits to the DCS.

$$\Delta \alpha_{0.95} / \alpha = 1 / \alpha \cdot t_{0.05(n-k)} \left[\frac{\chi^2}{(n-k) \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}} \quad (2)$$

In these equations, I_i and σ_i are the measured (arbitrarily normalized) and calculated (absolute) cross sections¹⁹ at each of n scattering angles, respectively, with the normalized weights g_i . For n data

points and k parameters, $t_{0.05}(n-k)$ is the appropriate Student t -distribution statistic for a 95% confidence level of the scaling factor α .²⁰ We point out that the $\Delta \alpha_{0.95}/\alpha$ statistical index is independent of the arbitrary normalization used in the experiment. Furthermore, it is statistically adjusted for the number of data points and fitted parameters, which should allow a more straightforward comparison between different potential forms, and between scattering results from different laboratories.

The potential function forms used in the data reduction are written in the reduced form

$$f(\rho) = \frac{V(r)}{\epsilon}, \quad \rho = \frac{r}{r_m}, \quad (3)$$

where r_m is the radius of the attractive minimum and ϵ is its depth. The zero of the potential, occurring at $r = \sigma$, may be related to r_m and the potential shape $f(\rho)$. The potential shapes we consider are

a) Lennard-Jones 12-6 (LJ 12-6)^{21a}

$$f(\rho) = \rho^{-12} - 2\rho^{-6} \quad (4)$$

b) Lennard-Jones n -6 (LJ n -6)^{21a}

$$f(\rho) = \frac{6}{n-6} \left\{ \rho^{-n} - \frac{n}{6} \rho^{-6} \right\} \quad (5)$$

c) Mores-Spline-van der Waals (MSV)²² and M²SV⁶

$$\left. \begin{aligned} f(\rho) &= e^{\frac{\beta(1-\rho)}{2}} \left[e^{\frac{\beta(1-\rho)}{2}} - 2 \right] && \text{for } \rho \leq \rho_1 \\ f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_2] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_2 \end{aligned} \right\} (6)$$

The s_i ($i = 1, 2, 3, 4$) are cubic spline coefficients, which are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 . The first spline point is taken as the inflection point of the Morse curve, $\rho_1 = 1 + \beta^{-1} \ln 2$. The second spline point may be treated as a fixed parameter but is held fixed at $\rho_2 = 1.6$.⁶ Remaining shape parameters are then β , governing the shape of the repulsive and well regions, and the dispersion series coefficients. We may modify this potential (MSV) by using a second Morse function for $r < \sigma$, joined smoothly to the first at $r = \sigma$. This M²SV potential then has the additional parameter β' and differs from above as:

$$\left. \begin{aligned} f(\rho) &= \frac{1}{\omega} e^{\frac{(\beta' - \rho\beta\omega)}{2}} \left[e^{\frac{(\beta' - \rho\beta\omega)}{2}} - 2 \right] && \text{for } \omega \equiv \frac{\beta' - \ln 2}{\beta - \ln 2} \\ &&& \text{and } \rho < 1 - \beta^{-1} \ln 2 \\ f(\rho) &= e^{\frac{\beta(1-\rho)}{2}} \left[e^{\frac{\beta(1-\rho)}{2}} - 2 \right] && \text{for } 1 - \beta^{-1} \ln 2 \leq \rho \leq \rho_1 \end{aligned} \right\} (7)$$

d) Simons-Parr-Finlan-Dunham (SPFD)²³

$$\left. \begin{aligned} f(\rho) &= b_0 \lambda^2 \left(1 + \sum_{i=1}^N b_i \lambda^i \right) - 1 && \text{for } \lambda = 1 - \frac{1}{\rho}, N = 3, \\ &&& \text{and } \rho < \rho_f \\ f(\rho) &= \sum_{i=1}^3 C_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_f \end{aligned} \right\} \quad (8)$$

Smoothness conditions at $\rho = \rho_f$ are used to fix the highest-order coefficients b_N and b_{N-1} . ρ_f may be treated as a variable but is fitted at $\rho_f = 1.6$; the $b_i (i=1, \dots, N-2)$ determine the shape of the potential; the dispersion series constants are also independent parameters. Since the SPFD potential often shows spurious maxima or oscillations below $\rho = 0.65$, an exponentially repulsive wall, i.e., $f(\rho) = A e^{-b\rho}$ is joined to the potential at $\rho = 0.7$ (A and b are fixed by smoothness conditions).

The LJ 12-6 and LJ n-6 potentials have been used in order to allow comparison with results of other DCS experiments¹⁶ and also to allow an assessment of simple combination rules. In previous studies for the He + Ar system,⁴ as well as for He+ molecule systems,^{7,9} more flexible parametric forms for $f(\rho)$ were found necessary to accurately describe the weak van der Waals interactions studied. However, for the $H_2(D_2) + Ar$ system,¹⁰ the LJ 12-6 form was seen to describe the intermolecular potential well, leading to the conclusion that the actual intermolecular potential had a form similar to that described by the LJ 12-6. A counter argument considered was that systems which have

collision energies that are small relative to ϵ ($\leq 10 \epsilon$) are not nearly as sensitive to the repulsive wall and hence do not require as great a flexibility in the potential form. (See Sec. IV for further discussion). Since both the $\text{H}_2(\text{D}_2) + \text{NH}_3$ and $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$ systems have relative collision energies of $\sim 7\epsilon$ and since scattering measurements were made only out to $\sim 18^\circ$ in the laboratory frame, we estimate that the experiment is only sensitive to values of $\rho > \sim 0.9$, i.e., the experiment has little, if any, sensitivity to the repulsive wall at values of r less than σ . Because very low-angle scattering data are lacking, we further estimate that the sensitivity of the present DCS data to the intermolecular potential is restricted to reduced distances $\rho \leq 1.8$.⁶

In Eqs. (6), (7), and (8), we fix $C_8 = C_{10} = 0$ and thus, obtain "effective" dispersion constants, labeled C'_6 for each interaction pair. The C'_6 ($= \epsilon r_m^6 C_6$) are expected to be greater than the corresponding correct C_6 constants because of the neglect of higher-order contributions. This neglect could have a substantial effect on the long-range part of the potential, especially for interactions of $\text{H}_2(\text{D}_2)$ with highly polar molecules like NH_3 and H_2O (for the $\text{He} + \text{NH}_3$, H_2O systems, the r^{-7} contribution to the dispersion energy at $\rho = 1.6$ has been estimated as $\sim 30\%$ of r^{-6} component⁹). However, since the dispersion expansion is only used for $\rho \geq 1.6$, the $C'_6 r^{-6}$ representation should provide a reasonable approximation to that part of the long-range potential which affects our experiment. Thus, the C'_6 parameter is permitted to vary in these fits instead of being fixed at a theoretical value.

A prerequisite for Eq. (3), together with the reduced potential forms of Eqs. (4) through (8), to provide an accurate description of the intermolecular interactions of the systems considered in the present paper, is that anisotropic contributions to the potential must be small over the intermolecular distance range to which the DCS data are sensitive. Although this central-field assumption may not be made a priori for the analysis of atom-molecule scattering experiments,⁷ we, nevertheless, base our extraction of intermolecular potentials on it. This procedure is justified in the following discussion (Sec. IV).

IV. RESULTS AND DISCUSSION

The measured¹⁹ DCS versus laboratory scattering angle curves, for the +v geometry are given as the points in Figs. 1 and 2. Signal to noise ratios range between 35 for the lowest angles and about 4 for the largest ones. The data points represent the average of several independent angular scans performed in several days' experimentation for each scattering pair; the error bars represent an estimation of the standard deviation of the measurements.⁴ The measurements for the other detection geometries are not displayed as figures but the resulting potentials are analyzed below.

A. Central-Field Analysis

Before discussing the central-field potentials which are obtained from a fit to these DCS measurements, let us consider the reasonability of such a central-field analysis. The molecule-molecule van der Waals interactions being considered are anisotropic and, as a result, the central-field potentials can only represent an approximation to them. To assess the validity of this approximation, we must address ourselves to two important questions: (1) Does the anisotropic component of the intermolecular potential have a negligible effect on our results? (2) If not, does the central-field approximation of Eq. (3) still provide an "effective" description of spherically averaged interactions?

In considering these questions, we recognize that, if the collision time scale is much longer than the molecular rotations, the collision would sample only the spherical average of the anisotropic potential for sufficiently weak interactions. This, however, does not apply to the present experiment. Typical rotation frequencies of the molecules are $\sim 10^{12}$ Hz while typical collision interaction times (to traverse ~ 8 Å) are $\sim 5 \times 10^{-13}$ sec, corresponding to only about half a revolution during the collision. The inversion frequency of NH_3 is ~ 50 times slower than the rotation frequency, and, therefore, does not contribute to averaging of the interaction. Consideration of spherically averaging collisions at set angles represents a different physical phenomenon and is examined below.

The significance of the anisotropic component of the inter-molecular potential has been addressed in three previous papers of this group.^{7,9,10} In the first study,⁷ it was seen that, if little evidence is found for the quenching of the observed rapid quantum oscillations, the effects of anisotropy are not likely to be significant. In fact, it was shown that the spherical averages of the anisotropic potentials extracted from an infinite-order sudden approximation analysis⁸ of the DCS data presented there were indistinguishable, within experimental error, from the potentials obtained by an accurate central-field analyses of these same data. This was shown to be true despite a van der Waals attractive minimum distance that was found to be up to 20% greater for linear configurations than

for the perpendicular one. These arguments were extended qualitatively to the $\text{He} + \text{NH}_3$ and $\text{He} + \text{H}_2\text{O}$ in the second study,⁹ since a quantitative validation would be difficult because of the additional parameters required to model the interaction of a polyatomic system compared to a diatomic one. The third study¹⁰ showed that anisotropy effects could be neglected for the range of distances sampled by the thermal DCS measurements and showed that a central-field intermolecular potential represents well the interaction of $\text{H}_2(\text{D}_2)$ with Ar. The shape of the hydrogen molecule is close to spherical.²⁴ In addition, the range of distances to which the DCS measurements being considered is sensitive is about 3.2 Å, 3.4 Å to 6.5 Å for the H_2O , NH_3 systems respectively, which are significantly larger than the H_2 bond length of 0.73 Å. We expect on this basis that the interactions of $\text{H}_2(\text{D}_2)$ with NH_3 or H_2O over this distance range will follow a central-field behavior, in analogy to the $\text{He} + \text{NH}_3$ and $\text{He} + \text{H}_2\text{O}$ systems. The assumption that, if quenching of the DCS is not observed, the effects of anisotropy can probably be neglected in the determination of the intermolecular potential, has furthermore been supported by the results of a counter example: damping of the rapid quantum oscillations (when compared with the $\text{He} + \text{Ar}$ oscillations) has been observed for scattering in the highly anisotropic quantum system, $\text{He} + \text{CO}_2$.²⁵

B. $\text{H}_2(\text{D}_2) + \text{NH}_3$

The central-field potentials obtained from the DCS measurements by the methods of the previous section are given in Table II. For the $\text{H}_2 + \text{NH}_3$ system, they include results obtained from three different detector geometries (+v, +h, and -h) as well as for the $\text{D}_2 + \text{NH}_3$ system in the +v configuration. Previous computer simulation studies⁶ have shown that the SPFD and M^2SV potential energy forms have the necessary flexibility for retrieving inter-molecular potentials from thermal energy DCS measurements. We have used these forms for the $\text{H}_2 + \text{NH}_3$ system for analyzing the +v and +h DCS results. For the -h measurements, convergence could not be obtained in the iterative fitting procedure using these potential forms. This indicates that the errors in these measurements are too large to permit a determination of the five parameters involved in those forms. For this reason, only the LJ 12-6 results are presented for this geometry in Table II and they should be viewed with suspicion. The potential $\text{H}_2 + \text{NH}_3$ parameters for the +v and +h geometries are seen from that table to be consistent with each other. The corresponding SPFD potentials when plotted are indistinguishable from one another within experimental error (see Fig. 3). The quality of the +v SPFD fit, as measured by the $\Delta\alpha_{0.95}/\alpha$ statistical index, is significantly higher than the +h one. Previous results for the $\text{He} + \text{Ar}$ ⁴ and the $\text{H}_2(\text{D}_2) + \text{Ar}$ ¹⁰ systems have also given indications that the +v configuration yielded better fits. For this reason, we limited ourselves to measurements

in this +v out-of-plane geometry for the $D_2 + NH_3$, $H_2 + H_2O$, and $D_2 + H_2O$ systems.

Comparison of the +v and +h SPFD potentials for the $H_2 + NH_3$ and the +v one for the $D_2 + NH_3$ system (see Fig. 3) shows them to be equivalent within experimental accuracy. The solid curves in Fig. 1 show the corresponding fit to the DCS data obtained from the +v SPFD potentials; the dashed curves are the corresponding LJ 12-6 fits, displayed for comparison purposes. It can be seen that the SPFD fits are superior to the LJ 12-6 ones, in agreement with the $\Delta\alpha_{0.95}/\alpha$ goodness-of-fit statistical index values given in Table II. The +v SPFD, M^2SV , and LJ 12-6 potential energy functions are displayed in Figs. 4 and 5 for the $H_2 + NH_3$ and the $D_2 + NH_3$ systems, respectively. It can be seen that the SPFD and M^2SV potentials for each of these systems agree within experimental error in spite of their different mathematical forms. The $H_2 + NH_3$ curves are indistinguishable from the $D_2 + NH_3$ ones (see Fig. 3), in spite of the different relative de Broglie wavelengths λ of 0.82 Å for the first and 0.60 Å for the second. This is particularly true if we compare the SPFD and M_2SV potentials for $H_2 + NH_3$, with the SPFD one for $D_2 + NH_3$, all of which fit the data very well ($\Delta\alpha_{0.95}/\alpha < 2.4$).²⁶ This independence of the potential on λ and on mathematical forms is consistent with the validity of the central-field assumption (over the range of intermolecular distances sampled by the experiment) and with the uniqueness of the potentials

obtained. This self-consistency argues for the reliability of these potentials.

As can be seen in Fig. 4, the LJ 12-6 curves differ from the SPFD and M_2SV ones. This difference is not as pronounced in Fig. 4, but as can be seen from Table II, the quality of fit index $\Delta\alpha_{0.95}/\alpha$ is appreciably better for the SPFD potential than for the LJ 12-6 one. The LJ 12-6 form is, therefore, considered not to provide as accurate a representation for this system as the SPFD one, a result which is not too surprising in view of the lack of flexibility of the form.⁶ Since, however, this was the only form used by Bickes et al.¹⁶ to analyze their $H_2 + NH_3$ DCS data, we compare in Fig. 6 and Table III their LJ 12-6 potential with our present ones and the ones obtained in our laboratory some time ago.¹⁵ It can be seen that our present LJ 12-6 potentials agree with our older ones within estimated experimental precision, in spite of modifications in the apparatus and extensive additional checks and calibrations^{4,10} performed between these two sets of experiments. On the other hand, these potentials differ noticeably from that of Bickes et al., more than allowed by the precision of the two experiments. The corresponding potential parameters are given in Table III. We are forced to agree with Bickes et al. that there is a true inconsistency between the two laboratories for this system. In attempting to resolve this inconsistency, we make a comparison with the results obtained for two additional systems studied by both laboratories: $He + Ar$ and $H_2(D_2) + Ar$.

For the He + Ar system, we have previously shown⁴ that the data of our laboratory and that of the Waterloo group²⁷ are consistent (although the final potentials are not, due to the different mathematical forms used in the data analysis). For the H₂ + Ar system, there is agreement between our LJ 12-6 potentials¹⁰ and those of Rulis et al.,¹¹ within experimental error. However, such an agreement did not exist with previous results of that laboratory.²⁸ Their apparatus was improved between their two sets of measurements and the velocity distribution of their primary beam was better characterized. This resulted in an increase of r_m of about 0.1 Å, bringing that value into agreement with ours, within experimental error. It is, therefore, possible that the difference between the H₂ + NH₃ results of the two laboratories could be decreased if new measurements were made by the Waterloo group. It should be noted, however, that these comparisons are based on a LJ 12-6 analysis of the data. As indicated above, this form is too inflexible to provide an optimal fit to the data, and a new reliable comparison should be based on more flexible potential function forms, such as the SPFD or the M₂SV.⁶

The differences in the shapes of the SPFD and LJ 12-6 potentials displayed in Figs. 4 and 5 in the well minimum and weakly repulsive well regions are noticeable. This differs from our H₂(D₂) + Ar results, for which the SPFD and LJ 12-6 shapes were quite close to one another.¹⁰ However, significant differences in potential shapes have been observed in all the He systems

reported by this laboratory.^{4,7,9} Because of the greater well depth, experiments for room temperature beams are less sensitive to the repulsive wall than the $\text{H}_2(\text{D}_2) + \text{Ar}$ experiments. Therefore, the satisfactory fit of the LJ 12-6 form to the DCS data for the latter system is not due to repulsive wall sensitivity considerations, and is probably fortuitous. All other systems we studied have required the flexibility of a 4 or 5 parameter potential form. This is further supported by the agreement between the M_2SV and the SPFD fits for each of these systems.

C. $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$

The central-field potential energy functions obtained from the +v data of Fig. 2, for the $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$ system are given in Table II. The solid curves of Fig. 2 show the fits to the data obtained from the SPFD potentials, whereas the dashed curves are the corresponding LJ 12-6 fits. As in the NH_3 system, the SPFD fits are better than the LJ 12-6, as also indicated by the corresponding values of $\Delta\alpha_{0.95}/\alpha$ in Table II. The potential energy functions for the H_2O systems are displayed in Figs. 7 and 8, including the SPFD, M_2SV , and LJ 12-6 ones. As for the NH_3 systems, the SPFD and M_2SV $\text{H}_2 + \text{H}_2\text{O}$ potentials are indistinguishable from each other within experimental precision but differ significantly from the LJ 12-6 one. For this system, the difference between the H_2 and D_2 potentials is greater than for the NH_3 case. This may be associated with the poorer quality of fit of the $\text{D}_2 + \text{H}_2\text{O}$ potentials

implied by the $\Delta\alpha_{0.95}/\alpha$ values of Table II as compared with the $D_2 + NH_3$ SPFD one. Although the LJ 12-6 potentials do not provide as adequate a representation of the actual potential as the SPFD one, it is the only one reported for $H_2 + H_2O$ by Bickes et.al.¹⁶ In order to provide a comparison of their results with ours, the corresponding LJ 12-6 potentials are given in Fig. 9 and Table III. It can be seen that the Bickes et al. curve is shifted towards lower internuclear distances relative to ours, as was the case for the NH_3 system, a further indication of the systematic differences between the two laboratories.

D. Trends in Well Depth and Position

The $H_2(D_2) + NH_3$ system involves the interaction of a nearly spherical homonuclear diatomic molecule with a polar symmetric top molecule, whereas, for the $H_2(D_2) + H_2O$ system, the second molecule is an asymmetric top instead. NH_3 and H_2O are isoelectronic hydrides and differ in molecular size, NH_3 being larger than H_2O . The NH bond length is 1.008 Å and the HNH bond angle is 107.3 for NH_3 , while for H_2O the OH bond length is 0.957 Å and the HOH bond angle is 104.5°. ²⁹ This difference correlates with the displacement of the repulsive walls for the two systems to the smaller molecular sizes in going from NH_3 to H_2O . We further note that conditioning in this isoelectronic sequence, the $D_2 + Ne$ interaction has $r_m = 3.31$ Å, ¹⁴ ~ 0.2 Å less than for the $D_2 + H_2O$ potential (Table II). The apparent lack of a strong anisotropic

effect in these potentials over the range of distances sampled by the thermal energy DCS experiments may be associated with the existence of lone-pair electrons in NH_3 and H_2O and their contribution to the interactions of these molecules with $\text{H}_2(\text{D}_2)$, despite their rather asymmetric arrangements.

A comparison of the $\text{H}_2 + \text{NH}_3$ and $\text{H}_2 + \text{H}_2\text{O}$ systems with the corresponding He+ molecule systems are made using the SPFD and LJ 12-6 potential parameters in Table IV. As expected, we observe that r_m decreases in going from NH_3 to H_2O for both the H_2 and He systems. Correlations for the well depth ϵ are not nearly as obvious. The well depths for the He + NH_3 and He + H_2O systems are the same within experimental error, while the depth for the $\text{H}_2 + \text{H}_2\text{O}$ system appears greater than that for $\text{H}_2 + \text{NH}_3$ (although the 10% error bounds on the latter just overlap). It has previously been noted⁹ that the He + H_2O , NH_3 and CH_4 well depths were very similar to one another. This is consistent with observations for other He systems: He + Ne, Ar, Kr, Xe^{30, 31, 32} and He + alkali - atoms.^{33, 34} The He + SF_6 well is, however, significantly deeper than the He + H_2O , NH_3 and CH_4 ones. Let us analyze the corresponding $\text{H}_2 + \text{molecule}$ potentials. Only LJ 12-6 parameters are available for all four systems $\text{H}_2 + \text{H}_2\text{O}$, NH_3 , CH_4 and SF_6 . Within this limitation, it seems nevertheless from Table IV that the $\text{H}_2 + \text{SF}_6$ well depth is not significantly different from those of the other $\text{H}_2 + \text{molecule}$ systems mentioned, in contradiction with the corresponding He+ molecule systems. The He + SF_6

potential (but not the $H_2 + SF_6$ one) thus provides a clear counter-example of previous empirical observations that it is primarily the least polarizable partner that is responsible for the magnitude of the van der Waals well depth.³⁵

E. Combination Rules

We have used the intermolecular potentials obtained in the present work to investigate the reliability of using combining rules to estimate potential parameters for unlike-pair interactions. The combination rules treated were:

a) simple geometric rules

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{\frac{1}{2}} \quad (9a)$$

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad (9b)$$

where σ_{AA} and σ_{BB} are the radii of the zero of the like-pair potentials and ϵ_{AA} and ϵ_{BB} are the well depths of the like pair potentials. (σ_{AB} and ϵ_{AB} are the unlike-pair potential parameters.)

b) rule of Hudson and McCoubrey³⁶

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{\frac{1}{2}} \frac{2(I_A I_B)^{\frac{1}{2}}}{I_A + I_B} \left\{ \frac{2(\sigma_{AA} \sigma_{BB})^{\frac{1}{2}}}{\sigma_{AA} + \sigma_B} \right\}^6 \quad (10)$$

where σ and ϵ are defined as above and I_X is the ionization potential of species X (X = A, B).

c) rule of Fender and Halsey³⁷

$$\epsilon_{AB} = 2\epsilon_{AA}\epsilon_{BB}/(\epsilon_{AA} + \epsilon_{BB}) \quad (11)$$

d) rules of Hirschfelder et al.²¹ for interaction of a polar and nonpolar molecule

$$\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{\frac{1}{2}}\xi^{\frac{1}{2}} \quad (12a)$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})\xi^{\frac{1}{6}} \quad (12b)$$

$$\xi = \left\{ 1 + \frac{1}{4} \frac{\alpha_A}{\sigma_A^3} \frac{\mu_B^2}{\epsilon_B \sigma_B^3} (\epsilon_{BB}/\epsilon_{AA})^{\frac{1}{2}} \right\}$$

where the subscript A refers to the nonpolar molecule and B refers to the polar molecule. Definitions are as above; α_X is the polarizability and μ_X is the dipole moment of species X.

The combination rules used are only a few that have been developed.³⁸ Historically, the use of such rules, only some of which are based upon theoretical or experimental conditions,²¹ may largely be due to difficulties in obtaining potential parameters from bulk sample measurements of unlike-pair properties. The validity of these rules relies upon the existence of a single reduced form or "universal function" for the interaction pairs considered which, in turn, is related to the "law of corresponding states" for the equation of state of real gases.²¹ However, this concept has been shown to be inappropriate for potentials determined by other means.^{3d, 6} Furthermore, combination rules for intermolecular

potentials ignore anisotropic contributions; while this neglect is valid for the present molecule-molecule systems for the range of the intermolecular distances sampled by our experiments, strong doubt exists for the validity of this assumption in the interaction of like-pair molecule-molecule interactions such as $\text{NH}_3 - \text{NH}_3$ or $\text{H}_2\text{O} - \text{H}_2\text{O}$. Moreover, experimental determinations of homomolecular interaction potentials have yielded widely different values for the potential parameters; and the values given in Table V for these parameters are merely representative, not necessarily accurate ones. Finally, these combination rules are generally used with data developed from simple potential forms, which are known to be crude estimates of the intermolecular potential. The results of the application of these combination rules are given in Table VI. For comparison purposes, the results for the corresponding He+ molecule parameters⁹ are also given. Examination of the resulting $\text{H}_2 + \text{NH}_3$, H_2O σ values shows that predictions are generally lower than experiment by ~ 0.1 to $0.3 \text{ \AA}$. The $\text{H}_2 + \text{NH}_3$, H_2O ϵ values predicted by combination rules shows that the simple geometric rule (Eq. 9a) or its variations (Eqs. 10 and 12a) give predictions which differ from the experimental SPFD ones by 20% to 50% (see Table VI) but the agreement with the experimental LJ 12-6 ones (see Table IV) is better. The situation is worse for the He+ molecule systems, for which not even the LJ 12-6 values of ϵ are reasonably predicted by these combination rules. Thus, it appears that combination rules can provide only crude estimates

of the well depths and radii of the potential zero for the interactions of simple polar molecules with $\text{H}_2(\text{D}_2)$.

V. SUMMARY AND CONCLUSIONS

Van der Waals potentials for the interactions of $\text{H}_2(\text{D}_2)$ molecules with NH_3 and H_2O have been extracted from differential cross sections (DCS), as measured by the crossed-beams technique. For systems showing only weak anisotropies, a suitable central-field analysis yields the spherically symmetric component of the interaction potential.⁷ The $\text{He} + \text{H}_2\text{O}$, $\text{He} + \text{NH}_3$ and $\text{H}_2(\text{D}_2) + \text{Ar}$ DCS measurements^{9,10} were consistent with a central-field assumption. Such an assumption was also made in analyzing the present data. Flexible potential forms such as the H_2SV or SPFD were found necessary to represent the intermolecular potential well.

We find a simple correlation between molecular size and the van der Waals radii for $\text{H}_2(\text{D}_2) + \text{NH}_3$ and H_2O interactions, which fall into order $\text{NH}_3 > \text{H}_2\text{O}$. This sequence may be extended to the isoelectronic $\text{H}_2(\text{D}_2) + \text{Ne}$ interaction. These results parallel closely the trends seen for the interaction of He with the same molecules/atoms. Simple combination rules appear to provide only crude estimates for the interactions of $\text{H}_2(\text{D}_2) + \text{NH}_3$ and H_2O , and they seriously fail for the corresponding He systems.

Table I. Beam Operating Conditions

Characteristic	Primary Beams		Secondary Beams	
	H ₂	D ₂	NH ₃	H ₂ O
Beam gas	H ₂	D ₂	NH ₃	H ₂ O
Inlet pressure/torr	500	500	4.8	3.9
Inlet temperature/°k	298	298	298	298
Angular FWHM ^a /deg	1	1	6	6
Most probable velocity/(k m/sec)	2.48	2.76	0.77	0.75
Velocity FWHM ^a , $\Delta v/v$	0.10	0.11	0.75	0.75
Mach number ¹⁹	20	18	1.5	1.5

^a Full width at half maximum.

Table II. Central-Field Intermolecular Potential Fits to the Experimental DCS's

System ^a	Potential Type ^b	Detector Configuration ^c	$r_m/\text{\AA}^d$	$\sigma/\text{\AA}^d$	ϵ/meV^d	Shape Parameters ^e	χ^2_f, g	$\Delta\alpha_{0.95}/\alpha^g$
$H_2 + NH_3$ (31) ^h	12-6	+v	$3.71 \pm .06$	3.30	$10.0 \pm .9$		71000(2)	3.03
	n-6		$3.68 \pm .06$	3.40	9.5 ± 1.2	$n=17.4$	30000(3)	2.01
	MSV		3.70	3.34	11.6	$\beta=7.21, c_e=1.98$	48000(3)	2.60
	M ₂ SV		3.69	3.35	12.0	$\beta=7.60, \beta^1=11.0, c_e=1.95$	40000(5)	2.33
	SPFD		3.68	3.38	12.3	$b_0=74.3, b_1=-6.59, c_e=1.75$	25000(5)	1.82
$H_2 + NH_3$ (29) ⁱ	12-6	+h	$3.65 \pm .11$	3.25	10.3 ± 1.6			5.16
	n-6		$3.65 \pm .09$	3.22	10.3 ± 1.1		250000(3)	5.20
	MSV		3.66	3.34	13.6	$\beta=7.83, c_e=2.34$	180000(4)	4.48
	M ₂ SV		3.67	3.34	13.5	$\beta=7.83, \beta^1=11.45, c_e=2.29$	170000(5)	4.20
	SPFD		3.67	3.37	13.1	$b_0=75.4, b_1=-6.45, c_e=1.82$	280000(5)	4.85
$H_2 + NH_3$ (28) ^j	12-6	-h	$3.57 \pm .07$	3.18	10.2 ± 1.2		2500(2)	4.18
	12-6	+v	$3.75 \pm .09$	3.34	$9.9 \pm .6$		940(2)	3.45
	n-6		$3.75 \pm .10$	3.40	10.0 ± 1.0	$n=16.0$	900(3)	3.43
	MSV		3.74	3.37	10.9	$\beta=6.97, c_e=2.24$	570(4)	2.77
	M ₂ SV		3.72	3.35	10.9	$\beta=7.00, \beta^1=10.67, c_e=1.85$	620(5)	2.95
$H_2 + H_2O$ (23) ^l	SPFD		3.70	3.40	11.9	$b_0=73.4, b_1=-6.65, c_e=1.85$	430(5)	2.29
	12-6	+v	$3.44 \pm .08$	3.07	10.1 ± 1.4		2700(2)	3.90
	n-6		$3.50 \pm .11$	3.12	9.9 ± 2.9	$n=11.2$	2700(3)	3.28
	MSV		3.51	3.21	14.1	$\beta=8.08, c_e=2.20$	630(4)	1.83
	M ₂ SV		3.53	3.23	14.3	$\beta=8.08, \beta^1=10.65, c_e=2.20$	640(5)	1.81
$D_2 + H_2O$ (36) ^m	SPFD		3.56	3.27	15.1	$b_0=77.15, b_1=-6.17, c_e=1.92$	730(5)	1.98
	12-6	+v	$3.53 \pm .09$	3.14	$10.5 \pm .7$		1200(2)	3.63
	n-6		$3.54 \pm .11$	3.15	$10.5 \pm .9$	$n=11.8$	1200(3)	3.68
	MSV		3.58	3.22	11.8	$\beta=6.84, c_e=2.13$	1100(4)	3.21
	M ₂ SV		3.53	3.18	12.3	$\beta=7.00, \beta^1=10.65, c_e=2.21$	890(5)	2.81
	SPFD		3.52	3.18	12.3	$b_0=51.11, b_1=-5.65, c_e=2.21$	1000(5)	2.97

Footnotes to Table II.

- ^a Experimental conditions given in Table I; the number of experimental points is given in parentheses.
- ^b Defined in Eqs. (3) - (8).
- ^c +v -- out-of-plane geometry, above plane of beams; +h -- in-plane geometry, detector moved from primary beam toward secondary beam in plane of beams; -h -- in-plane geometry, detector moved from primary beam away from secondary beam; See Section (II) for definition of configurations.
- ^d Error bars are given only as an indication of precision of fit; we prefer to base accuracy of fits on work done in ref. 6 and extended in refs. 7, 9.
- ^e Symbols have the same meaning as in Eqs. (3) - (8) of text. The MSV and M_2SV potentials also have $\rho_2 = 1.60$; the SPFD potential similarly has $\rho_f = 1.60$. The dispersion constant C_e' is obtained from the fitted reduced dispersion coefficient c_e , where $C_e' = \epsilon r_m^6 c_e$. The prime denotes an effective dispersion coefficient obtained by neglecting contributions from higher-order multipole terms.
- ^f Scattering normalized at $\Theta \sim 4.5^\circ$ -- exact values given in notes (h-m); the number of parameters varied is given in parentheses.
- ^g See Eqs. (1) and (2).
- ^h Relative collision energy = 68.5 meV; de Broglie wavelength = 0.82 Å; scattering intensity normalized to 5036. at $\Theta = 4.47^\circ$ in +v and $\Theta = 0.0^\circ$ in ±h.
- ⁱ Relative collision energy = 68.5 meV; de Broglie wavelength = 0.82 Å; scattering intensity normalized to 4425. at $\Theta = 4.88^\circ$ in +h and $\Theta = 0.0^\circ$ in ±v.
- ^j Relative collision energy = 68.5 meV; de Broglie wavelength = 0.82 Å; scattering intensity normalized to 500. at $\Theta = -4.63^\circ$ in -h and $\Theta = 0.0^\circ$ in ±v.
- ^k Relative collision energy = 70.6 meV; de Broglie wavelength = 0.80 Å; scattering intensity normalized to 500. at $\Theta = 4.66^\circ$ in +v and $\Theta = 0.0^\circ$ in ±h.
- ^l Relative collision energy = 68.5 meV; de Broglie wavelength = 0.81 Å; scattering intensity normalized to 500. at $\Theta = 4.60^\circ$ in +v and $\Theta = 0.0^\circ$ in ±h.
- ^m Relative collision energy = 70.8 meV; de Broglie wavelength = 0.59 Å; scattering intensity normalized to 500. at $\Theta = 4.60^\circ$ in +v and $\Theta = 0.0^\circ$ in ±h.

Table III. Potential parameters obtained from different DCS results for Lennard-Jones 12-6 potential.

System	$r_m/\text{\AA}$	ϵ/meV	ref.
$\text{H}_2 + \text{NH}_3$	$3.71 \pm .06$	$10.00 \pm .9$	this work
$\text{D}_2 + \text{NH}_3$	$3.75 \pm .09$	$9.97 \pm .6$	this work
$\text{H}_2 + \text{NH}_3$	$3.75 \pm .09$	$10.30 \pm .8$	15
$\text{D}_2 + \text{NH}_3$	$3.81 \pm .10$	$9.10 \pm .8$	15
$\text{H}_2 + \text{NH}_3$	$3.47 \pm .05$	$9.74 \pm .6$	16
$\text{H}_2 + \text{H}_2\text{O}$	$3.44 \pm .08$	10.12 ± 1.39	this work
$\text{D}_2 + \text{H}_2\text{O}$	$3.53 \pm .09$	$10.50 \pm .73$	this work
$\text{H}_2 + \text{H}_2\text{O}$	$3.28 \pm .07$	11.80 ± 1.0	16

Table IV. Potential parameters for the $H_2 + NH_3$, H_2O , CH_4 , SF_6 , systems and for the $He + NH_3$, H_2O , CH_4 , SF_6 systems.

System	Potential Form	$r_m/\text{\AA}$	$\sigma/\text{\AA}$	ϵ/meV
$H_2 + NH_3^b$	SPFD	3.68	3.38	12.3
	LJ 12-6	3.71	3.30	10.0
$He + NH_3^c$	SPFD	3.73	3.28	2.08
	LJ 12-6	3.67	3.28	2.5
$H_2 + H_2O^b$	SPFD	3.56	3.27	15.3
	LJ 12-6	3.44	3.07	10.1
$He + H_2O^c$	SPFD	3.38	3.01	2.27
	LJ 12-6	3.38	3.02	2.7
$H_2 + CH_4^d$	LJ 12-6	4.14	3.7	9.9
$He + CH_4^c$	SPFD	3.80	3.40	2.00
	LJ 12-6	3.81		2.44
$H_2 + SF_6^d$	LJ 12-6	4.53	4.05	10.4
$He + SF_6^c$	SPFD	4.23	3.77	4.79
	LJ 12-6	4.17	3.72	5.01

^a Parameters are determined using the SPFD (Eq. 8) and LJ 12-6 (Eq. 4) potentials.

^b This work

^c Ref. 9

^d Ref. 15

Table V. Like pair potential parameters, polarizabilities, dipole moments, and ionization potentials.

Gas	ϵ/meV	$\sigma/\text{\AA}$	$\alpha/\text{\AA}^3$ ^a	μ/D ^b	I/eV ^c
H ₂	3.05 ^d	3.00 ^d	0.79	---	15.43
He	0.91 ^d	2.66 ^d	0.205 ^e	---	24.5
NH ₃	31 ^f	3.42	2.26	1.47	10.5
H ₂ O	44 ^f	2.71	1.44	1.82	12.7

^a Ref. 39

^b Ref. 40

^c Ref. 41

^d Taken as most representative of H₂ + H₂, He + He elastic scattering data, Ref. 3a; MSV potential parameters for H₂ + H₂; ESMSV potential parameters for He + He.

^e Ref. 42

^f Ref. 43; LJ 12 potential parameters.

Table VI. Potential parameters from simple combination rules for $H_2 + NH_3$, H_2O and for $He + NH_3$ ^a

System	ϵ_{AB}^b	ϵ_{AB}^c	ϵ_{AB}^d	ϵ_{AB}^e	ϵ_{AB}^f	σ_{AB}^g	σ_{AB}^h	σ_{AB}^i
$H_2 + H_2O^j$	15.3	11.6	11.4	5.7	12.3	3.27	2.86	3.04
$H_2 + NH_3^j$	12.3	9.7	9.4	5.5	9.9	3.38	3.21	3.29
$He + H_2O^j$	2.27	6.3	6.2	1.78	6.6	3.01	2.68	2.80
$He + NH_3^j$	2.08	5.3	4.9	1.76	5.4	3.28	3.04	3.09

^a Values of ϵ are in meV and of σ in Å.

^b Experimental SPFD results of this work ($H_2 + H_2O$, NH_3) and of Ref. 9 ($He + H_2O$, NH_3).

^c See Eqn. (9a) in text.

^d See Eqn. (10) in text.

^e See Eqn. (11) in text.

^f See Eqn. (12a) in text.

^g Experimental SPFD results of this work ($H_2 + H_2O$, NH_3) and of Ref. 9 ($He + H_2O$, NH_3).

^h See Eqn. (9b) in text.

ⁱ See Eqn. (12b) in text.

^j Like-pair potential parameters given in Table V.

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Figure Captions

Figure 1. Laboratory differential cross sections for $\text{H}_2(\text{D}_2) + \text{NH}_3$ for out-of-plane scattering as a function of the out-of-plane laboratory scattering angle $\Theta_{\text{lab}}^\circ$. The points on the upper (lower) curve refer to scattering with $\text{H}_2(\text{D}_2)$ in the primary beam. The upper curve points are shifted upwards (by a factor of 10) with respect to the lower curve points for clarity of display. The solid curves are independent SPFD fits (central-field only) to each set of data; the dashed curves are independent LJ 12-6 fits (central-field only) to each set of data.

Figure 2. Laboratory differential cross sections for $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$ for out-of-plane scattering as a function of the out-of-plane laboratory scattering angle $\Theta_{\text{lab}}^\circ$. Points and curves are as defined in Fig. 1.

Figure 3. Spherically symmetric intermolecular potentials for $\text{H}_2(\text{D}_2) + \text{NH}_3$ as a function of intermolecular distance. Solid line: SPFD fit to positive out-of-plane, +v geometry for $\text{H}_2 + \text{NH}_3$; dashed line: SPFD fit to positive in-plane data, +h geometry, for $\text{H}_2 + \text{NH}_3$; dotted line: SPFD fit to positive out-of-plane data, +v geometry, for $\text{D}_2 + \text{NH}_3$.

Figure 4. Spherically symmetric intermolecular potentials for $\text{H}_2 + \text{NH}_3$ as a function of intermolecular distance. Solid line: LJ 12-6 potential; dashed line: SPFD potential; dotted line: M_2SV

potential. Error bar on the SPFD potential represents accuracy and precision with which it has been determined (based on results of Ref. 6), $\pm 12\%$ of the potential energy at the attractive minimum, $\pm 0.06 \text{ \AA}$ in the position of the repulsive wall at $\sim 0.0 \text{ meV}$.

Figure 5. Spherically symmetric intermolecular potentials for $\text{D}_2 + \text{NH}_3$ as a function of intermolecular distance. Symbols are as in Fig. 4.

Figure 6. Spherically symmetric intermolecular LJ 12-6 central-field intermolecular potentials for $\text{H}_2(\text{D}_2) + \text{NH}_3$ as a function of intermolecular distance. Solid lines represent fits to $\text{H}_2 + \text{NH}_3$ and $\text{D}_2 + \text{NH}_3$ data of this work. Dashed lines represent fits to $\text{H}_2 + \text{NH}_3$ and $\text{D}_2 + \text{NH}_3$ results of Ref. 15. Dotted line represents fit to $\text{H}_2 + \text{NH}_3$ data of Ref. 16. Error bars on the $\text{H}_2 + \text{NH}_3$ potentials for our data represent 95% confidence intervals. Error bars are displaced slightly in the position of the repulsive wall at $\sim 0.0 \text{ meV}$ and at attractive minimum for clarity of display.

Figure 7. Spherically symmetric intermolecular potentials for $\text{H}_2 + \text{H}_2\text{O}$ as a function of intermolecular distance. Symbols are as in Fig. 4.

Figure 8. Spherically symmetric intermolecular potentials for $\text{D}_2 + \text{H}_2\text{O}$ as a function of intermolecular distance. Symbols are as in Fig. 4.

Figure 9. Spherically symmetric intermolecular LJ 12-6 central-field intermolecular potentials for $\text{H}_2(\text{D}_2) + \text{H}_2\text{O}$ as a function of intermolecular distance. Solid line represents fit to $\text{H}_2 + \text{NH}_3$ data of this work. Dashed line represents fit to $\text{D}_2 + \text{NH}_3$ data of this work. Dotted line represents fit to $\text{H}_2 + \text{NH}_3$ data of Ref. 16. Error bars for our data represent 95% confidence intervals.

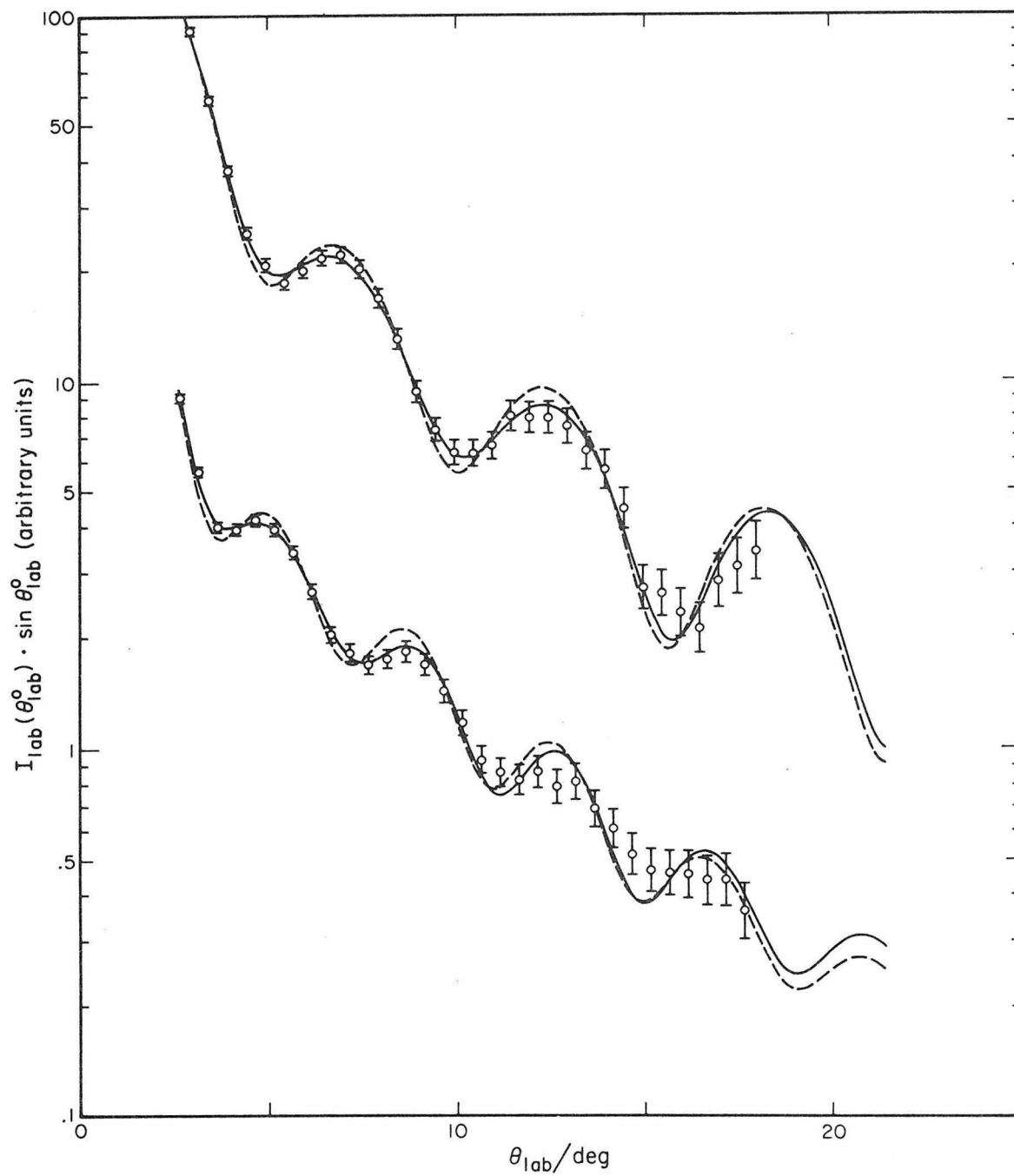


Figure 1.

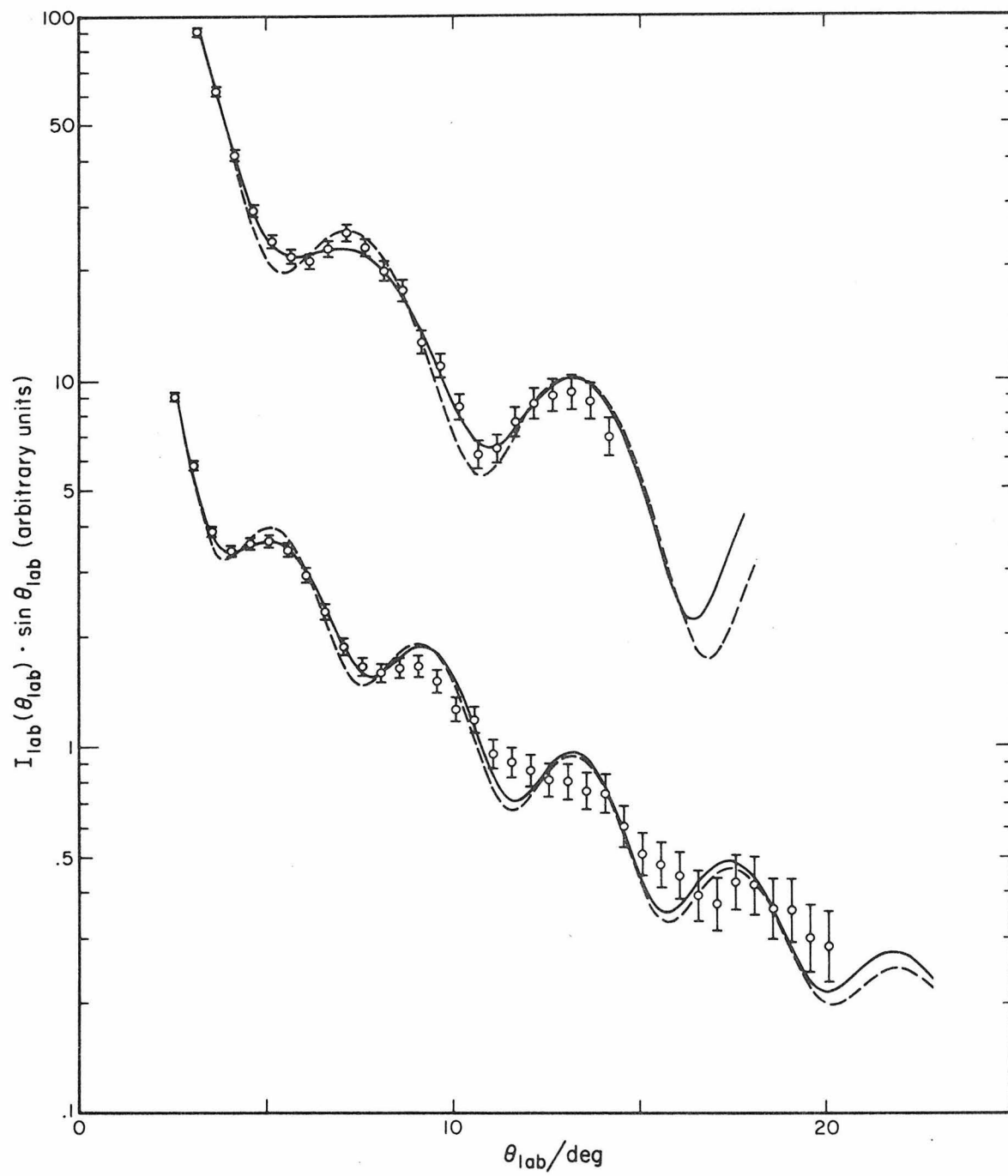


Figure 2.

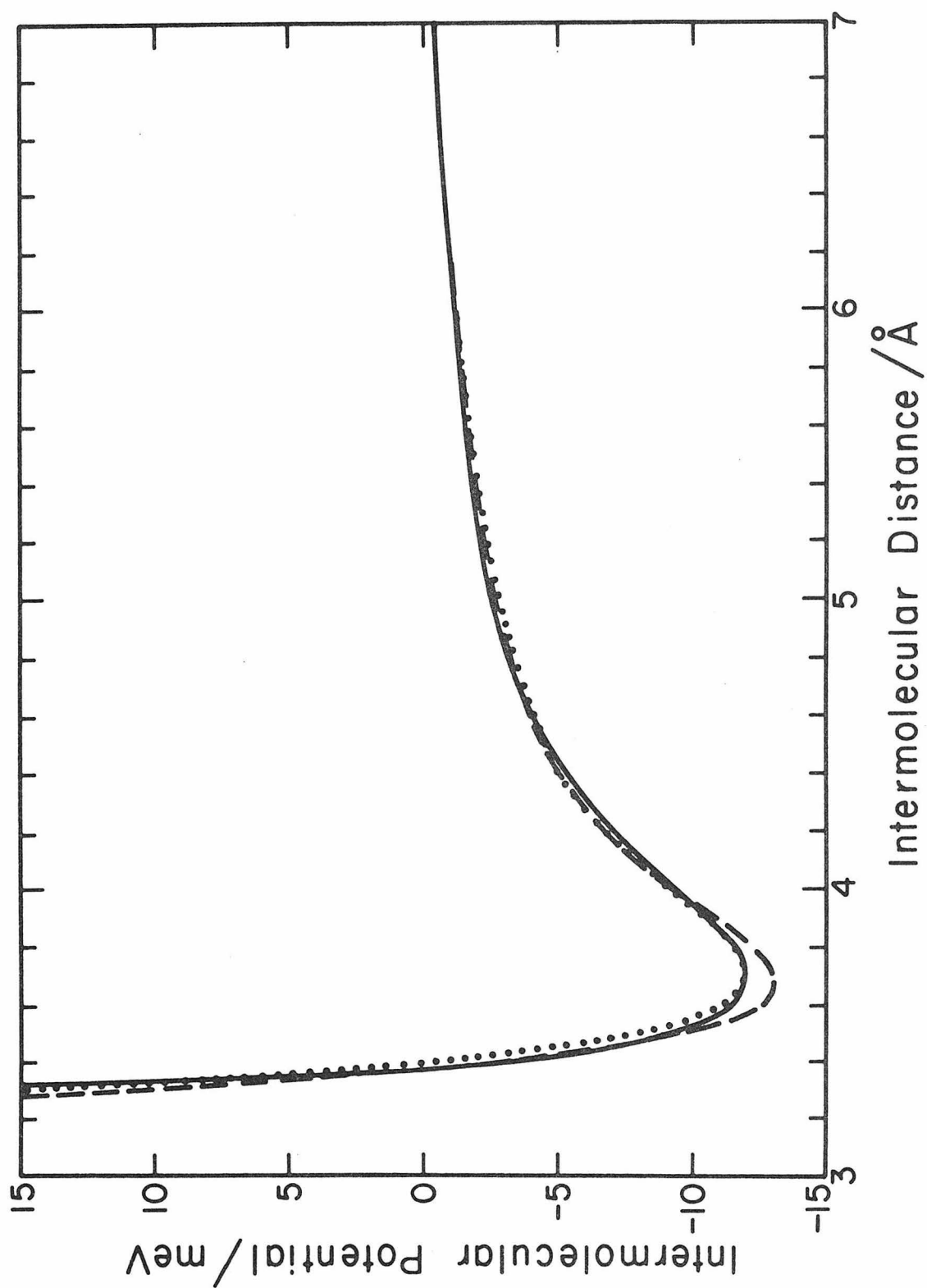


Figure 3.

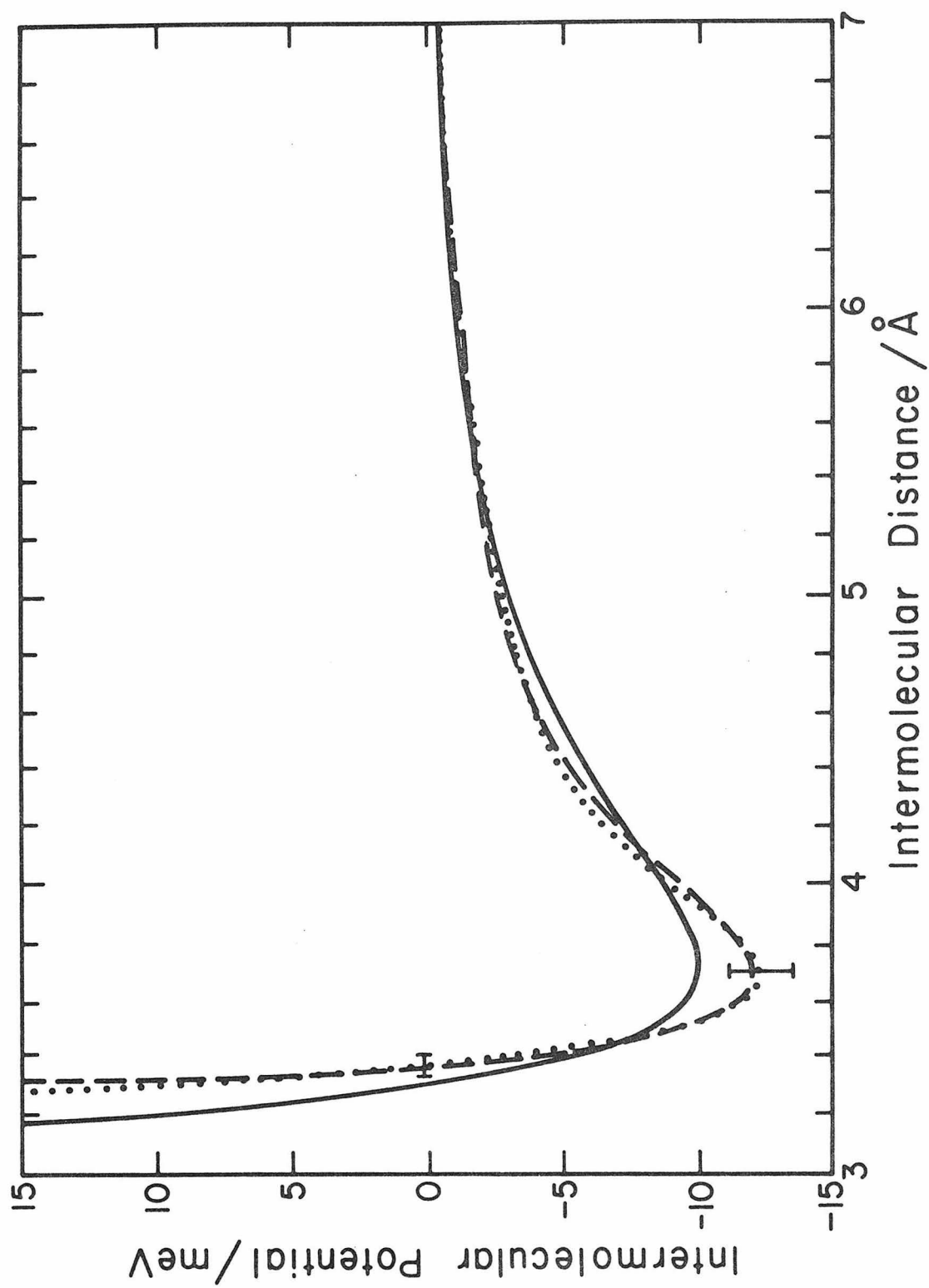


Figure 4.

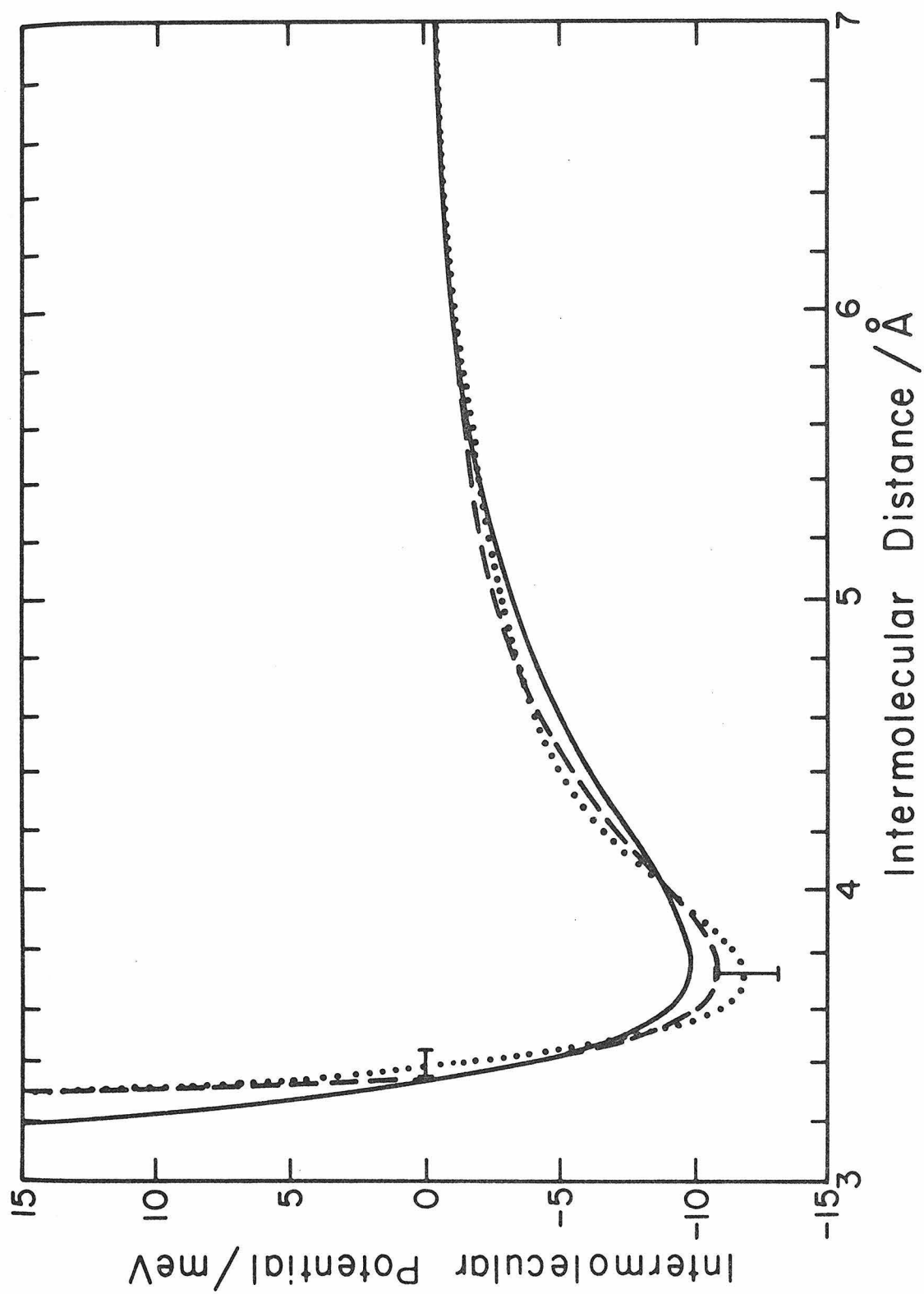


Figure 5.

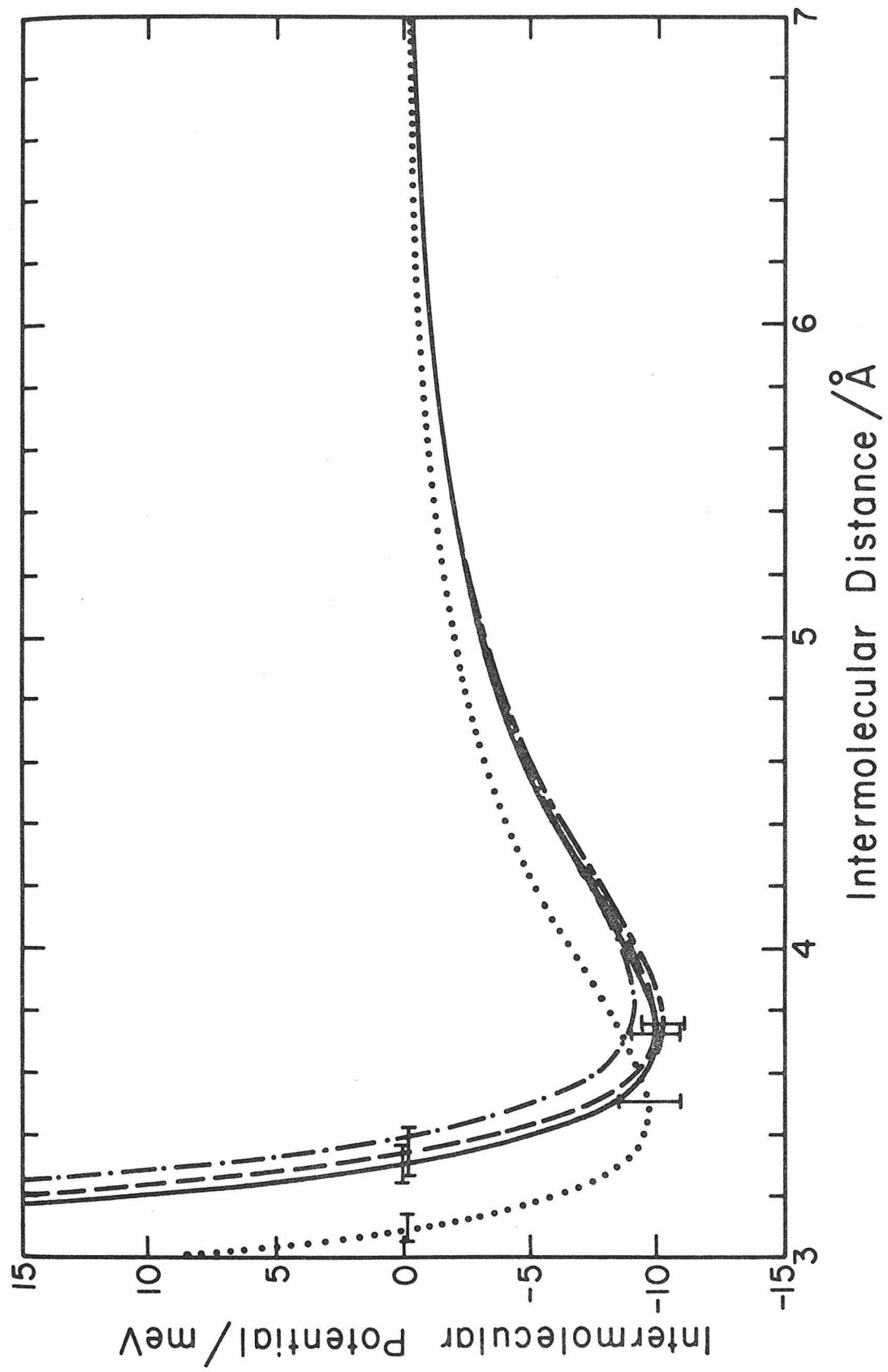


Figure 6.

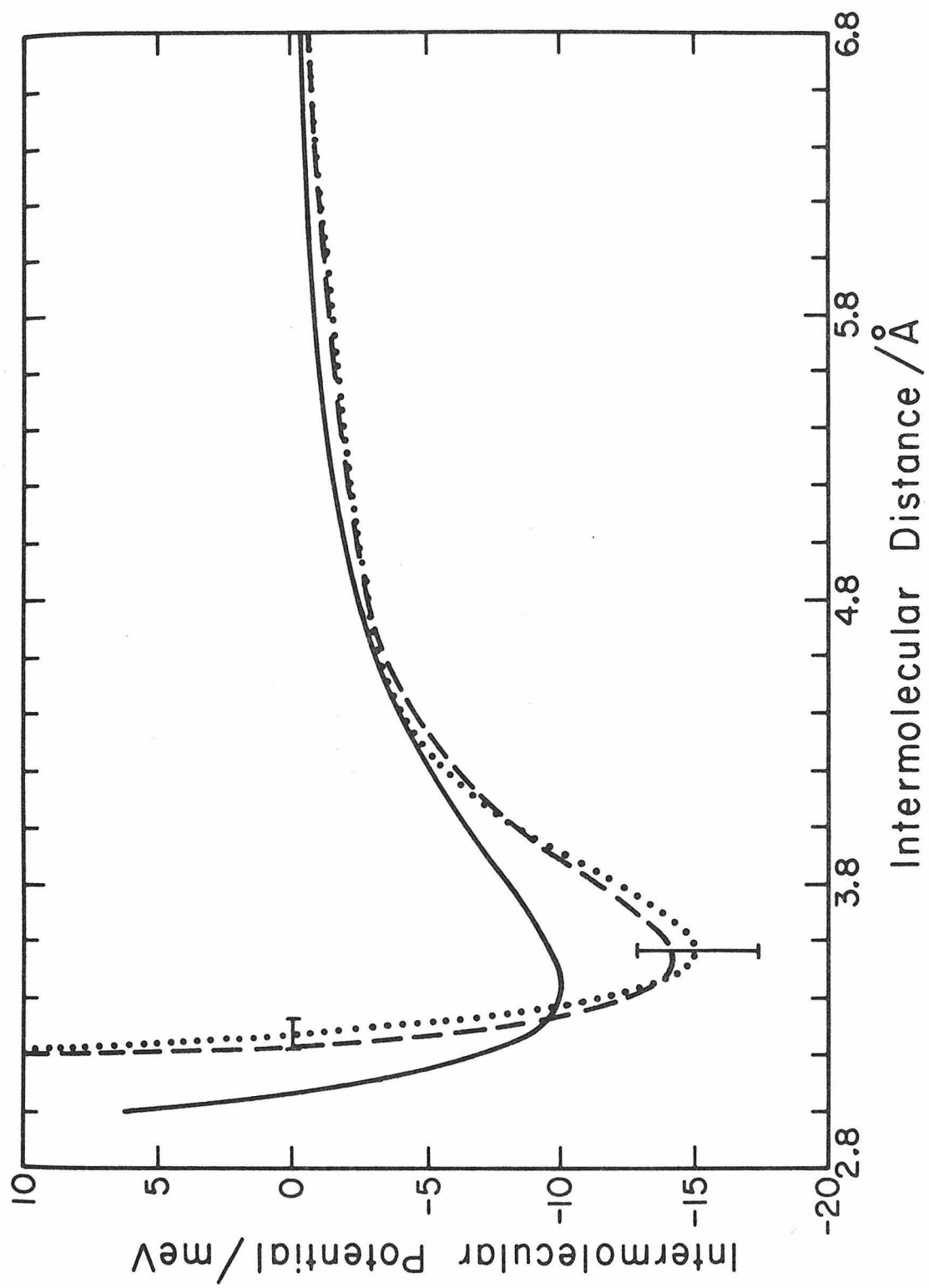


Figure 7.

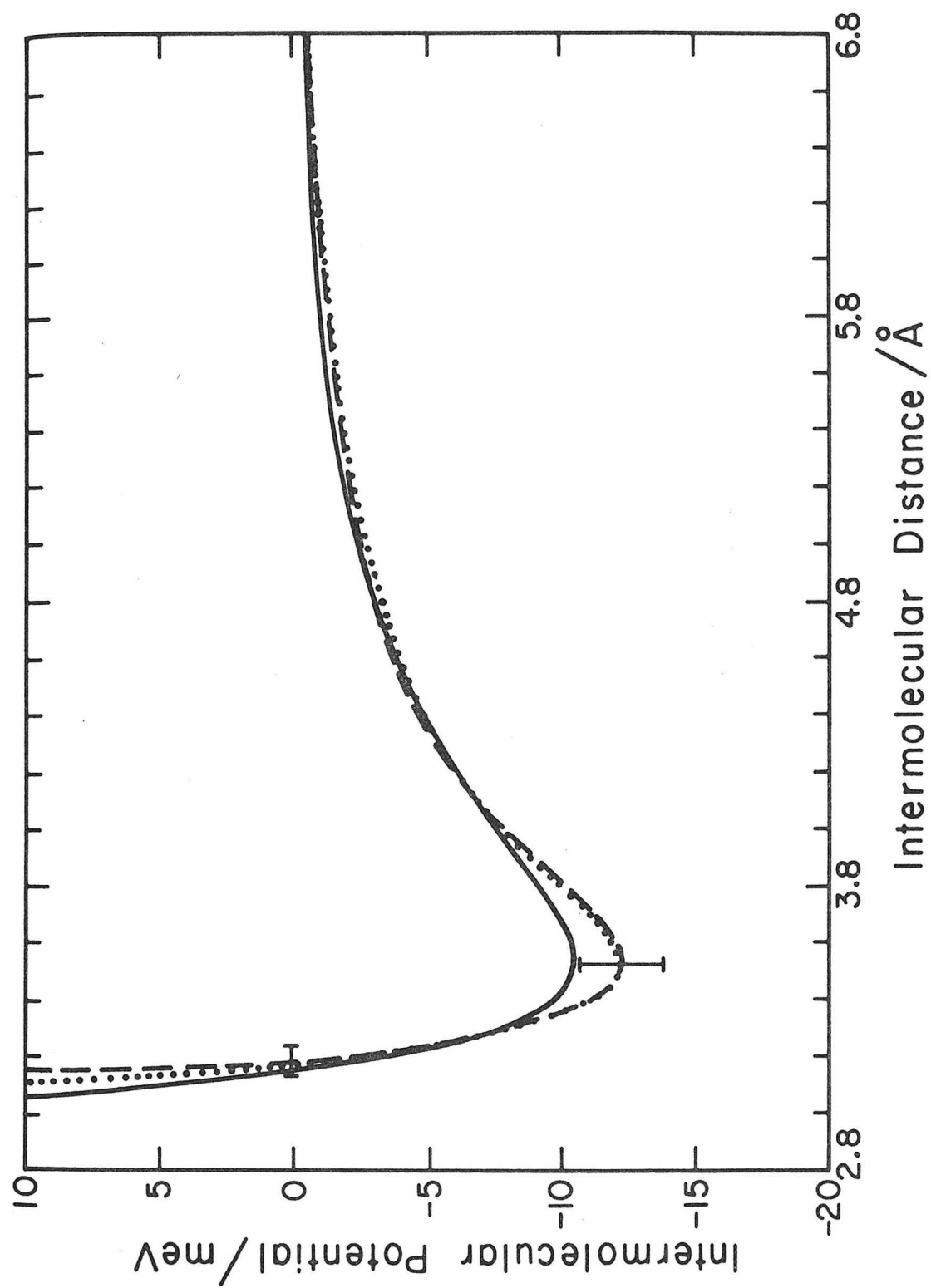


Figure 8.

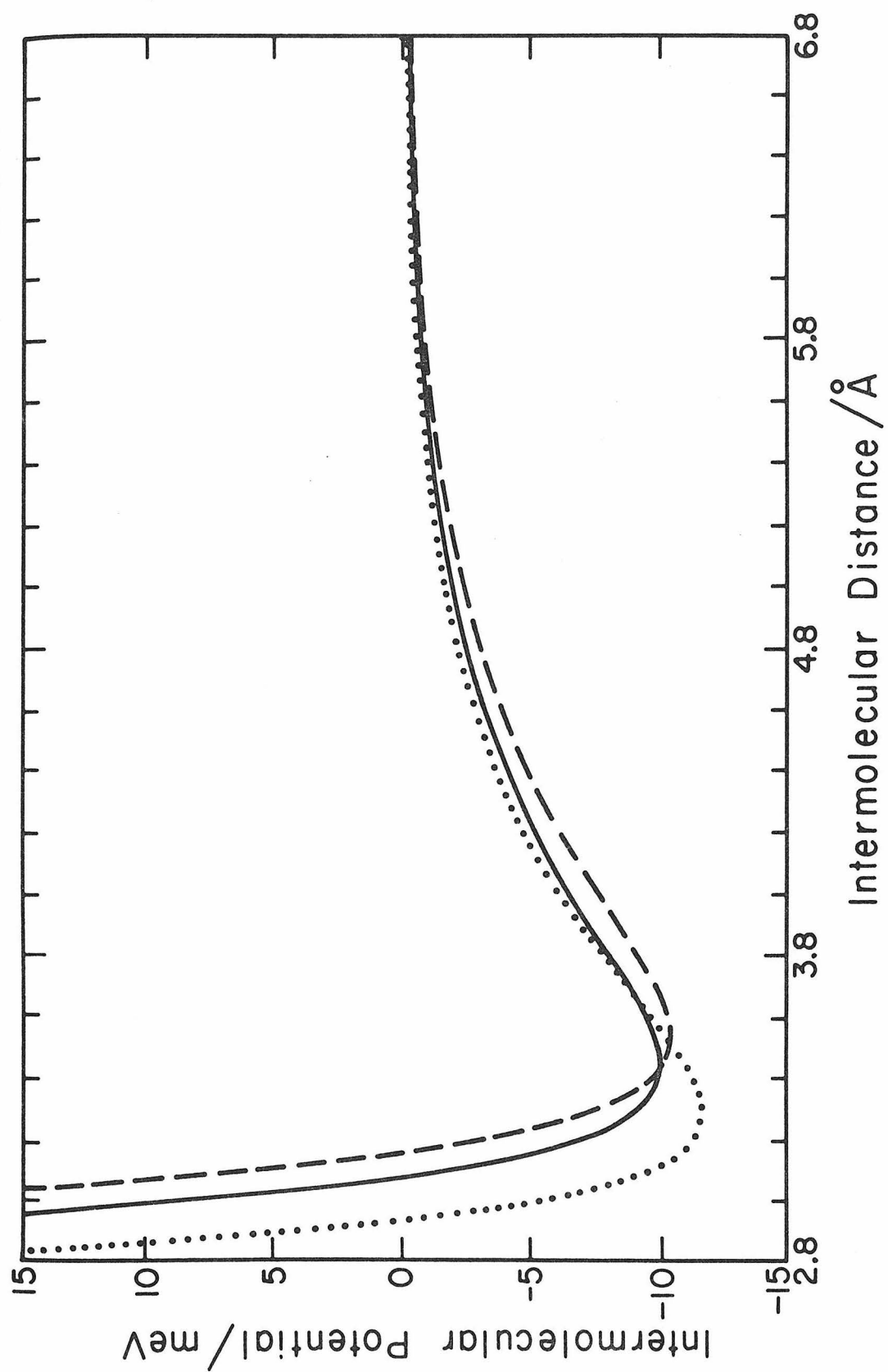


Figure 9.

CHAPTER 8

Summary and Conclusions

SUMMARY AND CONCLUSION

Van der Waals potentials in atom-molecule and molecule-molecule systems have been studied by means of scattering in "crossed beams." The observed scattering differential cross section contains information about the interaction potential between the collision partners. For the thermal energies we use, the region of the potentials around the well minimum is sampled over the reduced intermolecular distance (r/r_m) range of ~ 0.9 to ~ 1.8 . Elastic scattering is the only significant phenomenon observed under these conditions.

In Chapters 2 and 3 of this thesis, we briefly overviewed the theory associated with this experiment. The effects of the long-range and short-range regions of the intermolecular (interatomic) potentials on the scattering patterns were analyzed. The theory of elastic scattering was overviewed, including classical, semiclassical, and quantum approaches. For the systems studied in this work, quantum effects are very pronounced. Hence, while semiclassical approaches can provide a qualitative insight into the behavior of the systems, quantum mechanics must be used to describe fully the scattering process.

In Chapter 4 we reviewed the optimizations/characterizations made on the experimental apparatus. While this work did not have the glamour associated with the results discussed later, the characterizations/optimizations established confidence in the

apparatus and improved the signal-to-noise ratio by a minimum of a factor of three (i.e., only one-tenth the counting time was required to attain corresponding signal-to-noise ratios previously obtained on the apparatus!).

In Chapter 5 we presented our results for the $\text{H}_2(\text{D}_2) + \text{Ar}$ system which represents the first step away from the central-field $\text{He} + \text{Ar}$ system which was also studied by this group (see Appendix E). For the $\text{H}_2(\text{D}_2) + \text{Ar}$ system, the central-field approximation was found to represent well the spherically symmetric component of the interaction potential. Surprisingly it was found that the shape of the potential could be described well by the Lennard-Jones 12-6 Potential. This was not the case for the $\text{He} + \text{Ar}$ system where substantial changes in shape and well depth occur unless potentials such as the Simons-Parr-Finland-modified-Dunham potential (SPFD) or the Morse-Morse-Spline-van der Waals (M^2SV) are used--simple potentials provided only crude approximations for the actual intermolecular potential. Internal consistency in our apparatus was demonstrated by the agreement of the data fits, made for data taken in four different detector configurations and made for D_2 rather than H_2 as the primary gas collision partner. Close agreement was also found between our results and those of other laboratories which were determined by a variety of methods including total as well as differential cross section measurements and fits to spectroscopic measurements.

In Chapter 6, we presented our results for the $\text{He} + \text{CH}_4$, NH_3 , H_2O , SF_6 systems which represent a further excursion from physically

central-field systems such as He + Ar. These investigations which complement investigations done on the He + N₂, O₂, CO, NO systems (see Appendix F) address the validity of the central field approximation as the secondary gas collisions partner becomes more complicated in its structure. In all the systems studied, we found that the scattering data could be fit satisfactorily using the central-field analysis. We further found simple correlation between the molecular size and van der Waals radii of the He + CH₄, NH₃, H₂O interactions, falling in the sequence CH₄ > NH₃ > H₂O. No substantial effect of the large dipole moments of NH₃ and H₂O upon the long-range attractive potential could be found. The He + SF₆ potential, however, displayed an anomalous behavior in that it alone of all the He + atom (molecule) systems studied violated the usual supposition that only the least polarizable of the interacting atoms (molecules) are correlated with the van der Waals well depth. The well depth of the He + SF₆ system was twice as large as any well depth found for the other He + atom (molecule) systems.

In Chapter 7, we presented our results for the H₂(D₂) + NH₃, H₂O systems. These systems complement both the studies made in Chapter 6 for H₂(D₂) + Ar and in Chapter 7 for He + CH₄, NH₃, H₂O, and SF₆ systems. In the H₂(D₂) + NH₃, H₂O systems both collision partners are molecules. The validity of the central field approximation was again assumed and was supported not only by earlier results but also by the agreement in fit between the corresponding H₂ + molecule and D₂ + molecule systems (where the de Broglie

wavelength is substantially changed and where the anisotropic component would be expected to cause anisotropy effects such as quenching and shifting of extrema which would vary with the relative momentum, i.e., the de Broglie wavelength). Again as for the corresponding He + molecule systems, correlation existed between molecular size and the van der Waals radii in the order $\text{NH}_3 > \text{H}_2\text{O}$. Finally, it was seen that simple potentials such as the Lennard-Jones could not provide an adequate description of the intermolecular potential, i.e., the potential's shape changed as the mathematical form of the potential was made more flexible. However, more sophisticated potentials such as the five-parameter SPFD or M^2SV provide parameter-free descriptions, i.e., essentially the same potential as one another. The van der Waals radii we obtain for these two systems differ from those of another laboratory.

In conclusion, a number of He + atom (molecule) and $\text{H}_2(\text{D}_2)$ + atom (molecule) systems were studied. Results were found to be internally consistent and to agree in general with other laboratories. For all the systems studied the effects of anisotropy were found to be weak enough for a central-field analysis to yield the spherically symmetric component of the intermolecular potential. Finally, it was found that relatively sophisticated potentials such as the M^2SV or SPFD were necessary to lead to an intermolecular potential which was independent of the mathematical forms assumed.

APPENDIX A

Data Acquisition and Processing

APPENDIX A: DATA ACQUISITION AND PROCESSING

The acquisition and processing of experimental data have been described in the main body of this work. However, the specific details of the procedures were omitted to avoid unnecessary burdens of detail. In this section these procedures will be described and analyzed in detail to allow a basic understanding of how the data are not only acquired but also processed into final form.

Because signal-to-noise ratios are low, often less than one part in two thousand, AC detection techniques must be utilized in the experiment. Furthermore, since the AC background is a function of angle (note that the AC counting process automatically eliminates DC background), the AC background must be determined at each angle. This consequently requires two measurements: (1) AC signal including AC background and (2) AC background. The net signal is the difference of these two measurements.

As the data are taken over the range of scattering angles, the AC signal intensities are found to vary over a range of four decades. Hence, the sensitivities of the tuned frequency preamplifier and of the lock-in amplifier must be continually changed as the angle is varied. This keeps the output of the lock-in in the high section of full-scale, preventing possible errors in system linearity (linearity checks were made and are described later in this section).

The output of the lock-in is sampled by a minicomputer sixty times per second during the counting times which are predetermined

by teletype (TTY) input into the computer. Amplification and attenuation factors are also given to the computer by means of TTY input which the computer then uses to multiplex the sampled output by the given factors — this determines the relative magnitude of the sampled outputs. The outputs are then averaged over the counting period, and the AC measurement is determined. Figure 1 gives the flowchart of the computer software package used to reduce the data. Table I lists the hardware inputs and outputs. Following Table I is a minicomputer language (SCC 4700 Assembler) listing of the data reduction code. This is followed by a detailed explanation of the code using FORTRAN where possible.

TABLE I. Hardwire Inputs/Outputs for Data Reduction Software
Package

INPUTS

- A. Teletype (TTY) inputs for counting parameters
 - 1. Number of times to count (input called FLAGS)
 - 2. Number of seconds counting per time (input called TIME)
 - 3. Wait time between counting times (input called TAU)
 - 4. Amplification factor for HR-8 (input called PAR)
 - 5. Amplification factor for tuned preamp. (input called AC)
- B. Analog-to-Digital (A/D) channel -- output of HR-8, i.e.,
the signal
- C. Analog-to-Digital (A/D) channel -- output of abort switch

OUTPUTS

- A. Teletype (TTY) output
- B. Digital-to-Analog (D/A) channel to select secondary beam position
- C. Digital-to-Analog (D/A) channel to indicate system status on
flashing light

Figure A.1: Flowchart for data processing.

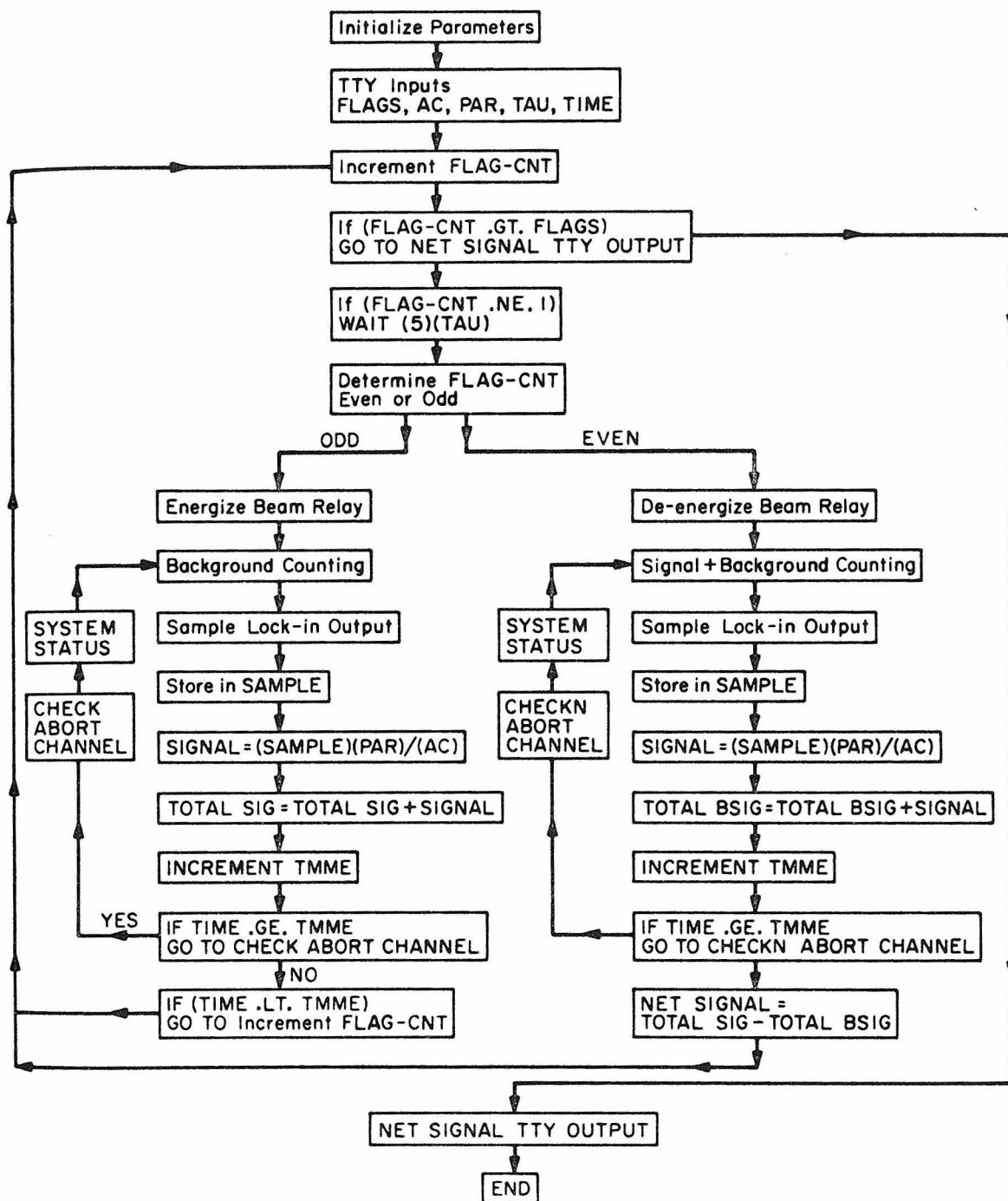


Figure A.1

TITLE 'MOLECULAR BEAM DATA COLLECTION SYSTEM'

* 'MBDA10' THIRD MOLECULAR BEAM PROGRAM. FEB. 2, 1971:

* ALL USE OF MAGNETIC TAPE ELIMINATED. TELETYPE
ACTIVATED

#〈COPY;&SCC.PRIME〉

START REL

ENTRY MBDA10

EXTRN DINTOC, CTOBIN, PRINT, KEYIN, SATOD, ATIME,

BMOVE

BUDD_LNG EQU 81

DA EQU X'0F'

SPACE 3

MBDA10 ENTER

STO DA, RESET, DUMMY, 2

WAIT DA

STO DA, FLIPFLOP, DUMMY, 2

WAIT DA

LDL 1

STA L(POSITION)

SPACE 3

CALL PRINT, (B(MESSAGE1))

CALL KEYIN, (B(TTY_BUFF))

CALL CTOBIN, (B(TTY_AREA), 1)

STA L(COUNT)

CALL PRINT, (B(MESSAGE 4))

CALL KEYIN, (B(TTY_BUFF))

```
RECYCLE    MIN    L(COUNT)
           LDA    L(COUNT)
           CALL   BINTOC, (B(MESSAGE6 8) 1)
           CALL   PRINT, (3(MESSAGE6))
STRTHEAD   CALL   PRINT, (B(MESSAGE7))
           CALL   KEYIN, (B(TTY_BUFF))
           CALL   PRINT, (B(MESSAGE5))
           CALL   KEYIN, (B(TTY_BUFF))
INPUTPAR   CALL   PRINT, (B(MESSAGE8))
           CALL   KEYIN, (B(TTY_BUFF))
           JSL    L(VALID)
           CALL   CTOBIN, (B(TTY_AREA), 3)
           STF    PAR
INPUT_AC   CALL   PRINT, (B(MESSAGE9))
           CALL   KEYIN, (B(TTY_BUFF))
           JSL    L(VALID)
           CALL   CTOBIN, (B(TTY_AREA), 3)
           STF    AC
           DFS    AC1
           RCPY   A, A, Z
           JMP    ACTEST2
           LDF    AC
           DFD    ACC1
           STF    AC
           JMP    GET_FACT
```

ACTEST2 LDF AC
 DFS AC2
 RCPY A,A,Z
 JMP ACTEST3
 JMP GET_FACT

ACTEST3 LDF AC
 DFS AC3
 RCPY A,A,Z
 JMP ACTEST4
 LDF AC
 DFD ACC3
 STF AC
 JMP GET_FACT

ACTEST4 LDF AC
 DFS AC4
 RCPY A,A,Z
 JMP INPUT_AC
 LDF AC
 DFD ACC4
 STF AC

* AMPLIFICATION FACTOR IS COMPUTED.

GET_FACT LDF PAR
 DFD AC
 DFM F1
 DFD F2
 STF FACTOR

```

                                DFM    AC4
                                STF    FACTOR2
INPUTTAU    CALL    PRINT, (B(MESSAG10))
                                CALL    KEYIN, (B(TTY_BUFF))
                                JSL     L(VALID)
                                CALL    CTOBIN, (B(TTY_AREA), 1)
                                STA     L(TTAU)
                                MPY     FIVE
                                STA     L(TAU)
                                CALL    PRINT, (B(MESSAG12))
                                CALL    KEYIN, (B(TTY_BUFF))
                                JSL     L(VALID)
                                CALL    CTOBIN, (B(TTY_AREA), 1)
                                STA     L(TTIME)
                                MPY     SIXTY
                                XAB
                                STD     L(TIME)
                                CALL    PRINT, (B(MESSAC14))
                                CALL    KEYIN, (B(TTY_BUFF))
                                JSL     L(VALID)
                                CALL    CTOBIN, (BTTY_AREA), 1)
                                STA     L(FLAGS)
RUN          CALL    KEYIN, (B(TTY_BUFF))
                                JSL     L(VALID)
                                JNP     RUN
```

* INITIALIZATION OF RUNNING VARIABLES INCLUDING CLOCK.

```
CLEAR      LDL      X'00'
           RCPY     A,E
           RCPY     A,B
           STA      L(FLAG_CNT)
           STD      NN
           STD      N1
           STD      N2
           STF      SUM1
           STF      SUM2
           STF      SUM11
           STF      SUM22
           STF      SS1
           STF      SS2
           STA      L(QUERY)
GET_TIME   CALL     ATIME, (B(DAYTIME))
           CALL     PRINT, (B(DAYTIME))
           TIME
           DAD      L(TIME)
           STD      TIME_LIM
           SPACE 3
```

* DATA ACQUISITION CYCLE. FLAG SECONDARY BEAM IF
NECESSARY

```
START      TIME
           DSB      TIME_LIM
           RCPY     A,A,N
```

	JMP	FLAG	T>TIME_LIM
	JMP	SENSE	T<TIME_LIM
FLAG	STO	DA, FLIPFLOP, DUMMY, 2	
	WAIT	DA	
	LDA	L(POSITION)	
	XDL	1	
	STA	L(POSITION)	
	LDL	0	
	SKN	L(POSITION)	
	JMP	TOGWAIT	
	LDD	N1	
	DSB	NN	
	DF		
	STF	EN	ASSUME N1=N2 FOR NOW
	LDD	N1	
	STD	NN	
	LDF	SUM11	
	DFS	SUM22	
	STF	SAVE	
	LDF	SUM2	
	STF	SUM22	
	LDF	SUM1	
	STF	SUM11	
	DFS	SUM2	
	DFS	SAVE	
	DFM	FACTOR	

```

                                DFD    EN
                                CALL   BINTOC, (B(MESSAG17), 3)
                                CALL   PRINT, (B(MESSAG17))
TOGWAIT  MIN    L(FLAG_CNT)
                                LDA     L(FLAGS)
                                SKN     L(FLAG_CNT)
                                JMP     END_PT
                                LDL     0
                                SUB     L(TAU)
                                STA     L(TAU2)
WAITING   LDA     L(SIXTY)
                                WAIT_TIME
                                SI      DA, FLOPFLIP, DUMMY, 2
                                WAIT    DA
                                MIN     L(TAU2)
                                LDA     L(TAU2)
                                RCPY    A, A, P
                                JMP     QUIT
                                JMP     DONE
QUIT      LA3
                                STA     L(QUERY)
                                LDL     2
                                SUB     L(QUERY)
                                RCPY    A, A, Z
                                JMP     NOT_TWO
                                JMP     END_PT
```



```
NOT-TWO    CALL    SATOD, (6)
            IF
            DFM     FACTOR2
            RCPY    A, A, P
            JMP     END_PT
            JMP     WAITING

DONE        TIME
            DAD     L(TIME)
            STD     L(TIME_LIM)

* CHECK FOR QUERY STATUS.

SENSE       LAS
            RCPY    A, A, Z
            JMP     NONZERO
            JMP     REMOTE

NONZERO     SKN     L(QUERY)
            JMP     REMOTE
            STA     L(QUERY)
            JMP     INTRUPT

REMOTE      STA     L(QUERY)
            CALL    SATOD, (6)
            IF
            DFM     FACTOR2
            FI
            RCPY    A, A, P
            JMP     END_PT
```

* SAMPLE THE ATOD AND UPDATE THE DATA SUMS.

```
CONTINUE    LDA    L(PERIOD)
            WAIT_TIME
            LDA    L(POSITION)
            RCPY   A,A,Z
            JMP    BEAM_ON
            CALL   SATOD,(7)
            IF
            STF    SAVE
            DFA    SUM2
            STF    SUM2
            LDF    SAVE
            DFM    SAVE
            DFA    SS2
            STF    SS2
            MIN    L(N2+2)
            SIO    DA,FLOPFLTP,DUMMY,2
            WAIT   DA
            LDL    0
            SKN    1(N2+2)
            JMP    FIXN2
            JMP    START
FIXN2       MIN    L(N2)
            JMP    START
BEAM_ON     CALL   SATOD,(7)
            IF
```

```
STF    SAVE
DFA    SUM1
STF    SUM1
LDF    SAVE
DFM    SAVE
DFA    SS1
STF    SS1
MIN    L(N1+2)
SIO    DA, FLOPFLIP, DUMMY, 2
WAIT   DA
LDL    0
SKN    L(N1+2)
JMP    FIXN1
JMP    START
FIXN1  MIN    L(N1)
JMP    START
SPACE 3
```

* INTERRUPTION PROCEDURE.

```
END_PT  LDL    2
STA     L(QUERY)
CALL    ATIME, (B(DAYTIME))
CALL    PRINT, (B(DAYTIME))
LDL     1
SKN     L(POSITION)
JMP     INTRUPT
STA     L(POSITION)
```

	STO	DA, FLIPFLOP, DUMMY, 2
	WAIT	DA
INTRUPT	LDL	3
	SUB	L(QUERY)
	RCPY	A, A, P
	JMP	CONTINUE
	TIME	
	STD	L(SAVETIME)
	LDL	0
	SKN	L(N1+2)
	JMP	SKIP1
	LDD	N1
	CALL	BINTOC, (B(MESSAG17), 2)
	CALL	BMOVE, (B(MESSAG17+4), B(MESSAG13+3), 7)
	LDD	N1
	DF	
	STF	EN
	LDF	SUM1
	DFM	FACTOR
	STF	FSUM
	LDF	SS1
	DFM	FACTOR
	DFM	FACTOR
	STF	FSS
	LDF	FSUM
	DFD	EN

```
STF      AV1
CALL     BINTUC, (B(MESSAG17), 3)
CALL     BMOVE, (B(MESSAG17), B(MESSAG13+15), 7)
CALL     BMOVE, (B(MESSAG17+11), B(MESSAG13+22), 4)
LDF      FSUM
DFM      FSUM
DFD      EN
STF      SAVE
LDF      FSS
DFS      SAVE
STF      SAVE
LDF      EN
DFS      ONEF
STF      EN
LDF      SAVE
DFD      EN
DFD      AV1
DFD      AV1
STF      SQ1
CALL     BINTUC, (B(MESSAG17), 3)
CALL     BMOVE, (B(MESSAG17), B(MESSAG13+30), 7)
CALL     BMOVE, (B(MESSAG17+11), B(MESSAG13+37), 4)
CALL     PRINT, (B(MESSAG13))
SKIP1    LDL      0
          SKN      L(N2+2)
          JMP      SKIP2
```

```
LDD    N2
CALL   BINTOC, (B(MESSAG17), 2)
CALL   BMOVE, (B(MESSAG17+4), B(MESSAG15+3), 7)
LDD    N2
DF
STF     EN
LDF     SUM2
DFM     FACTOR
STF     FSUM
LDF     SS2
DFM     FACTOR
DFM     FACTOR
STF     FSS
LDF     FSUM
DFD     EN
STF     AV2
CALL   BINTUC, (B(MESSAG17), 3)
CALL   BMOVE, (B(MESSAG17), B(MESSAG15+15), 7)
CALL   BMOVE, (B(MESSAG17+11), B(MESSAG15+22), 4)
LDF     FSUM
DFM     FSUM
DFD     EN
STF     SAVE
LDF     FSS
DFS     SAVE
STF     SAVE
```

```
LDF    EN
DFS    ONEF
SIF    EN
LDF    SAVE
DFD    EN
DFD    AV2
DFD    AV2
STF    SQ2
CALL   BINTUC, (B(MESSAG17), 3)
CALL   BMOVE, (B(MESSAG17), B(MESSAG15+30), 7)
CALL   BMOVE, (B(MESSAG17+11), B(MESSAG15+37), 4)
CALL   PRINT, (B(MESSAG15))
LDF    AV1
DFS    AV2
CALL   BINTUC, (B(MESSAG17), 3)
CALL   BMOVE, (B(MESSAG17+11), B(MESSAG16+14), 4)
CALL   BMOVE, (B(MESSAG17+11), B(MESSAG16+14), 4)
LDA    L(TTIME)
DIV    L(TTAU)
IF
STF    1OVERTAU
LDF    AV2
DFD    AV1
DFM    SQ2
DFA    SQ1
DFD    1OVERTAU
```

```
CALL  BINTOC, (B(MESSAG17), 3)
CALL  BMOVE, (B(MESSAG17), B(MESSAG16+22), 7)
CALL  BMOVE, (B(MESSAG17+11), B(MESSAG16+29), 4)
CALL  PRINT, (B(MESSAG16))

SKIP2  TTHE
      DSB  L(SAVETIME)
      DAD  L(TIME_LIM)
      STD  L(TIME_LIM)
      LDL  2
      SKN  QUERY
      JMP  MORE
      JMP  L(CONTINUE)
MORE   JMP  L(RECYCLE)
      EJECT
```

* SUBROUTINE TO CHECK FOR ERRORS AND BEGIN DATA TAKING.

```
      BSS  1
VALID  PAR  A(*-2)
      LDH  L(TTY_AREA)
      XOL  C'S'
      RCPY A, A, Z
      JMP  ERR-TEST
      JMP  L(CLEAR)
ERR_TEST LDH  L(TTY_AREA)
      XOL  C'E'
      RCPY A, A, Z
      JMP  I(VALID-2)
```


	JMP	L(INPUTPAR)
	EJECT	
AC	BSS	3
AC1	FPAR	.01
AC2	FPAR	.1
AC3	FPAR	1.
AC4	FPAR	10.
ACC1	FPAR	1.156
ACC3	FPAR	.987
ACC4	FPAR	.978
AV1	BSS	3
AV2	BSS	3
COUNT	BSS	1
DAYTIME	BBSS	9
DUMMY	BPAR	0,0
EN	BSS	3
FACTOR	BSS	3
FACTOR2	BSS	3
F1	FPAR	40
F2	FPAR	32767
FIVE	PAR	5
FLAG_CNT	BSS	1
FLAGS	BSS	1
FLIPFLOP	BPAR	3
FLOPFLIP	BPAR	2
FSS	BSS	3

FSUM	BSS	3
MESSAGE1	BCIE	'THIS IS MBDA10. WHAT WAS YOUR LAST COUNT NUMBER?'
MESSAGE4	BCIE	'DATE = MM/DD/YY'
MESSAGE5	BCIE	'ANGLE='
MESSAGE6	BCIE	'COUNT = S _____'
MESSAGE7	BCIE	'COMMENTS?'
MESSAGE8	BCIE	'PAR='
MESSAGE9	BCIE	'AC='
MESSAG10	BCIE	'TAU='
MESSAG11	BCIE	'PERIOD='
MESSAG12	BCIE	'TIMF='
MESSAG13	BCIE	'N1=_____ AV1=_____ S1=_____'
MESSAG14	BCIE	'FLAGS='
MESSAG15	BCIE	'N2=_____ AV2=_____ S2=_____'
MESSAG16	BCIE	'SIGNAL=_____ SS=_____'
MESSAG17	BCIE	'_____'
N1	BSS	2
N2	BSS	2
NN	BSS	2
ONEF	FPAR	1
PAR	BSS	3
PERIOD	PAR	1
POSITION	BSS	1
QUERY	BSS	1
RESET	BPAR	X '0F'

SAVE	BSS	3
SAVETIME	BSS	2
SIXTY	PAR	60
SO1	BSS	3
SO2	BSS	3
SS1	BSS	3
SS2	BSS	3
SUM1	BSS	3
SUM2	BSS	3
SUM11	BSS	3
SUM22	BSS	3
TAU	BSS	1
TAU2	BSS	1
TIME	BSS	2
TIME_LIM	BSS	2
TOVERTAU	BSS	3
TTAU	BSS	1
TTIME	BSS	1
TIY_BUFF	BPAR	BUFF_LNG
TTY_AREA	BBSS	BUFF_LNG
END		

DATA REDUCTION CODE
MBDAID "FORTRAN EQUIVALENCE"

```
* Title Card
* Compile assembler card # (COPY; ESCC. PRIME)
START
*          FORMAT for assembler
ENTER MBDAID
* LIST SUBROUTINES CALLED
  BUFF_LING = 81
  DA = hex contents of 0F
10 START
* Start Input/Output for DA, RESET, DUMMY, 2
* DA is unit address, RESET is order, DUMMY is data, 2 is
  # bytes counted
  WAIT DA
* Program halted until interrupt received from RESET
* Start Input/Output for DA, FLIPFLOP, DUMMY, 2
  WAIT DA
* Computer waits 15, 0F in hexadecimal, counts of time clock,
  i.e., 15/60 second
  POSITION = 1
  PRINT _ _ _ MESSAGE 1
* MESSAGE 1: This is MBDAID. What was your last count number?
  ENABLE TTY (KEYIN subroutine)
* This is input on teletype TTY of fast count number.
  TRANSLATE TTY character to binary
```

```
COUNT = "last count number"
PRINT _ _ _ MESSAGE 4
* MESSAGE 4 = "DATE = MM/DD/YY
  ENABLES TTY (KEYIN subroutine)
11 COUNT = COUNT + 1
  PRINT MESSAGE 6 + 8
* MESSAGE 6 is printed with value of COUNT displaced in
  MESSAGE 6.
* by 8 characters
12 PRINT MESSAGE 7
* MESSAGE 7: Comments?
  ENABLE TTY
  PRINT MESSAGE 5
* MESSAGE 5: ANGLE =
  ENABLE TTY
13 PRINT MESSAGE 8
* MESSAGE 8: PAA =
  ENABLE TTY
* We can now type input for PAR
  GO TO VALID
  STORE LOCATION in VALID
20 IF (S = TTY_AREA) GO TO 19
* TTY_AREA = halfword read on TTY
21 IF (E = TTY_AREA) GO TO 13
  GO TO VALID = 2
* This is to see if input for PAR is an approved (valid) input
```

```
*      Return to location after JSL command
      PAR = "value printed on TTY, given on TTY"

14  PRINT MESSAGE 9

*      Message 9: AC =
      ENABLE TTY

*      We can now type input for AC
      GO TO 20

20  IF (S = TTY_AREA) GO TO 19

*      TTY_AREA halfword read on TTY

21  IF (E = TTY_AREA) GO TO 13
      GO TO VALID-2

*      This is to see if input for AC is an approved (valid) input
      AC = "value given on TTY"
      IF((AC - AC1).EQ. 0) AC = AC1/ACC1, GO TO 16
      IF ((AC - AC2) .EQ. 0) AC = AC2, GO TO 16
      IF ((AC - AC3) .EQ. 0) AC = AC3/ACC3, GO TO 16
      IF ((AC - AC4) .NEQ. 0) GO TO 14
      AC = AC4/ACC4

16  FACTOR = ((PAR/AC) * F1)/F2
      FACTOR 2 = FACTOR * AC4

17  PRINT MESSAGE 10

*      MESSAGE 10: TAY =
      ENABLE TTY
      GO TO 20

      (VALID -2 = "location of instruction after GO TO")
```

```
20 IF (S .EQ. TTY_AREA) GO TO 19
21 IF (E .EQ. TTY_AREA) GO TO 13
    GO TO VALID - 2
    TTAU = 'value for TAU read in on TTY'
    TAU = 5 * TTAU
    PRINT MESSAGE 12
*   MESSAGE 12: TIME =
        (VALID - 2 = 'location of instruction after GO TO)
    GO TO 20
20 IF (S .EQ. TTY_AREA) GO TO 19
21 IF (E .EQ. TTY_AREA) GO TO 13
    GO TO VALID - 2
    TTIME = 'Value of time read in on TTY'
    TIME = 60 * TTIME
*   NOTE: because of convention used in multiplication,
        A & B registers must be exchanged
    PRINT MESSAGE 14
*   MESSAGE 14: FLAGS =
        ENABLE TTY
        VALID - 2 = 'Present address of instruction after GO TO
        statement'
20 IF (S .EQ. TTY_AREA) GO TO 19
21 IF (E .EQ. TTY_AREA) GO TO 13
    GO TO VALID - 2
        Flags = 'value for flags read in on TTY'
18 READ TTY COMMAND
```

```
IF (TTY COMMAND .EQ. S) GO TO 19
IF (TTY COMMAND .EQ. E) GO TO 13
GO TO 18
19  CLEAR REGISTER
93  A = 0
    FLAG_CNT = 0
    NN = 0
    N1 = 0
    N2 = 0
    SUM1 = 0
    SUM2 = 0
    SUM11 = 0
    SUM22 = 0
    SS1 = 0
    SS2 = 0
    QUERY = 0
100 CALL TIMEPRINT
    *   This converts binary-code time-of-day to ASC11 (TTY language)
        TIME_LIM = TIMEF (X) + TIME
    *   TIMEF (X) is initialized with the value of 60 times value read
        on TTY
    *   TIME is time-of-day
101 IF (TIME - TIME_LIM).LT. 0) GO TO 102
103 CALL DATOG (I0)
    POSITION = XORF (POSITION, 1)
    IF (POSITION .EQ. 0) GO TO 104
```



```
EN = N1 - NN
NN = N1
SAVE = SUM11 - SUM22
SUM22 = SUM 2
SUM11 = SUM1
T = (SUM1 - SUM2 - SAVE) *FACTOR/EN
PRINT T
*   T is not signal, i.e., the difference between signal of 2 flags
    (flag set)
104  FLAG_OUT = FLAG_OUT + 1
      IF (FLAGS .EQ. FLAG_OUT) GO TO 105
      TAU2 = - TAU
*   TAU is 5 times time constant  read in TTY, i.e., waiting period
106  CALL DELAY (60)
      CALL DATOG (0I)
      TAU2 = TAU2 + 1
      IF (TAU2 .GT. 0) GO TO 107
108  QUERY = SLITET (X)
      IF (QUERY .EQ. 2) GO TO 105
109  CALL SATOD (6, T)
*   SATOD (6, T) samples abort A/D channel
      IF ((T * FACTOR 2) .GT. 0) GO TO 106
*   This 106 to last IF-statement is our delay time between flags
      GO TO 105
*   This is out/abort path, if we go to 105
107  TIME_LIM = TIMEF (X) + TIME
```

```
102  IF (SLITET (X) .EQ. 0) GO TO 110
      IF (SLITET (X) .EQ. QUERY) GO TO 110
      QUERY = SLITET (X)
      GO TO 112
110  QUERY = SLITET (X)
      CALL SATOD (6,T)
      IF (T * FACTOR " .LE. 0) GO TO 105
113  CALL DELAY (1)
      IF (POSITION .NE. 0) GO TO 114
      CALL SATOD (7,T)
      SAVE = T
      SUM 2 = SUM 2 + T
      SS 2 = SAVE * SAVE + SS 2
      N2 = N2 + 1
*    This is double word, in assembler + 2 words
      CALL SATOD (7,T)
      CALL DELAY (DA = 15)
*    Double Word fix routine
      GO TO 101
114  CALL SATOD (7,T)
      SAVE = T
      SUM 1 = T + SUM 1
      SS 1 = SS 1 + SAVE * SAVE
      N 1 = N 1 + 1
      CALL DATOG (0I)
      CALL DELAY (DA = 15)
```

```
*      Double Word fix routine
      GO TO 101
105    QUERY = 2
      CALL TIMEPRINT
      IF (POSITION .EQ. 1) GO TO 112
      POSITION = 1
      CALL DATOG (I0)
      CALL DELAY (DA = 15)
112    IF ((3-QUERY) .LE. 0) GO TO 113
      SAVETIME = TIME
      IF ((N 1 + 2) .NE. 0) GO TO 115
*      FORMAT   N 1 to print
          EN = N 1
          FSUM = SUM 1 * FACTOR
          FSS = SS 1 * FACTOR * FACTOR
          AV 1 = FSUM/EN
*      FORMAT   AV 1 to print
          SAVE = FSUM * FSUM/EN
          SAVE = FSS - SAVE
          EN = EN - 1
          SQ 1 + SAVE/(EN * AV 1 * AV 1)
*      FORMAT   SQ 1 to print
          PRINT   N 1, AV 1, SQ 1
115    IF ((N 2 + 2) .NE. 0) GO TO 116
*      FORMAT   N 2 to print
          EN = N 2
```

```
FSUM = SUM 2 * FACTOR
FSS = SS 2 * FACTOR * FACTOR
AV 2 = FSUM/EN
*   FORMAT  AV 2 to print
      SAVE = FSUM * FSUM/EN
      SAVE = FSS - SAVE
      EN = EN - 1
      SQ 2 = SAVE/(EN * AV 2 * AV 2)
*   FORMAT  SQ 2 to print
      PRINT      N 2, AV 2, SQ 2
      MESS (17) = AV 1 - AV 2
      MESS (16 + 7) = MESS (17)
*   7 most significant characters in message 17 are transferred to
      message 16 and displaced 7 characters
*   Next 4 characters in message 17 are transferred to message 16
      TOVERTAU = TTIME/TTAU
      MESS (16 + 22) = ((AV 2/AV 1)(SQ 2) - SQ 1)/TOVERTAU
*   Value put in message at 22nd character -- count starts with 0
      PRINT      MESS(16 + )
      GET_TIME
      TIME_LIM = GET_TIME - SAVETIME + TIM_LIM
      IF (QUERY .EQ. 2) GO TO 117
      GO TO 113
117      GO TO 98
*   98 is start of new count with new TTY inputs required
```

"FORTRAN EQUIVALENCE" of MBDAID

EQUIVALENCE of LOCATIONS:

Assembler Location	Fortran Location
GET_TIME	100
START	101
SENSE	102
FLAG	103
TOGWAIT	104
END POINT	105
WAITING	106
DONE	107
QUIT	108
NOT_TWO	109
REMOTE	110
NONZERO	111
INTRUPT	112
CONTINUE	113
BEAM_ON	114
SKIP 1	115
SKIP 2	116
MORE	117
CLEAR	99
RECYCLE	98
MBDAID	10

RECYCLE	11
STRTHEAD	12
INPUTPAR	13
INPUT_AC	14
ACTEST 4	15
GET_FACT	16
INPUTTAU	17
RUN	18
CLEAR	19
VALID	20
ERR_TEST	21
ACTEST 2	22
ACTEST 3	23

System Linearity Checks:

Whenever data are being taken over a wide range of sensitivities, there is a natural concern whether the data acquisition and processing system has adequate linearity, i.e., are errors due to nonlinear behavior a concern. As a consequence test signals, as indicated in Figure 2, were introduced into the data acquisition and processing system. A wide range of intensities were used; and as the results of Table II indicate the system was linear within $\pm 1.0\%$ for typical run conditions.

Linearity was also checked as a function of the same scale; results are in Table III. Linearity was well within $\pm 0.25\%$ for typical run conditions.

Figure A.2: Schematic for check of linearity in data acquisition/
processing system.

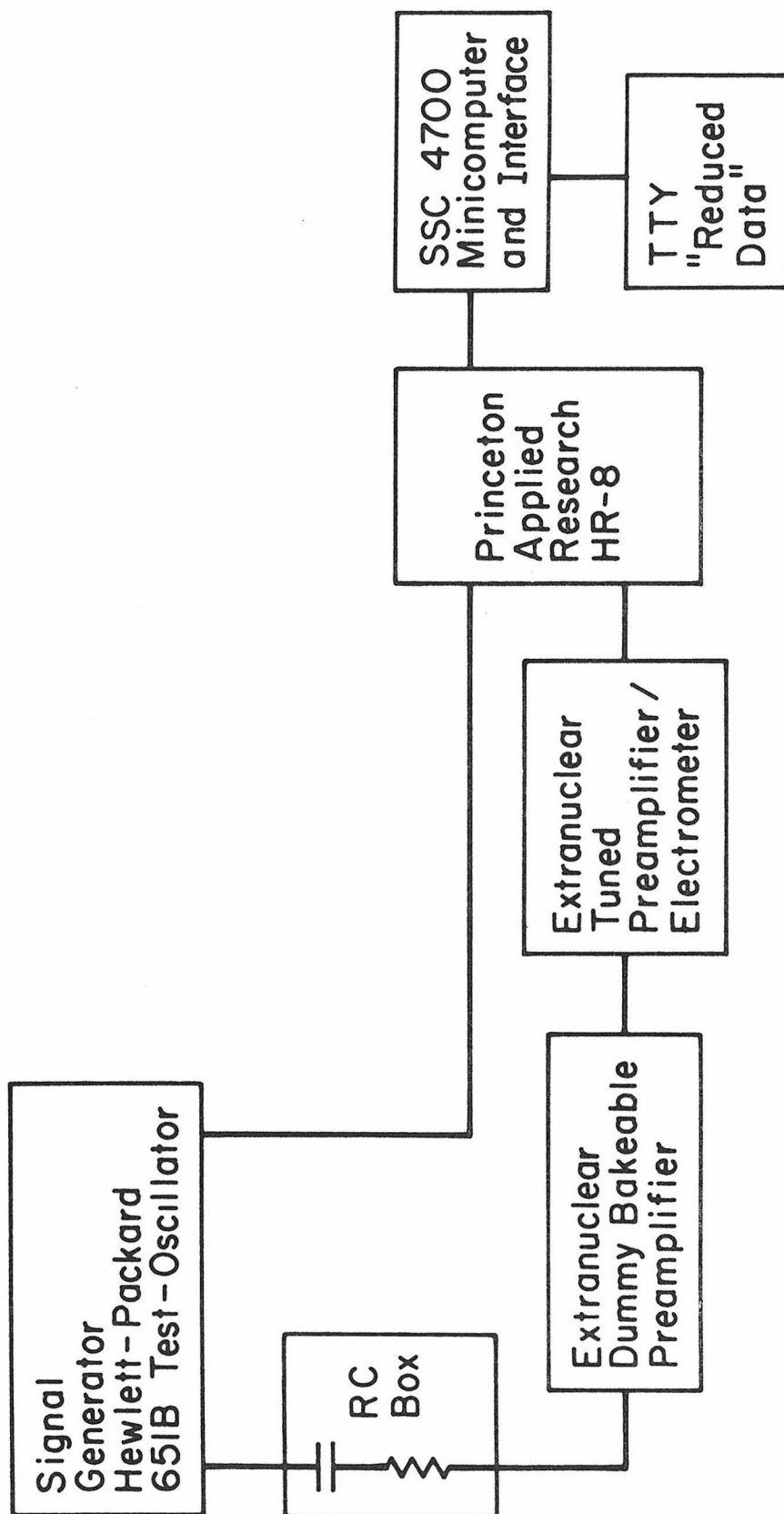


Figure A.2

TABLE II: LINEARITY CHECKS

Arbitrary Test Signal Number	HR-8	Tuned Pre	Signal	Average	% Deviation
1	50	0.1	4397/4408		
1	100	0.1	4420/4426		
1	50	0.1	4395/4400		
1	200	0.1	4390/4404		
1	50	0.1	4395/4407		
1	500	0.1	4371/4429		
1	50	0.1	4387/4395		
2	50	0.1	4425		+0.18
2	500	0.1	4378	4417	-0.88
2	500	1.0	4448		+0.70
3 ^a	50	1.0	467.3		+0.021
3	100	1.0	476.2		+1.92
3	50	1.0	465.5		-0.36
3	200	1.0	462.8	467.2	-0.94
3	50	1.0	469.6		+0.51
3	500	1.0	464.0		-0.68
3	50	1.0	470.0		+0.60
3	500	10.0	462.0		-1.07
4 ^b	50	0.01	54630		-0.2
4	100	0.01	54860		+0.2
4	50	0.01	54640		-0.16
4	200	0.01	54760	54740	+0.04

4	50	0.01	54700		-0.07
4	500	0.01	54950		+0.38
4	50	0.01	54670		-0.13
5	500	0.1	46950	4728	-0.69
5	500	0.01	47620		+0.69
6	500	1.0	2770	2759	+0.40
6	100	0.1	2748		-0.40
7	200	0.1	17230	1732	-0.58
7	50	0.01	17420		+0.58
8	500	1.0	3040	3027	+0.43
8	50	0.1	3015		-0.43
9	500	10.0	282.4	284.7	-0.81
9	50	1.0	287.0		+0.81

a) Weak signal, represents problem of measurement because reference signal is too weak.

b) Strong signal, easy measurement.

TABLE III. LINEARITY CHECKS

Input Voltage	Signal	Expected signal (based on full scale)	% Deviation
.1872	9013	9013	--
.1664	8010	8011	0.01
.1456	6997	7010	0.18
.1248	5991	6008	0.28
.1040	4997	5007	0.20
.0832	3994	4006	0.30
.0624	2993	3004	0.37
.0416 ^a	1985	2002	0.86
.0208 ^a	967	1001	3.52

^a) Weak signal, problem in measurement because reference signal is weak.

APPENDIX B

Pulse Counting

APPENDIX B: PULSE COUNTING

In the experimental section of this work and in the previous appendix section, the current mode of acquiring and processing data was described. However, there are limitations with this technique. As the signal decreases, the point is finally reached when thermal noise, etc. in the detection and processing apparatus overcomes the signal and makes any attempt to retrieve the signal impossible. An alternative technique of acquiring and processing data does exist: the response of the detector is put into a short pulse whose magnitude is much greater than the background noise. This technique is preferable only at low signal-to-noise ratios where signal levels are comparable to thermal, environmental noise. Current mode counting is generally preferred because bandwidth suppression of the frequencies not in the immediate range of the chopping frequency (which contains the signal information) eliminates the majority of the background noise. As a result, in regimes where the signal has enough intensity, current mode counting will outperform pulse mode counting by a factor of six since pulse mode counting sees the entire spectrum of background noise.¹ It must be emphasized at this point that the process of AC or UP-minus-DOWN counting involves the subtraction of two relatively large numbers that are primarily DC background. In order to get a meaningful result, the statistical nature of the process has to be recognized and enough time has to be given to acquire meaningful statistics.

The first experimental efforts to use the pulse counting mode

used a Spiraltron detector (SEM) with an inhouse-designed pulse amplifier and counter. Nothing was obtained that even indicated a possibility of success. The next step was to use a commercial amplifier and counter. While tests indicated that the signals indeed were being counted, analysis and observation soon showed that significant RF noise was being counted. This, of course, destroyed the statistical behavior and meaning of the data. Examination of the detector circuit revealed that the resistor used to determine the voltage between the detector/multiplier and the collector was not only too small by a factor of one hundred but also was improperly grounded to the body of the mass spectrometer. This area is the worst possible for RF noise. The circuit was rewired as shown in Figure 1. Again tests were made with the commercial amplifier and counter; this time the tests were successful. The data obtained did follow statistical behavior!! A point should be made here that RF noise could still be observed; however, the noise had been reduced to a level at which the amplifier could discriminate against it.

The next step was examination of the inhouse-designed preamplifier and the inhouse-designed counter. The preamplifier worked well in breadboard checks at 1000 Hz both in amplification and in discrimination. The UP-minus-DOWN counter did not work--the gating system did not pass a single pulse. This counter had previously been described in detail;² however, the gating circuit had been modified. As a consequence, the entire gating circuit was changed and all that remained of the original unit was the counter and display circuit

(Circuit B-4 in reference 2). Since the HR-8 lock-in amplifier was dedicated to the molecular beam experiment, the phase-shifted reference signal generated by the lock-in could be used. This then was used to trigger the gates for UP or DOWN counting. When the reference saw an $\uparrow$ pulse, i.e., transmitting, the UP-counting gate was triggered; when the reference saw a $\downarrow$ pulse, i.e., nontransmitting (chopped) the DOWN counting gate was triggered. Of course, the opposite gate was disabled throughout this sequence. Preliminary tests indicated that these modifications allowed statistical counting to be made. One final change was made to the gating system. Because of edge effects in chopping, an overlap occurred between UP and DOWN counting. To eliminate this error, to eliminate the error introduced by imprecise phase shifting, and to eliminate the error introduced in the reference by imprecise frequency matching of the chopper and lock-in, a time delay after each trigger was introduced followed by a well-defined counting interval, nominally the center 80% of the UP or DOWN counting period. A megahertz clock was used to time the counting interval, which results in a maximum error of 1 out of 2000.

Tests of the counter under normal experimental conditions appeared reasonable, i.e., signal-to-noise was in the expected regime of values and signals had expected relative size at intermediate angles (i.e., 5° - 8°). However, the scan of an ethane primary beam indicated anomalous behavior at low angles (see Figure 2). Further investigations and analyses showed that a number of factors had to be considered in the system performance:

- I. The detector/multiplier loses linear behavior when the counts exceed 10% dynode bias current.³

a. $B = \frac{V}{\Omega}$

where B is bias current

V is applied voltage

Ω is resistance of Spiraltron

- b. Ω for new Spiraltron is $1 - 1.3 \times 10^{+9}$

As Spiraltron gets old or is subjected to bakeouts,

Ω increases. 2×10^9 is reasonable value.

- c. $I = GNC$

where I = current due to counts

G = gain

N = counts

C = charge

- d. G is a function of applied voltage, age of multiplier, and number of counts.

i. new multiplier: $V = 3KV \Rightarrow_1 G = 10^8$

$V = 2.7 KV \Rightarrow_2 G = 5 \times 10^7$

ii. $N = 10^4 \Rightarrow G \approx 10^8$

$N = 10^6 \Rightarrow G \approx 10^7$

- e. $B \sim 3 \times 10^{-6}$ amps

- f. For linearity: $I = 0.10 B = 3 \times 10^{-7}$ amps = GNC

$3 \times 10^{-7} = (10^7)(1.9 \times 10^{-19})N$

$N \approx 1.5 \times 10^5$ counts/sec

i.e., for linear behavior $N \leq 1.5 \times 10^5$ counts/sec

- II. With high AC signal, i.e., UP counts are much larger than background, two significant problems occur:⁴
 - a. The pulse height of the UP counts is significantly lower than those of the DOWN counts. Discrimination in the preamplifier becomes touchy, i.e., we do not want to discard weak UP-count pulses.
 - b. A d.c. shift occurs which causes the preamplifier to discriminate against DOWN-pulses which have been shifted down in size.
- III. The bandwidths of all electronics must be large, i.e., in the megahertz regime to prevent pulse pile-up, i.e., pulses overlap and are not counted.
 - a. The counter was tested and found to have a 20 MHz bandwidth.
 - b. The Spiraltron pulses had widths less than a micro-second, i.e., a bandwidth larger than a MHz.
 - c. The preamplifier was tested and found to have satisfactory performance at 1 kHz; however, as the bandwidth tests were increased beyond 10 kHz, severe degradation of performance was observed.

As a consequence of these observations, two recommendations were made: (1) replace the preamplifier with a commercial unit supplied by Galileo Electro Optics which had a bandwidth in the megahertz regime and (2) investigate the use of DC filters if the counting system was planned to be used at very low angles.

Figure B.1: Spiraltron (detector) circuit.

Figure B.2: Plot of Ethane Beam Intensity as a Function of Angle
 $\blacktriangle$ - intensity measured by current detector, $\odot$ - intensity measured
by pulse detector.

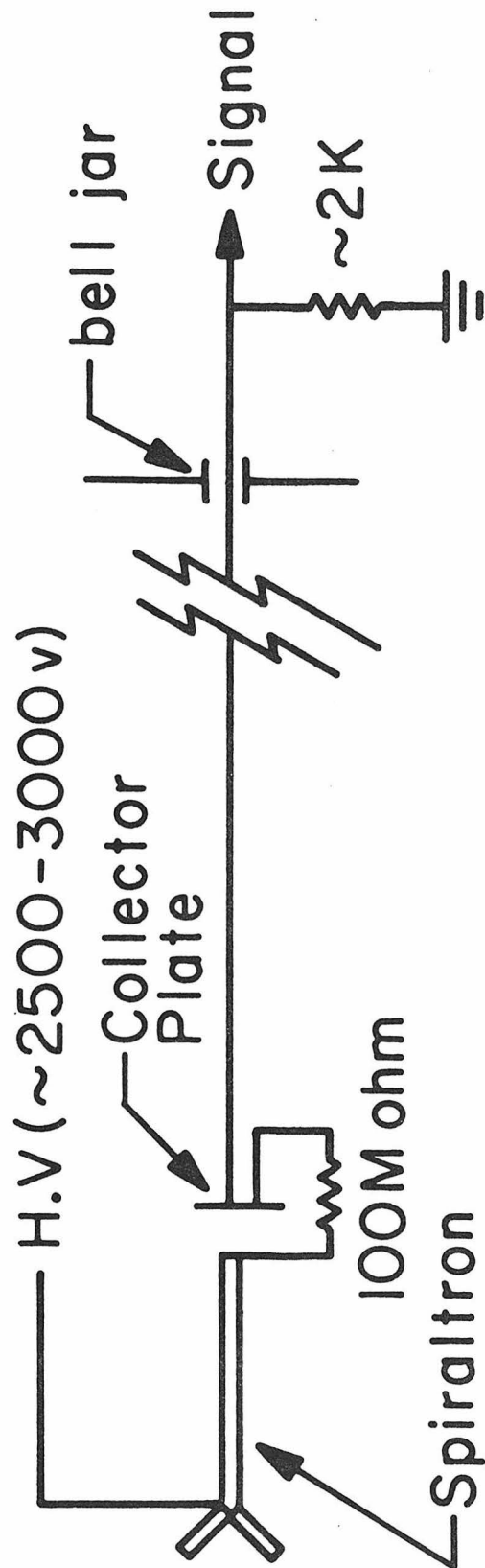


Figure B.1

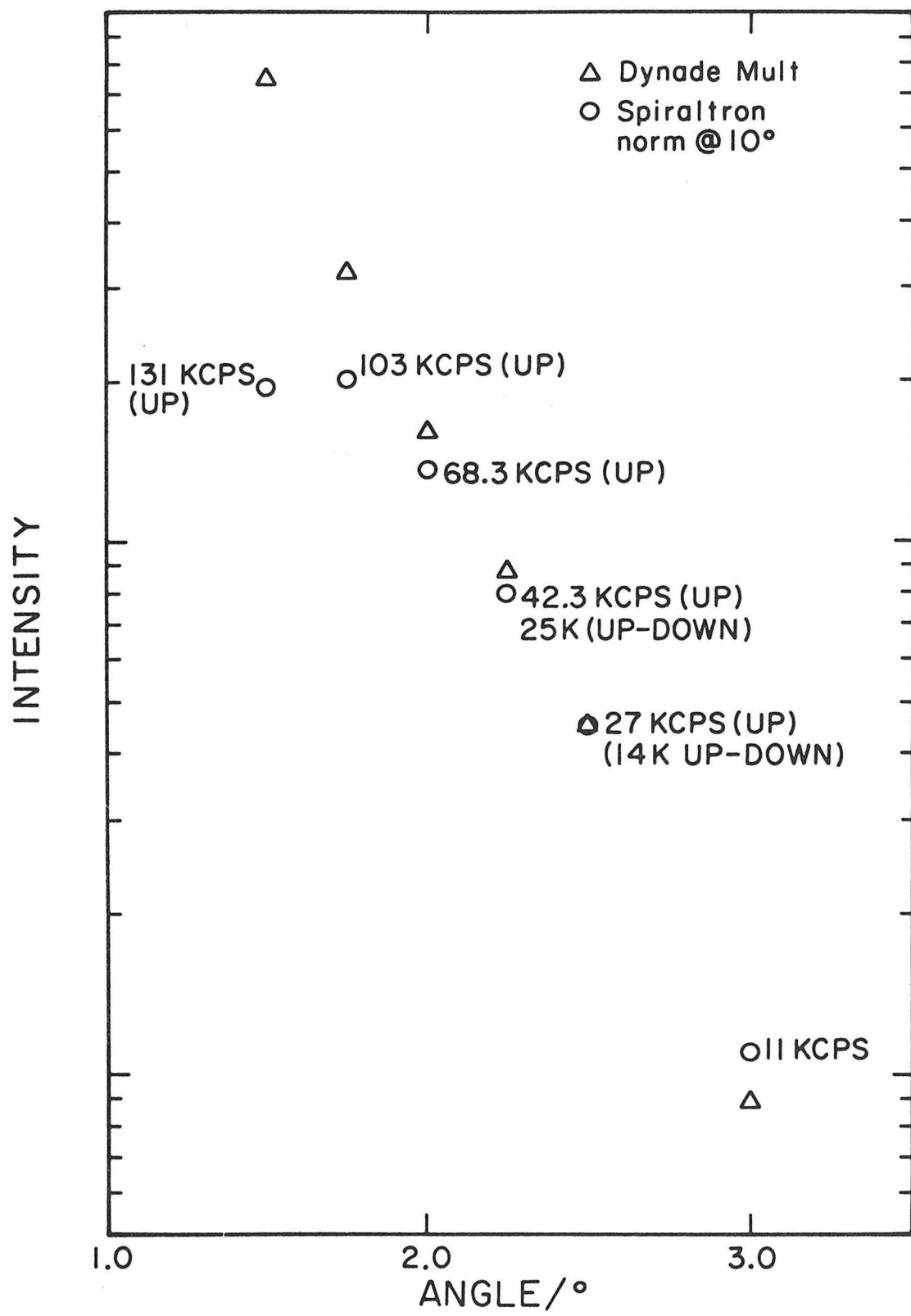


Figure B.2

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2. M. J. Coggiola, Ph.D. Thesis, California Institute of Technology, 1975, Appendix B.
3. Private Communication, Ray Ray, Galileo Electro-Optics.
4. Private Communication, Irv Moskowitz, Electronics Shop, Department of Chemistry, California Institute of Technology.
5. Pulse Amplifier - Discriminator, Galileo Electro-Optics Corp., Galileo Park, Sturbridge, Mass. 01518, (617)347-9191.
12MHz counting rate.

APPENDIX C

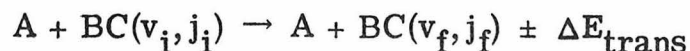
Molecular Beam Inelastic Scattering Experiment

APPENDIX C:
MOLECULAR BEAM INELASTIC SCATTERING EXPERIMENT

Introduction and Overview of Theory:

Vibrationally and rotationally inelastic scattering are simple energy-transfer collision processes which play a significant role in many physical phenomena such as the kinetics of gas-phase chemical reactions and as the energy balance in plasmas and astrophysical systems. Perhaps their most glamorous role today is in the operation of gas-phase lasers.

The simplest of all inelastic collision processes is given by



where A, B, and C are atoms, and v and j are the vibrational and rotational quantum number respectively. The index i denotes the initial state; the index f the final state. ΔE_{trans} denotes the change in relative translational energy. Understanding of such processes provide insight into the dynamics of molecular collisions and should provide the foundation for better definition of reactive collisions. Considerable work has been done on these systems over the past few years. The work of Rapp and Kassal remains the best description on the theoretical methods developed for describing energy transfer.¹ Experimental work has been done in bulk studies and a number of good reviews exist.^{2, 3} Work done with beams has been much more limited. A good review is given by Toennies.⁴ Two fundamentally

different experimental techniques are used: the state selecting and the energy change methods. In the ideal state-selecting experiment, molecules are prepared in a definite state before scattering and the scattered molecules are analyzed for their final rotational and/or vibrational state by an appropriate "state filter" which permits only molecules in the specified state to arrive at the detector. In the energy-change experiments, the final velocity of one of the partners is measured after collision. If the initial velocities of both particles are sufficiently defined, the inelastic energy loss observed after the collision can be used to determine what vibrational or rotational state has been excited. This experiment generally involves a small cross section and hence a small signal making it a difficult experiment to run. Farrar et al. have studied in the $\text{CO}_2\text{-Ar}$ and the $\text{N}_2\text{O-Ar}$ systems rotationally inelastic collisions,⁵ as examples of the energy-change experiment.

Velocity distributions of particles are normally measured either by filters which allow only those particles with a specific velocity to pass or by analyzers which determine the time of flight, i.e., the time it takes a particle to travel a known distance. The first method, in practice, requires five or six disks to provide reasonable resolution and measures only one velocity at a time. In the second method the beam is chopped to introduce a pulse of particles into the system. The particles spread out in time and the detector sees them as a function of time. For good resolution, the pulse must be short and the pulses must be separated far enough in time to prevent overlap.

This consequently results in low signal with poor statistics forcing many measurements, since the technique has only approximately 0.5% duty cycle. This duty cycle can, however, be increased to nearly 50.0% by use of correlation techniques which can and do separate information from overlapping pulses. In this method the beam is modulated with an approximation to white noise, a pseudo-random sequence; and the resulting signal at the detector is cross-correlated with the modulating sequence (function) to produce the time-of-flight spectrum.

The mathematics of this approach is described by Visser et al.,⁶ Sköld,⁷ Hirschy and Aldridge,⁸ and Allen.⁹ In general, the response $y(t)$ to an excitation function $x(t)$ is given by the convolution integral

$$y(t) = \int_0^{\infty} h(\tau) x(t - \tau) d\tau \quad (1)$$

where $H(t)$ is the impulse response of the system. In order to measure $h(t)$, the unit impulse $\delta(t)$ is substituted for $x(t)$.

$$y(t) = \int_0^{\infty} h(\tau) \delta(t - \tau) d\tau = h(t). \quad (2)$$

This is a direct measurement of the residence time distribution and represents time-of-flight measurement of a short pulse. The more efficient method is provided by a cross-correlation measurement in which the impulse response $h(t)$ is obtained by cross correlating the excitation function $x(t)$ and the response $y(t)$. The cross correlation $R_{xy}(\tau)$ of $y(t)$ in (1) is defined as

$$R_{xy}(\tau) = A\{x(t) y(t - \tau)\} \quad (3)$$

where A is the statistical average. This may further be developed

$$A\{x(t - \tau) y(t)\} = A\left\{x(t - \tau) \int_0^{\infty} x(t - \lambda) h(\lambda) d\lambda\right\} . \quad (4)$$

If $x(t)$ is a stationary time function,

$$A\{y(t) x(t - \tau)\} = \int_0^{\infty} A\{x(t - \tau) x(t - \lambda) h(\lambda) d\lambda\} \quad (5)$$

$$= \int_0^{\infty} A\{x(t - \tau) x(t - \lambda)\} h(\lambda) d\lambda \quad (6)$$

$$= \int_0^{\infty} R_{xx}(\tau - \lambda) h(\lambda) d\lambda . \quad (7)$$

If $x(t)$ is chosen as a stationary random function with an autocorrelation function $\psi_{xx}(\tau) = \delta(\tau)$, it follows

$$R_{xy}(\tau) = \int_0^{\infty} \delta(\tau - \lambda) h(\lambda) d\lambda = h(\tau) , \quad (8)$$

i. e. , the residence time distribution $h(\tau)$ has been obtained.

This method may be specifically applied to a fast response detector whose signal has been chopped by a pseudo-random function periodic in character. Use of a pseudo-random function is dictated because its spectral density is highest, optimizing signal-to-noise ratios.⁶ The periodic nature of the function is also advantageous since integration times are minimized in comparison with a true

random function.¹⁰ Let the transmission function be

$$F(i) = \frac{1}{2} \{a(i) + 1\} \text{ where } F(i) = 1 \text{ open, transmitting interval}$$

$$F(i) = 0 \text{ closed, nontransmitting interval}$$
(9)

Let $a(i)$ be a maximum sequence of length $L-1$

$$\sum_{i=0}^{L-1} a(i) = 1$$
(10)

$$\sum_{i=0}^{L-1} a(i) a(i+j) = \begin{cases} L & j = 0 \\ -1 & j \neq 0 \end{cases}$$
(11)

Hence, we have a transmitting function $F(i)$ which is a sequence of L distinct intervals i , each of which corresponds to a transmitting or a nontransmitting of particles with a distribution in time $S(t)$. The total number of counts which the detector sees in one interval is given by

$$I(i) = \sum_{t=0}^{L-1} [F(i-t) S(t) + B(t)]$$
(12)

where $B(t)$ is the background noise. Cross correlation gives

$$R(\tau) = \sum_{t=0}^{L-1} a(i-\tau) I(i) = \sum_{t=0}^{L-1} \sum_{t=0}^{L-1} \{a(i-\tau) \frac{1}{2} [a(i-t) + 1] S(t) + a(i-t) B(t)\}$$
(13)

$$R(\tau) = \frac{1}{2} \{L + 1\} S(\tau) + B(\tau) + \sum_{t=0}^{L-1} B(t)$$
(14)

where $S(\tau)$ is the probability distribution in time, $B(\tau)$ is the coherent noise associated with the signal and $B(t)$ is the incoherent noise. For N revolutions, L intervals, the average signal may be written

$$I(i) = \frac{1}{N} \left\{ N \sum_{t=0}^{L-1} [F(i-t) S(t) + \sqrt{N} B(t)] \right\}, \quad (15)$$

i. e., the signal and associated coherent noise accumulates proportional to N while the incoherent noise accumulates to an rms, $\sqrt{N}$. For a large number of N , since $B(t)$ is random and should be constant for all intervals, $B(t)$ can be estimated closely from minimum values of $R(\tau)$ and subtracted. Our measured distribution is thus given as

$$R(\tau) = \frac{1}{2} \{L + 1\} S(\tau) + B(\tau)$$

$$\frac{2}{L + 1} R(\tau) = S(\tau) + \frac{2}{L + 1} B(\tau) = P(\tau).$$

Thus, the calculated distribution in time differs from the true distribution by a term $\frac{2}{L + 1} B(\tau)$. If the distance between the chopper and the detector can be characterized as DIS, the velocity distribution can readily be obtained by changing from the variable τ to v where $v = \text{DIS}/\tau$. The amplitude must be corrected for the detection method, i. e., by multiplying $R(\tau)$ by the corresponding time.

The Multichannel Scaler:

The multichannel scaler acts as a storage buffer for a mini-computer. It is necessary to store data in a 2-to-10 μ sec time interval synchronously with well-defined discrete intervals on the chopping wheel. Since data acquisition and storage time on a minicomputer is characteristically longer, the data cannot be stored on-line. Hence the need for a buffer exists.

The multichannel scaler can be subdivided into four sections: timing, data acquisition, gating, and storage (see Figure 1).

The timing section determines the time length (period) of each interval and hence determines the speed of the motor, since each revolution has 255/(1020) or 256/(1024) intervals. The light pulse from the chopper, which represents the beginning of a new revolution, is used to correct any phase difference between the actual motor speed and generated time by resetting everything at the beginning of each revolution.

The data acquisition section is comprised of two parts which alternately count or store data depending on whether the interval number (address) is even or odd (low or high). This permits continuous counting with no time necessary for resets, etc.

The storage section allows data for corresponding intervals to be accumulated over a large number of revolutions. This provides counting efficiency times of greater than 90%.

The gating section must be divided into subsystems which often interconnect and overlap in their functions. These subsystems can be categorized as: timing, data acquisition, storage, and clearing.

Figure C.1: Block-diagram of multi-channel scalar.

Figure C.2: Schematic of multi-channel scalar.

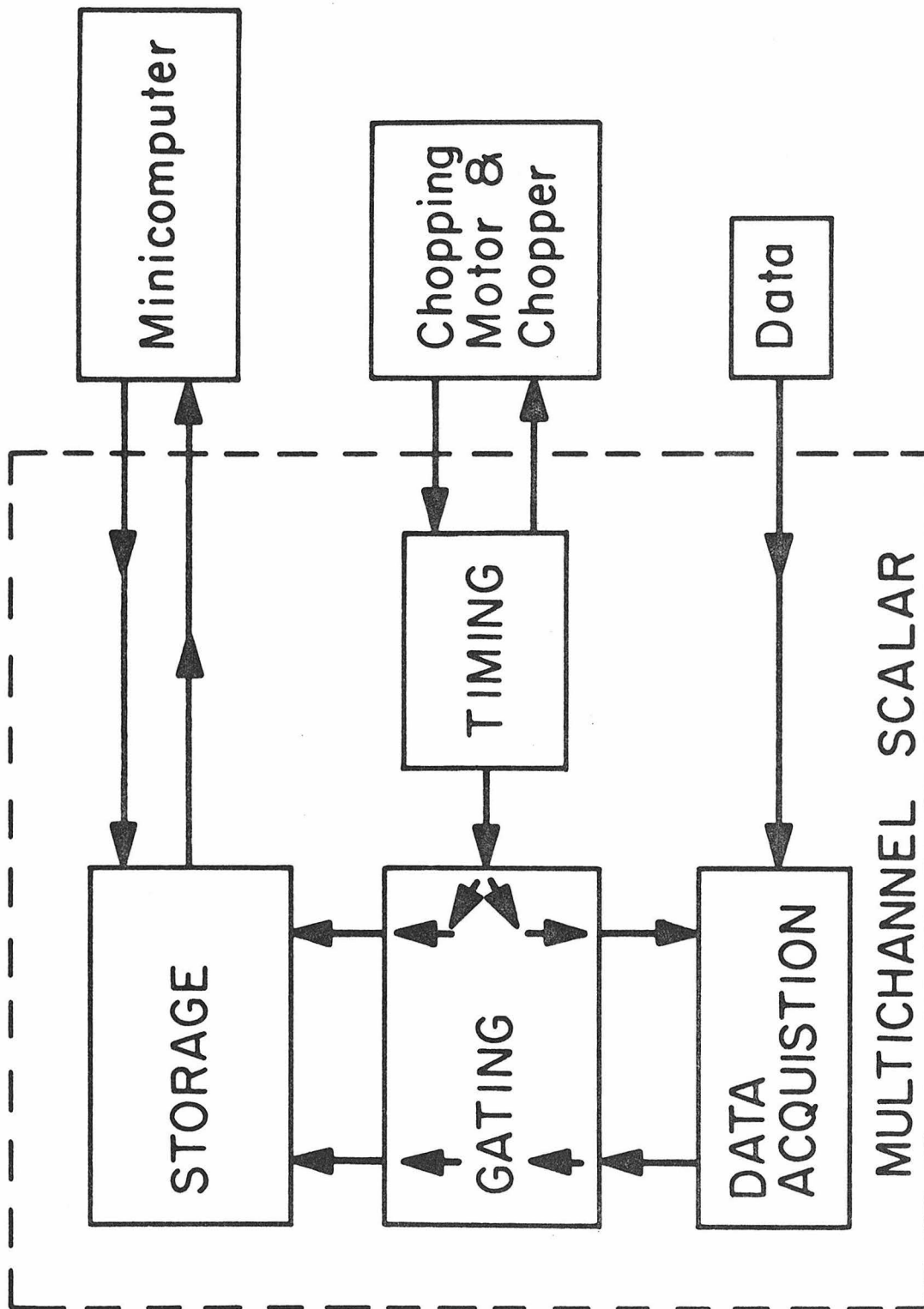


Figure C.1

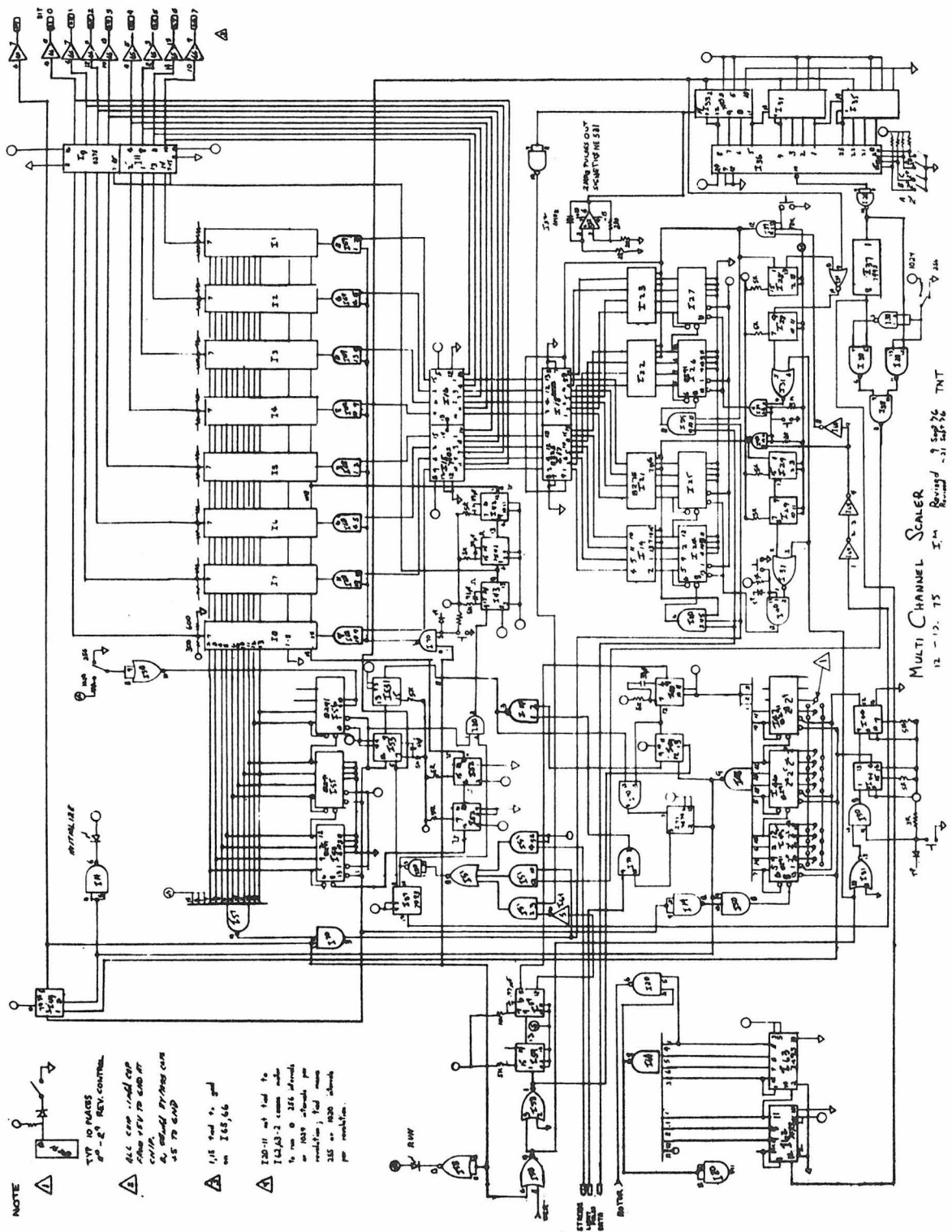


Figure C.2

Timing Section

Chip	Description of Function
I32	Provides 2MHz pulses
I33, 34, 35	Count pulse output of I32
I36	12-input multiplexor, determines time length (period) associated with an interval
I51	Gate through which square wave from I38 must pass
I37-1, 8	Divide by four. When 255 wheel is used, it drives both motor and address registers; when 1023 wheel is used, it drives only motor register
I38-4, 5, 6;8, 9, 10;11, 12, 13	Selects either 255 or 1020 <u>or</u> 256 or 1024 intervals per revolution
I62, 63, 61, 20-4, 5, 6;11, 12, 14	Determines motor speed (one revolution for every 255/1020 or 256/1024 intervals)

Data Acquisition Section:

The data acquisition section has two identical parts which alternately count or store data depending on whether the first bit of a binary counter is high or low.

Chip		Function
I20-1, 2, 3		Puts data acquisition cycle in phase with I36 squarewave output
I37-14, 12		Determines whether part A or part B counts or stores data (parts A and B defined below)
Part A	Part B	
I40-3, 4, 56	I39-8, 9, 10, 11	AND-gate for data input
I24, 25	I26, 27	Count data pulses depending on I37-12
I19, 21	I22, 23	Latch data count from previous interval
I40-8, 9, 10, 11	I39, 1, 2, 12, 13	AND-gate, part of high/low selection gating
I29	I28	one-shots to clear counters
	I31-8, 9, 10	insures data counter B is cleared for the initial interval

Data Storage:

This section has six subsections plus gating.

Subsection	Cip	Function
(1)	I1, 2, 3, 4, 5, 6, 7, 8	RAM's for storing accumulated counts
(2)	I17, 18	Multiplexor to select stored counts
(3)	I9, 11	Latcher to hold stored counts from RAM's for interval just completed (old stored value)
(4)	I15, 16	Adds counted data with stored data to give updated input for RAM's (updated input = old stored value + new counts)
(5)	I54, 55, 56	Address register--gives interval counting is on but does not advance until RAM's have updated input.
(6)	I45, 46, 47	Revolution register--fives number of revolutions plus one that chopper has completed

Gating

I43-13	Causes data in RAM's to be latched
I42	100nsec after data is latched, it produces a write-enable pulse of 100 nsec to store updated input
I52	40 nsec after end of write-enable pulse, it produces a pulse to advance address register

Data Storage (cont):

	Chip	Function
Gating	I53	Produces rest pulse for address register, for binary counter I37-12, 14, and for interval squarewave from I36; advances revolution register, disenable I30-1, 2, 3 during reset to prevent spurious pulse from firing I43 one-shot if output of I20-3 is high
	I44	One shot for resetting I45, 46, 47 on clear
	I48	NAND-gate, goes down when number of revolution specified is completed

Gating Section:

With the exception of the enable and clear gates, gates have been referenced in other sections.

Chip	Function
I70-8, 9, 10	Does not admit further light pulses once number of specified revolutions obtained
I14-1, 2, 3	Does not admit light pulse during clear pulse
I48	Goes down when specified number of revolutions are obtained
I71-5	Goes down when specified number of revolutions are obtained and <u>when</u> counting for last revolution is complete
I57-9	Goes down when all intervals during a revolution have been completed (motor is slower than clock)
I49-5	Goes down when specified number revolutions are obtained and <u>when</u> next light pulse clocks, i.e., goes down after end of final revolution
I70-3	Goes down when either number of intervals in a revolution have been completed or when number of revolutions have been completed (end of last revolution)

Normal Operation (Overview):

1. Computer software is programmed to receive, through the teletype (TTY), the number of data dumps, i.e., sets of revolutions, that should be received by the computer.
2. Execute command is given to the computer through TTY.
3. Computer sends command to the Multichannel Scaler (MCS) for clear.
4. MCS clears and then starts accepting data at the beginning of the next revolution (light pulse into I14-1).
5. After specified number of revolutions (as determined by switches on MCS; MCS no longer accepts data and then sends pulse to computer that it is ready for data dump (I49-5)).
6. Status of MCS:
 - (1) I54, 55, 56 -- memory address set to 0
 - (2) I8 thru I1 -- RAM's set to output address determined by
I54, 55, 56 {I8 least significant bit, i.e., 2^0 }
 - (3) I54, 55, 56 cannot be advanced by square wave output (I36-10)
" " " " " " " direct clock (I32)
" " " " " reset by light pulse (I14-3)
" " " can be advanced by strobe input
 - (4) I24, 25, 26, 27 cannot accept data
7. Computer reads first data byte (8 bits) from I9, 11; adds contents to that already stored for first interval (address 00000000 in binary). Command is sent to advance I54, 55, 56; computer reads second byte, etc.; computer reads 255th byte (1023rd byte).

Normal Operation (Overview) (cont):

8. Computer compares number of dumps made with number specified through TTY input, returns to step 3 unless specified number of dumps have been made.
9. Computer processes data. This is arithmetic with file just read in; and also at end of dumps this is the cross-correlation.

Clear Command (thru I58-5):

At the start of the run, the manual reset is hit. The reset consists of five switches ganged together which clear the data registers and the revolution register. The MCS is now ready for a clear pulse from the computer. Command from the computer (I58-5) causes a positive pulse at I58-4 which in turn is sent to the following locations:

- (i) I31-3 $\Rightarrow$ I24,25 are cleared
- (ii) I31-6 $\Rightarrow$ I26,27 are cleared
- (iii) I31-13 $\Rightarrow$ generates a 40 nsec negative pulse which immediately reset I45,46,47 and I49-1;
I45,46,47 are also strobed about 40 nsec later to set values to those selected by panel switches
- (iv) I59-12 $\Rightarrow$ $\sim$ /msec pulse which allows direct clock inputs (2MHz) to advance address register
- (v) I59-5 $\Rightarrow$ $\sim$ /msec pulse at whose end a pulse is generated in I43-12. This clocks I49-11 causing I49-9 to go high and enable I14-1.
This also clocks I71-3 which enables I70-9.

Clear on I45,46,47 makes I48 go high

I48 high enables I50-10 (AND-gate to I45,46,47)

Light pulse in (I14-1) causes I53 to generate reset pulse on I54,55,56; I33,34,35; and I49-3 (clock). I49-5 goes high. I57-9 is now also high.

$\Rightarrow$ I51-9 is enable (interval drive)

$\Rightarrow$ I50-10 into I45,46,47 is enabled

Clear Command (thru I58-5) (cont):

⇒ I40-4 and I39-10 are high; data may be accepted

∴ data can now be accepted

address register can be advanced by I36-10 square wave

Data Acceptance:

status: I45, 46, 47 have been cleared, have one revolution counted

I24, 25, 26, 27 are clear

I19, 21, 22, 23 are clear

I17, 18 are clear

I8 thru I1, RAM's are clear

I9, 11 are clear

I15, 16 are clear

start: I14-3 clears I54, 55, 56; I33, 34, 35

I14-3 causes I49-3 clock to drive I49-5 high which drives

I70-3 high enabling data acceptance and address
register advance

I33, 34, 35 generate a square wave whose period (multiples of
two megahertz oscillator pulses) is determined by I36 —
output square wave from I36 is start high to low

Output of I37-12 is low for first interval (address
00000000 in binary)

Low on I37-12 causes I24, 25 to be cleared after a 40nsec delay;

causes I19, 21 to be held; causes I17, 18 to pass contents of
I19, 21 to I15, 16; and causes I26, 27 to count data pulses

High on I37-12 causes opposite: I26, 27 to be cleared; I22, 23 to be held;

I17, 18 to pass contents of I22, 23 to I15, 16; and I24, 25 to count
pulses

Data Acceptance (cont):

When the output from I36 goes low, I37-12 sees a count and I43-13 generates a pulse. I9,11 are latched with contents old stored data for first address; I37-12 has already gone high. I24,25 are now counting. I15,16 now add contents of I17,18 (latched data counts from I26,27) with latched stored old data from I9,11.

After time delay in I42, new updated counts are written in RAM's I8 thru I1 (i.e., contents of memory address 00000000 plus counts from 00000000 interval just completed go into memory address 00000000). I54,55,56 are advanced by one after 40 nsec delay in I53.

When second interval is complete, the squarewave from I36 goes down. This causes I37-14 to go low. I26,27 are now counting. I9,11 are latched with contents of old stored data for second address.

I15,16 now add contents of I17,18 (latched data counts from I24,25) with latched stored old data from I9,11. After time delay in I42, new updated counts are written in RAM's I8 thru I1 (i.e., contents of memory address 00000001 plus counts from 00000001 interval just completed go into memory address 00000001).

I54,55,56 are advanced by one after 40 nsec delay in I53.

Each time a period is generated in I36, the process is repeated.

In general: For the first revolution contents of the i^{th} memory address correspond to data pulses counted in the i^{th} interval. For the second and succeeding revolutions, contents of the i^{th} memory address are added with the counts from the i^{th} interval and then written into the i^{th} memory address.

Data Acceptance (cont):

⇒ In the i^{th} memory address is stored the accumulated counts for the i^{th} interval; counts are counted in each interval for a full period except at the end of the revolution if the motor is faster than the clock (everything is immediately set back to the first interval - address 00000000).

I36 continues generating square waves which continue advancing I54, 55, 56.

As I54, 55, 56 approach 256, two cases can occur:

(i) wheel is faster than clock

⇒ light pulse through I14-1 resets I54, 55, 56; I33, 34, 35 and advances I45, 46, 47 by one

(ii) wheel is slower than clock

⇒ I54, 55, 56 reach 256th interval (memory address 11111111)
I57 NAND-gate goes down, I70-3 goes down. Data cannot be accepted; memory address register cannot be advanced.
Finally wheel catches up and light pulse resets as in case (i)
Data counting starts out at first interval again (00000000 address) and repeats described operation).

The switches associated with I45, 46, 47 determine the number of revolutions before a data dump. When the light pulse resets I54, 55, 56 and advances I45, 46, 47 to the desired number, I48-9 goes down. When that revolution's counting is completed, i.e., another light pulse into I14-1, I54, 55, 56 are reset; I33, 34, 35 are reset; and I49-5

Data Acceptance (cont):

goes low. I45,46,47 can no longer be advanced because I50-9 is disabled. I49-5 low disables MCS--data cannot be accepted nor can I54,55,56 be advanced.

Data Dump:

Status: I54,55,56 are at address 00000000

I8 thru I1 output at address from I54,55,56

I8 thru I1 buffered in I9,11, I65,66

"Computer reads" byte from I9,11; sends advance command to I51-4; I54,55,56 advanced by one; I8 thru I1 output address now advanced by one; "computer reads" byte, etc.

When "computer has read" all desired memory addresses, clear command is sent to I58-5.

Clear cycles in MCS; process is repeated for data counting/storing until computer has data from the desired number of dumps.

Computer software processes data.

Timing - Data Taking (cont)

level; I26, 27 are reset so that counts from previous interval before reset are not counted.

I37 must fire on ↓, not ↑

After one full interval, I37 changes level which causes counts from completed interval to be output by I17, 18.

I51-8, I20-3 change causes I43-13 to produce a 200 nsec long pulse which latches stored data in RAM's for interval just completed.

100 nsec after end of I14-13 pulse, I42 gives a 100 nsec pulse to write into RAM's the sum of stored and just counted data for interval just completed.

After 40 nsec more, I54, 55, 56 are advanced by one to give address of current interval.

Although the multi-channel scaler just described (schematic given in Figure 2) was built to be compatible with any minicomputer, considerable work was done to interface it to the SCC 4700 minicomputer, which formerly was alive and well computing in the Noyes sub-basement. Following is given the time sequence of operations (see Figure 3); the schematic for the minicomputer - scaler interface (see Table I and Figure 4); the Fortran program to reduce raw data and to obtain velocity distributions; and finally the SCC 4700 Assembler Language Program for acquiring, storing, and reducing data obtained through use of the multichannel scaler.

Timing — Initialize

Switch I (SW-1)	disenable AND-gates to RAM's
Switch II (SW-II)	clears I45, 46, 47 $\Rightarrow$ I48-9 goes high $\leq$ 80 nsec strokes I45, 46, 46 for 40 nsec, 40nsec after clear clears I49-5 (definitely low)
Switch IIIA (SW-IIIA)	resets I24, 25, 26, 27 disenables I40-5 (no data can be accepted)
Switch IIIB (SW-IIIB)	disenables I39-11 (no data can be accepted)
Switch IV	resets I24, 25

Timing — Computer Clear (This assumes manual initialize)

Clear pulse from computer causes positive pulse I58-4.

Positive pulse I58-4 resets I24, 25, I26, 27 within 40 nsec

" " " " I45, 46, 46 within 40 nsec

" " " clears I49-5 (Q low) within 40 nsec

" " " creates pulse in I59 $\sim$ 1 msec long

I59-12 negative pulse enables I51 AND-gate input of 2MHz oscillator
pulses

I59-5 positive pulse at end ($\sim$ 1 msec) causes I43-12 to clock I49-9
flip-flop which enables light pulse through I14-1 AND-gate and
causes I71 flip-flop to be clocked to enable I70-9 AND-gate
which also enables light pulse to pass, i.e., both I14-1 and
I70-9 must be enabled to allow light pulse to pass through to I53.

Timing — Computer Clear (cont)

Light pulse through I-14 clears I54, 55, 56; I33, 34, 35 after ~ 40 nsec

" " " " clocks I49-3 (~ 40 nsec) to cause I49-5 to go
high

" " " " resets I37

" " " " disenables I30-1 to prevent spurious address
register advance

" " " " enables AND gates for data and address
register

" " " " causes I26, 27 to be reset (before reset from
I37)

START TAKING DATA

Timing — Data Taking

Light pulse into I14-1 marks start of data-acquisition cycle.

Pulse into I53 produces 100 nsec pulse after 40 nsec delay.

I53-12 — clears I54, 55, 56 (memory address register)

— clears I33, 34, 35 (square wave generator -time of interval)

— clocks I49-3

I53-5 — resets I37

— disenables I30-1 for 100 nsec (does not allow data from
interval before reset to be stored nor does it allow
address register to falsely be advanced by one)

— inputs to I28-9 thru I31-9 a reset pulse ~ 20 nsec after
reset pulse from I37 — this is in case I37 did not change

Figure C.3: Time Sequence of Operation.

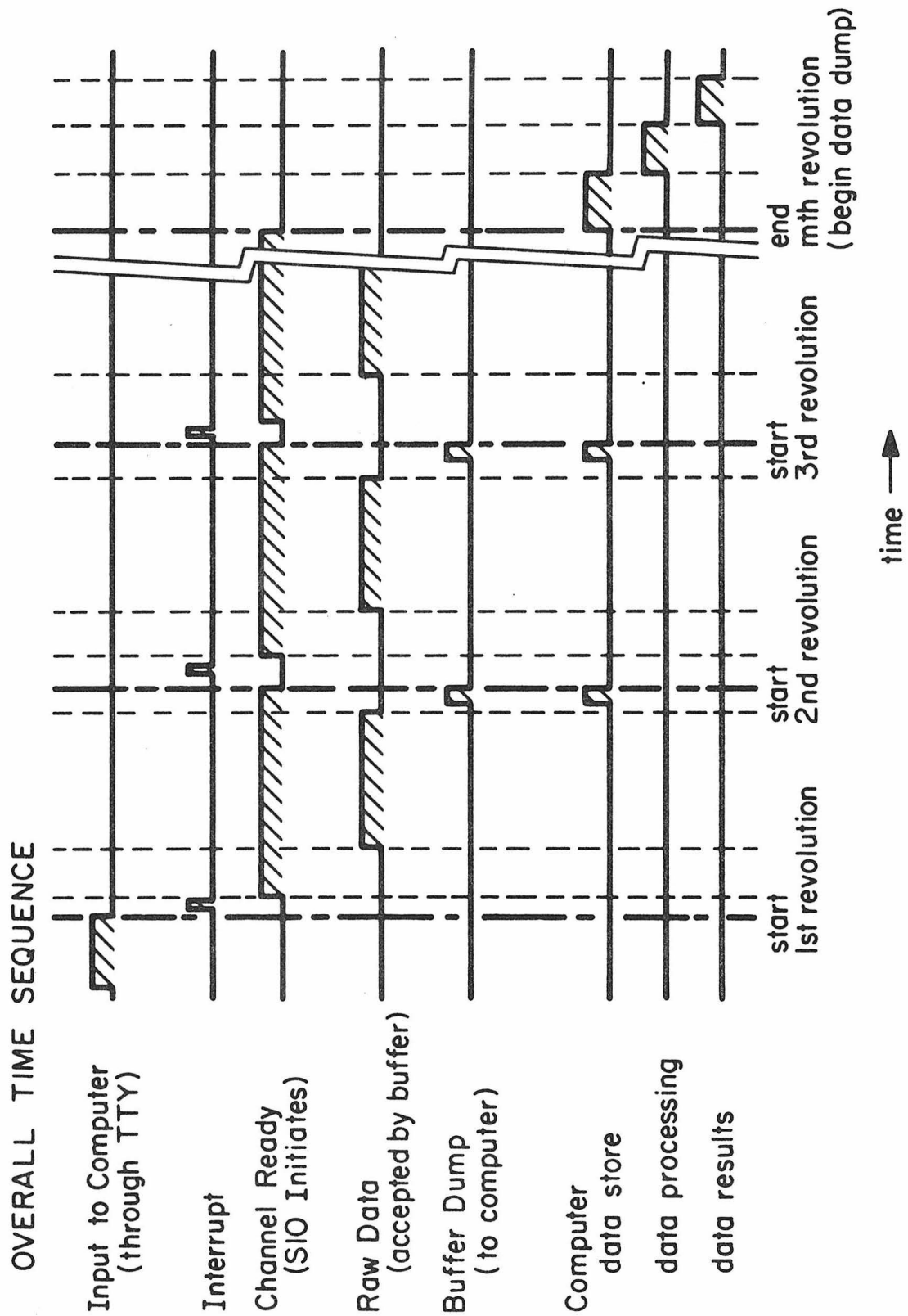


Figure C.3

Table I. Interface between Correlation Chopper Interface and
SCC 4700 Multiplexor – Multiplexor Pin Description

Pin ^a	Function Description
1	Channel Ready: d.c. positive level means channel is ready for input; remains true until interrupt is received (end of input to computer)
2	Input Response: positive pulse generated by computer signifying data byte has been transferred
4	Input Request: positive pulse to command computer to accept data byte transfer
6	Interrupt: positive pulse to command computer that no more data is to be transferred
22	Date Input Bit on Channel 8: 2 ⁷ byte position
23	" " " " " " " : 2 ⁶ " "
24	" " " " " " " : 2 ⁵ " "
25	" " " " " " " : 2 ⁴ " "
26	" " " " " " " : 2 ³ " "
27	" " " " " " " : 2 ² " "
28	" " " " " " " : 2 ¹ " "
29	" " " " " " " : 2 ⁰ " "

^aAll signal lines to and from multiplexor are TTL positive true.

Figure C.4: SCC-4700-Minicomputer/Multichannel-Scaler Interface

I – NOR gate; II – inverter; III – AND gate; IVA and IVb – 74123's, monostable vibrators; V and VI – inverters; VII – AND gate; VIIIA and VIIIB – 74123's.

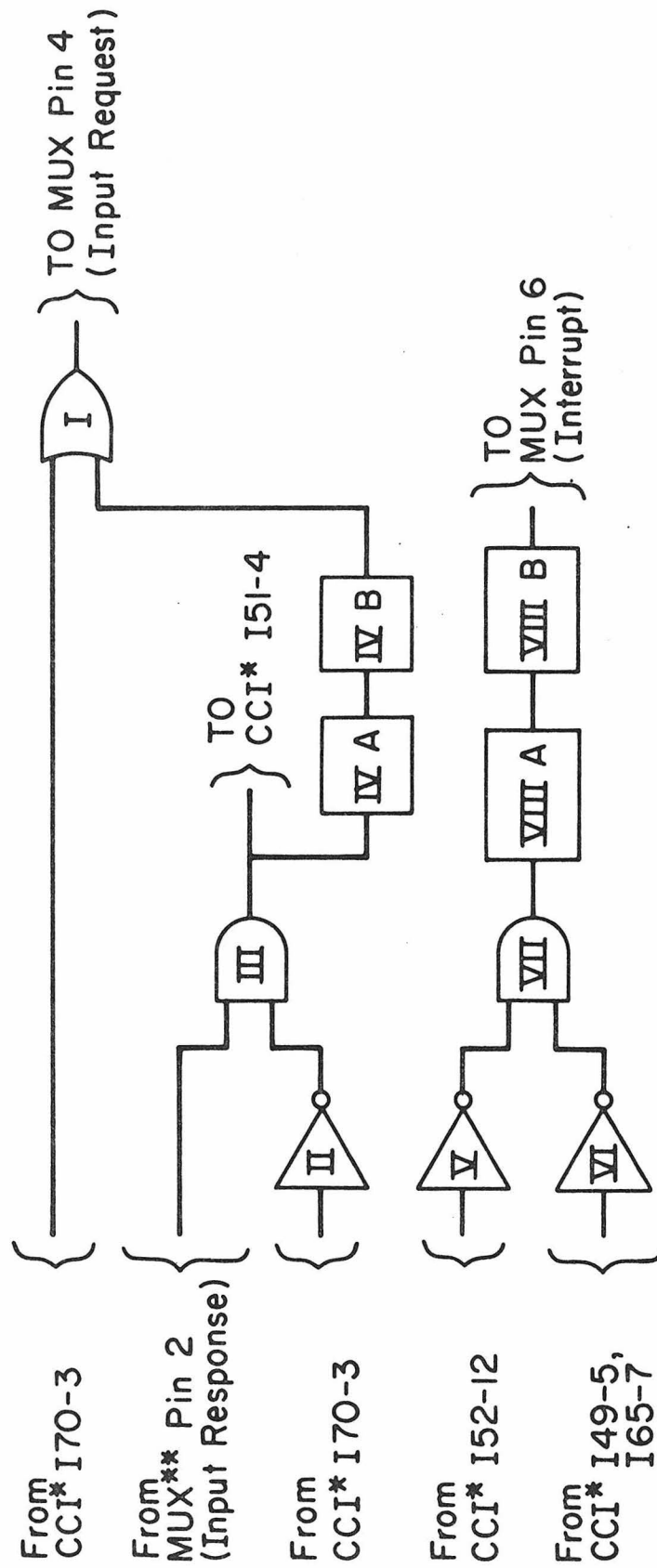


Figure C.4

REDUCE DATA

[This is the Fortran program which cross-correlates the detected signal and gives both the time distribution $P(\tau)$ and the corrected velocity distribution (PRRAY(J) vs VRRAY(I). Adapted from Allen.⁹

```
      M = 0
      M1 = 0
      DO 200 K = 1, 255
      SUM = 0
      DO 100 N = 1, 255
      NM = M + N
100    SUM = SUM + DRRAY (N) * MRRAY (NM)
      M1 = M1 + 1
      CRRAY (M1) = SUM
200    M = M + 1
      TC = 1./ (RPS * 255)
      OFFS = 0.5 * TC
      DO 300 I = 1, 255
300    TRRAY(I) = TC * I - OFFS
      J = 255
      DO 400 I = 1, 255
      VRRAY(I) = DIS/TRRAY(J)
      PRRAY(J) = CRRAY(I) * TRRAY I
400    J = J - 1
```

ASSEMBLER PROGRAM FOR ACQUIRING,
STORING, AND REDUCING DATA

* This is initialization section of the program

GET DUMPS BSS 0

 CALL PRINT, (B(DUMPNESS))

* This causes TTY to print request for number of dumps

 CALL CTOBIN, (B(AREA), 1)

* This converts ASCII TTY input into binary

 RNEG A, A, N

 JMP TOO_FEW

 STA DUMPS

 LDL 0

* We initialize 225 byte and word vectors to 0

 CALL BFILL, (B(BUF2), 255)

 CALL BFILL, (B(FINAL), 510)

* Load into A register, the byte address of BUF2

 LDA B(B.UF.2)

* Store byte address at WORK

 STA WORK

* This is acquisition section for 255 bytes transferred from multi-channel scanner. S10 is command, that (through interface line CHOPPER_ORDER) 255 bytes are to be transferred into computer and stored sequentially starting at location WORK

LOOP BSS 0

 SIO CCHOP, CHOPPER_ORDER, 0 + 0, 255


```
LDA      D(-255)
STA      COUNT
RXOR     X,X
LDA      WORK
STA      FROM
```

* LOOP2 stores data in vector FINAL: X

```
LOOP2   BSS      0
        LDH      I(FROM)
```

* Add contents of FINAL: X (stored raw data for interval X) to register which has newly acquired data for interval X in the corresponding address of BUF2 vector (FROM is address of 1st interval)

```
        ADD      FINAL: X
        STA      FINAL: X
        MIN      FROM
        RINC     X, X
        MIN      COUNT
```

* Return to beginning of loop to process interval (X + 1)

* Skip next step if COUNT 255

```
        JMP      LOOP2
```

* When multichannel scaler is cleared (255 bytes read) and ready to start next dumps, it sends minicomputer a signal. When signal is received by minicomputer interface, a signal is sent to minicomputer (CCHOP) and back to multichannel scaler to start next data acquisition cycle (data dump)

* Computer waits until CCHOP signal is received

```
        WAIT     CCHOP
```

- * Increment value of DUMPS (stored initially as a negative value.

If DUMPS is positive, skip step after increment

MIN DUMPS

JMP LOOP

- * These next three steps are "housekeeping" for previous sections of the program. We are now ready for data reduction section

TOO_FEW BSS O

CALL PRINT, (B(TURKEY))

JMP GETDUMPS

- * This is the section of program for reducing data, i.e., the Assembler Language Program for the Fortran Program "Reduce Data" given earlier

LDL 0

STA M

STA M1

LDA D(-255)

STA KS

STA II

LOOP3 BSS 0

LDL 0

STA SUM

LDA D(255)

ADD KS

STA K

```
LOOP4  BSS      0
        LDA      D(255)
        ADD      NS
        STA      N
        ADD      M
        STA      NM
        XAX
        LDA      FINAL: X
        STA      RAWX
        LDA      N
        XAX
        LDA      POLY: X
        MPY      RAWX
        XAB
        ADD      SUM
        STA      SUM
        MIN      NS
        JMP      LOOP4
        LDA      N
        XAX
        LDA      SUM
        STA      CRY: X
        MIN      KS
        JMP      LOOP3
        LDA      1
        DFD      255
```

	DFD	RPS
	STA	TC
	MPY	0.5
	STF	OFFS
LOOP5	BSS	0
	LDA	D(255)
	ADD	II
	XAX	
	STF	II
	MPY	TC
	XAB	
	DFS	OFFS
	STF	TRY: I
	MIN	II
	JMP	LOOP5
	LDA	D(255)
	STA	J
	STA	JJ
	LDA	D(-255)
	STA	LL
LOOP6	BSS	0
	LDA	J
	XAX	
	LDF	DIS
	DFD	RES
	SDF	VRY: X

```
LDF    CRY: X
DFM    TRY: X
DFS    DRES
LDA    J
XAX
LDF    DRES
DFS    PRY: X
XAX
SUB    1
STA    J
MIN    LL
JMP    LOOP6
```

* Format Support

TURKEY	BCIE	"POSITIVE NUMBER OF DUMPS!"
DUMPNESS	BCIE	"HOW MANY DUMPS"
BUFF	BPAR	81
AREA	BBSS	81
DUMPS	BSS	1
BUF 2	BBSS	255
FINAL	BSS	255
WORK	BSS	1
CHOPPER_ORDER	BPAR	1
C CHOP	EQU	8
COUNT	BSS	1
FROM	BSS	1
TOO_FEW	BSS	0

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APPENDIX D

Cryogenics

APPENDIX D: CRYOGENICS

The most important improvement made on the molecular beam apparatus is the cryogenic liquid helium pump described in the experimental section. This improvement represents an increase in the signal-to-noise ratio of a factor between 2 and 10 depending upon the experiment. Great concern exists, therefore, to maximize the holding time of liquid helium and to maximize its reliability. Unfortunately, these considerations are at odds, since a maximized holding time leads to minimized heat loss and thus to thin walls which by definition are hard to weld and seal. As a consequence of these considerations, the heat transfer characteristic of the liquid helium dewar and its associated liquid nitrogen jacket were investigated to define the controlling parameter of behavior.

A schematic of the liquid helium dewar with its liquid nitrogen jacket is shown in Figure 1. Because of the high vacuum, no convective heat transfer mechanisms need consideration. However, because of the low temperatures involved, radiative heat transfer as well as conductive heat transfer has to be considered. Based on a length of 22.5 cm, the total heat of vaporization available of the liquid helium in a filled dewar is taken to be 2820 joules.¹ This will serve as the base for determining theoretical holding times. First, the effects of conduction will be examined; next the effects of radiation from the dewar jacket will be investigated; and then a review of the effects of the ionizer will be made. After these considerations on the liquid helium system, considerations on the liquid nitrogen system will be reviewed.

Figure D.1: Liquid-Helium Dewar with Liquid-Nitrogen Jacket.

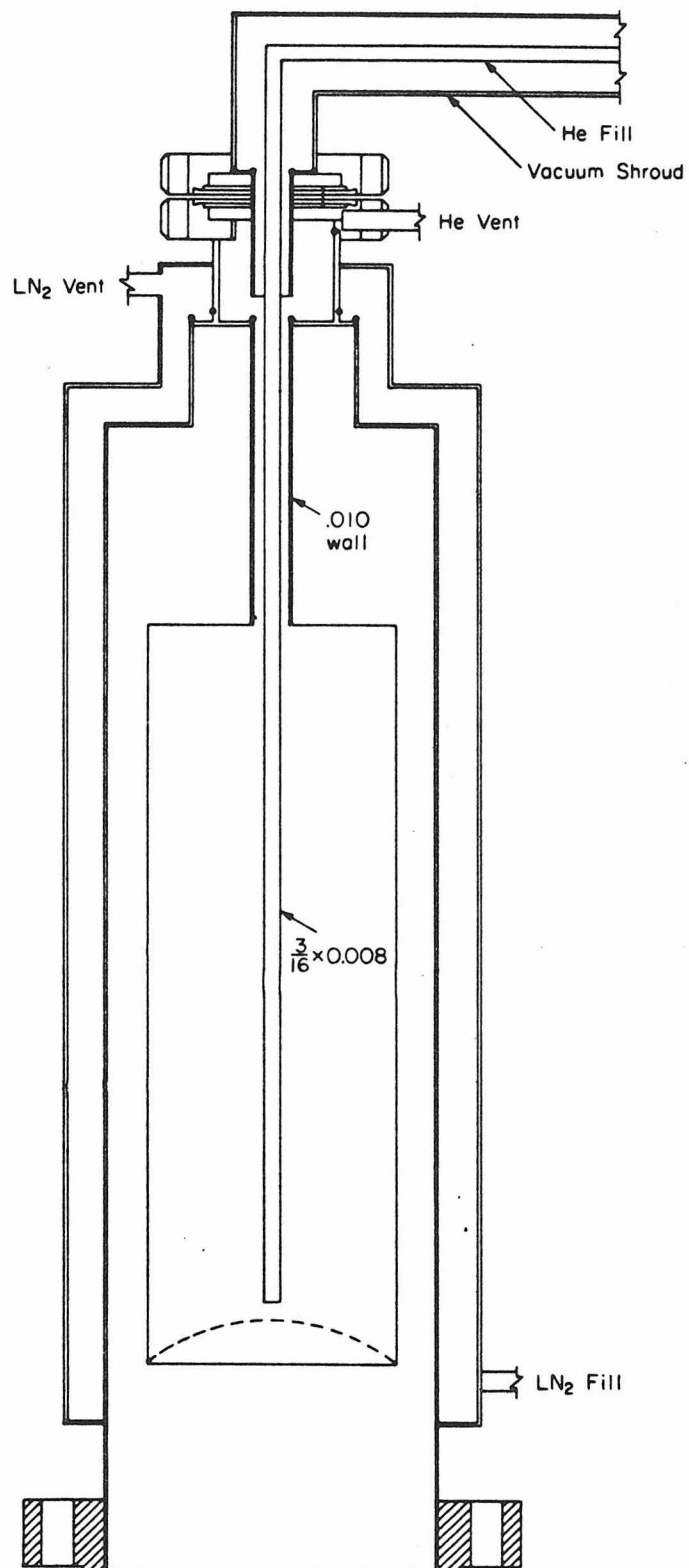


Figure D.1

Conductive heat transfer:

The best approach to describe the conductive heat transfer in the dewar is to assume steady-state behavior where the heat transfer to the liquid helium from the top neck of the dewar is equal at all locations. Define the neck to be at temperature T_4 at its top where the dewar is suspended from the liquid nitrogen jacket; define the neck to be at temperature T_3 at its base where it supports the dewar; define the outer top edge of the dewar to be at T_2 . Further define the radius of the neck as r_2 and the radius of the dewar as r_3 . Finally define the liquid helium level of the dewar at L_1 below the top of the dewar where the temperature is T_{He} .

At steady-state we can now divide the dewar into three sections for consideration of the heat transfer: (1) the dewar wall of radius r_3 between the liquid helium level and the top of the dewar (length is L_1); (2) the annular top of the dewar; and (3) the neck of the dewar. We can now write:

$$q = KA_1 \frac{T_2 - T_{\text{He}}}{L_1} = K t_3 \pi (r_1 + r_2) \frac{T_3 - T_2}{r_2 - r_1} = kA_2 \frac{T_4 - T_3}{L_3}$$

$$A_1 \approx 2 \pi r_2 t_1, \quad A_2 \approx 2 \pi r_1 t_2$$

$$T_2 - T_{\text{He}} = q \frac{L_1}{KA_1} = q B_1$$

$$T_3 - T_2 = q \frac{r_2 - r_1}{k t_3 \pi (r_1 + r_2)} = q B_2$$

$$T_4 - T_3 = q \frac{L_3}{KA_2} = qB_3$$

$$T_4 - T_{He} = q (B_1 + B_2 + B_3)$$

or

$$q = \frac{T_4 - T_{He}}{B + B_2 + B_3} .$$

Typical numbers for B_1 , B_2 , and B_3

$$B_1 = \frac{L_1}{KA_1} = \frac{0.12 \text{ m}}{2k\pi(0.0375\text{m})(0.00076\text{m})} \quad t_1 \approx 0.030 \text{ in} = 0.076 \text{ cm} = 0.00076 \text{ m}$$

$$B_1 \approx \frac{670}{K}$$

$$B_2 = \frac{r_2 - r_1}{Kt_3\pi(r_1 + r_2)} = \frac{0.0375 - 0.0125}{K(0.00150)\pi(0.0375 + 0.0125)} = \frac{106}{K}$$

$$B_3 \approx \frac{0.12}{2K\pi(0.0125)(0.00076)} = \frac{2010}{K} \quad t_3 \approx 0.030 \text{ in}$$

$$\Rightarrow q \approx T_4 - T_{He} \left\{ \frac{1}{670 + 106 + 2010} \right\} K$$

K ranges from 0.3 to 15 watts/m °K over temperature range of 4°K to 300°K.

Assume $\bar{K} \approx 10 \text{ } \omega/\text{m } ^\circ\text{K}$ and $T_4 \approx 300^\circ\text{K}$

$$q \approx \frac{295^\circ\text{K} \cdot 10}{2800} \approx 1 \text{ watt} .$$

This rate can be slowed in two ways: (1) increase the sum of B_1 , B_2 and B_3 which essentially means increase B_3 and (2) decrease ΔT , i. e., decrease T_4 . Since t_3 can be decreased from 0.030 in to 0.013 in, which increases B_3 by a factor greater than 2, since T_4 can readily be decreased to 100°K which is a factor of 3, and since a more realistic value of K would be $2 \text{ } \omega/\text{m } ^\circ\text{K}$ which is a factor of 5, it can safely be assumed that conductive heat transfer is not a consideration for 2-hr holding times or less. Note: the thickness of the dewar can and top essentially are negligible parameters.

II. Radiative Heat Transfer from dewar jacket walls:

If one black body is completely @ T_1 surrounded by a second black body at a higher temperature T_2 , the net rate of heat transfer to the inner body is

$$q_r = \sigma A_1 (T_2^4 - T_1^4) .$$

If, however, the bodies do not behave as black bodies, the equation is modified to

$$q_r = \sigma A_1 F_{1-2} (T_2^4 - T_1^4) .$$

In the case of coaxial cylinders ($L \gg r$),

$$F_{1-2} = \frac{e_1 e_2}{e_2 + \frac{A_1}{A_2} (1 - e_2) e_1}$$

$$\Rightarrow F_{1-2} = \frac{(0.05)e_2}{e_2 + \frac{3.75}{5.00}(1 - e_2)(0.05)}$$

$$\text{if } e_2 \approx 0.05 \Rightarrow F_{1-2} = \frac{0.05}{1 + \frac{3.75}{5.00}(0.95)} = 0.0295$$

$$\text{if } e_1 = e_2 = 0.08 \Rightarrow F_{1-2} = \frac{0.08}{1 + \frac{3.75}{5.00}(0.92)} = 0.0473$$

$$\text{if } e_1 \approx 0.08, e_2 \approx 0.16 \Rightarrow F_{1-2} = \frac{0.08 \cdot 2}{2 + \frac{3.75}{5.00}(0.84)} \approx 0.06$$

$$T_2 \gg T_1$$

$$\Rightarrow q_r = \sigma A_1 F_{1-2} T_2^4 = F_{1-2} (5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4) (\pi) (0.075) (0.25) T_2^4$$

Temperature	300°K	100	20
black-body: q_r/A (W/m^2)	460	5.67	9×10^{-3}
our system: q_r (W)	$27.0 F_{12}$	$0.33 F_{12}$	$0.53 \times 10^{-3} F_{12}$
$F_{1-2} \approx 0.06$	1.62	0.02	0.000030

Since 100°K is an attainable temperature if liquid nitrogen (77.K) is being used to cool the jacket walls, it is obvious that radiation from the dewar jacket is also negligible.

III. Ionizer:

Since conductive heat transfer and radiative heat transfer from the LN_2 jacket walls have both been shown to be negligible, radiative heat transfer from below the liquid helium dewar must be the dominating mechanism which determines holding time. Because of the fourth power temperature dependence on the heat radiated from any source (the wall of the mass spectrometer chamber, the focusing elements of the mass spectrometer, the ionizer), efforts must be made to minimize the temperatures of any possible source. This, however, is not straightforward. It is almost impossible to cool the elements of the mass spectrometer, especially the ionizer. Cooling the walls of the mass spectrometer chamber effectively does not appear feasible since the chamber is of stainless steel construction with notoriously slow cooling times. Any baffling or spoiling of the radiation path will be helpful; in fact, a small annular ring at the base of the LN_2 jacket has been found to improve holding times significantly. However, any such approach must be carefully studied, since any baffling of the radiation also directly decreases the pumping capacity, i.e., adds conductance.

Liquid Nitrogen Heat Transfer Problems:

Investigation of the heat loss associated with the armaflex-insulated liquid nitrogen transfer lines was made in order that the loss of liquid nitrogen could be assessed.

$$q = KL\pi(r_1 + r_2) \frac{t_1 - t_2}{r_1 - r_2} ,$$

where r_1 = outside radius of annular armaflex insulation
 t_1 = outside temperature of annular armaflex insulation
 r_2 = inside radius of annular armaflex insulation
 t_2 = inside temperature of annular armaflex insulation
 K = coefficient of thermal heat conduction
 L = length of annulus
 q = rate of heat transfer.

For armaflex, $K \approx 0.05$ Btu/hr °F ft

$$r_1 \approx \frac{1}{4} \text{ in, } r_2 = \frac{3}{4} \text{ in, } L = 1 \text{ ft}$$

$$\Delta t = t_1 - t_2 \approx 180^\circ \text{C}$$

$$\Rightarrow q \approx 100. \text{ Btu/hr .}$$

∴ For each foot of insulated line, approximately 100 Btu/hr of heat is transferred to the liquid nitrogen.

Latent heat of vaporization $\text{LN}_2 = 199 \text{ KJ/Kg}$

Density = 810 Kg/m^3

$1\text{KJ} = 0.9478 \text{ Btu}$

$$\begin{aligned}\therefore \text{Heat of vaporization} &= 1.61 \times 10^5 \text{ KJ/m}^3 \\ &= 1.61 \times 10^2 \text{ KJ/l} \\ &= 1.52 \times 10^2 \text{ Btu/l}\end{aligned}$$

$\therefore$ For each foot of insulated line, approximately $\frac{2}{3}$ liter LN_2 is lost per hour.

Conductive heat transfer of the liquid nitrogen transfer line at the bell-jar feedthrough was estimated

$$q = Kt\pi(r_1 + r_2) \frac{T_1 - T_2}{r_1 - r_2}$$

where k = coefficient of thermal heat conduction

t = thickness of feedthrough

r_1 = radius of transfer line

r_2 = radius of feedthrough

T_1 = temperature of transfer line ($\sim 77^\circ\text{K}$)

T_2 = temperature of outer radius of feedthrough ($\sim 240^\circ\text{K}$)

$$\Rightarrow q \approx 100 \text{ Btu/hr}$$

$\therefore$ Approximately $\frac{2}{3}$ liter of liquid nitrogen is consumed per hour due to heat transfer through feedthrough.

As a result of these considerations an insulated LN_2 reservoir with a vacuum-shrouded transfer line was recommended to save

significant quantities of LN_2 .

Heat transfer in mass spectrometer:

$$q = KA \frac{T_2 - T_1}{L}$$

where A is cross-sectional area

T_2 is room temperature

T_1 is LN_2 temperature

L is length of assumed annulus.

If an annulus 8 inches in diameter, $\frac{1}{4}$ in thick, 4 in long is used to model worst case heat transfer in mass spectrometer, heat transfer is approximately 80 watts.

If thickness is taken as $\frac{1}{8}$ in and length is taken as 12 in, heat transfer is approximately 13 watts.

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APPENDIX E

The He-Ar van der Waals potential

Scattering of thermal He beams by crossed atomic and molecular beams.

II. The He-Ar van der Waals potential^{a)}

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ABSTRACT

Differential cross sections for He-Ar scattering at room temperature have been measured. The experimental consistency of these measurements with others performed in different laboratories is demonstrated. Despite this consistency, the present van der Waals well depth of 1.78 meV, accurate to 10%, is smaller by 20% to 50% than the experimental values obtained previously. These discrepancies are caused by differences between the assumed mathematical forms or between the assumed dispersion coefficients of the potentials used in the present paper and those of previous studies. Independent investigations have shown that the previous assumptions are inappropriate for providing accurate potentials from fits to experimental differential cross section data for He-Ar. We use two forms free of this inadequacy in the present analysis: a

a) This work was supported in part by a contract (EY-76-S-03-767) from the Department of Energy. Report Code: CALT-767P4-167.

b) Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

c) Contribution No. 5762.

modified version of the Simons-Parr-Finlan-Dunham (SPFD) potential, and a double Morse-van der Waals (M^2SV) type of parameterization. The resulting He-Ar potentials are shown to be equal, within experimental error, throughout the range of interatomic distances to which the scattering data are sensitive. The SPFD or M^2SV potentials are combined with a repulsive potential previously determined exclusively from fits to gas phase bulk properties. The resulting potentials, valid over the extended range of interatomic distances $r \gtrsim 2.4 \text{ \AA}$, are able to reproduce all these bulk properties quite well, without adversely affecting the quality of the fits to the DCS.

I. INTRODUCTION

Recent experimental and theoretical efforts directed towards the determination of interatomic potentials for rare gas van der Waals interactions have improved remarkably the characterization and understanding of such potentials.¹ Early investigations of homonuclear interactions did much to elucidate the nature of their short-^{2,3} and long-range⁴ components, while later results for the same systems provided accurate information about the important attractive minimum region.⁵⁻⁷ As a result of these concerted efforts, the van der Waals potentials for the homonuclear rare gas pairs have been determined quite accurately; experimental data of many different kinds may be predicted satisfactorily from these potentials.¹

The outstanding success with which these homonuclear potentials have been determined unfortunately is not attained for the more complicated case of heteronuclear interactions.¹ This is of course partially due to less intensive investigations of the heteronuclear rare gas pairs as compared to those of the homonuclear ones; there are also significant experimental difficulties. For example,^{8,9} macroscopic heteronuclear interaction properties may be derived only indirectly from corresponding measurements of the mixtures, due to contributions of like-atom interactions.¹⁰ Historically, the incentive for the extensive development of various "combination rules", only some of which are soundly based upon theoretical or experimental considerations,^{10,11} may in part be attributed to these difficulties. These rules are predicated upon the validity of the "corresponding states" assumption. Here,

some "universal function" may be used to predict the potential for a particular interaction, given appropriate distance and energy scaling parameters.¹⁰ The concept of such a universal functions has however, been abandoned in describing homonuclear interaction potentials, which could not formerly be obtained with sufficient accuracy.^{1c} As more data become available for the determination of heteronuclear interatomic potentials, it is increasingly apparent that flexible potentials are also needed to describe these interactions accurately.¹² Indeed, in a recent computer simulation study¹³ hereafter referred to as Paper I, it was shown that the assumption of too rigid a mathematical form (e.g., having only two or three parameters) for the analysis of low-energy differential cross section (DCS) scattering data can introduce significant biases into the potentials extracted from such data. Such biases can be avoided only by using appropriately flexible mathematical forms in the analysis of the DCS data. Consequently, the use of excessively simple potentials and their combination rule progeny should be abandoned. It is important to use a more realistic approach to determine accurate heteronuclear potentials for simple van der Waals interactions.

In the present paper, we apply such an approach to the determination of the He-Ar potential, which has often served as a prototype for discussions of heteronuclear rare gas pair interactions. Experimental details for the acquisition of the DCS data presented in this study are described in Sec. II. The data reduction procedure used to analyze these DCS measurements are outlined in Sec. III. In Sec. IV we present our DCS data and several potentials obtained from them. By comparing one of these potentials (of the Morse-spline-van der Waals form) with

those obtained in two other laboratories,^{14,15} using the same mathematical form, we analyze in Sec. V the equivalence of the DCS scattering data of the three laboratories. We also discuss in that section the appropriateness of the forms used in Section IV, and those used in previous studies,¹⁴⁻¹⁶ for accurately describing the interatomic potential. In Sec. VI we examine the consistency of our potentials with integral cross section scattering data,^{17,18} and use these to potentials to predict the zero-point dissociation energy of the bound He-Ar diatom for which spectroscopic measurements are not yet available.¹⁹ We also adjust our M^2SV ²⁰ and SPFD^{21,22} potentials for interatomic distances to which the DCS data are insensitive,¹³ to provide a modified potential appropriate for a description of equilibrium²³⁻²⁵ and of gas transport²⁶⁻²⁹ properties. Finally, in Sec. VII, we present a concise characterization of the He-Ar potential.

A preliminary account of the present studies has been published previously.³⁰

II. EXPERIMENTAL

The crossed molecular beam apparatus used in our laboratory is shown schematically in Figs. 1 and 2. The major components are a movable, differentially pumped mass spectrometer detector, a fully supersonic primary beam, and an intense but only slightly supersonic secondary beam. The present version of the apparatus is an extensive improvement over earlier ones, which have been described elsewhere.^{31, 32}

The two beam sources and detector support arc are mounted to the base of a 1200-liter vacuum chamber, as shown in Fig. 1. All internal components of the apparatus are serviced via feedthroughs (FT) placed around the base circumference. The upper part of the chamber is a stainless steel bell jar which may be lifted free of the internal components, allowing access for work on them. The main vacuum chamber is pumped by four liquid nitrogen (LN₂-) trapped 25 cm oil diffusion pumps (DP₁ through DP₄), with a combined measured pumping speed of $S = 1600$ l/sec.

The primary beam (PB) is of the supersonic design,³³ with nozzle (Nz) and skimmer (Sk) diameters of 0.07 mm and 0.64 mm, respectively. The nozzle is fitted to the end of a gas inlet tube which, serving as a piston, is mounted to a motor-driven translator. With this arrangement, the nozzle-skimmer distance may be adjusted remotely, while maintaining an accurate beam alignment. The nozzle stagnation chamber is evacuated by a fifth 25 cm oil diffusion pump (DP₅; $S = 400$ l/sec.); a second chamber downstream of the skimmer is differentially pumped by a 25 cm LN₂-trapped mercury diffusion

pump (DP_6 ; $S = 120$ l/sec.). This buffer chamber houses a mechanical beam chopper (Ch) which modulates the primary beam, simultaneously generating a square wave signal with an infrared light-emitting diode and photocell arrangement. This signal is used as a reference input to a phase-sensitive lock-in detection system (see below). Also enclosed in the primary beam buffer chamber is a mechanical slotted-disk velocity selector (VS),³⁴ used for beam velocity distribution measurements. The modulated primary beam, which may be interrupted by a pneumatically-operated beam flag (Fl), emerges into the main (scattering) chamber through a collimator of 1.6 mm diameter. This final collimator (C_1) is located 79 mm from the scattering center (SC), as depicted in Fig. 2.

Returning to Fig. 1, the secondary beam (SB) is shown as consisting of a glass capillary array (CA),^{35, 36} through which the beam gas is admitted directly into the scattering chamber (SCh). The array is 0.61 mm thick with individual capillary diameters of 0.002 mm, and has a transparency to gas flow of 50%. The area of the array actually used is defined by a retaining cap with a hole of 1.6 mm diameter (C_2), located 6 mm from the SC (Fig. 2). The retaining cap also seals the array to the gas feed tube to prevent leakage around it. This assembly is mounted in a block which may be tilted upwards by remote activation of a pneumatic bellows, uncrossing the beams. Turning the secondary beam "off" in this fashion, the modulated background signal can be measured without affecting it as seriously as a beam flag would, since the secondary beam gas flow is uninter-

rupted. The bottom surface of the block is machined flat, which in mating to a similarly flat support structure, ensures precise alignment each time the beam is lowered to intersect the primary.

Although optimum operating conditions could be estimated theoretically for these beam sources,^{33, 36} the approximations involved make it worthwhile, in addition to design calculations, to perform experimental optimization studies. For the primary beam, it was generally found in these studies that intensity maximization and velocity spread minimization (with respect to gas inlet pressure and nozzle-skimmer separation) were complementary characteristics, while the beam angular spread was independent of these variables. The primary beam nozzle-skimmer distance is optimized at 7 mm ; the differential chambers pumped by DP₅ and DP₆ are operated at pressures of 3×10^{-4} torr and 2×10^{-5} torr, respectively.

Optimization of the secondary beam on the other hand, required a compromise between intensity and angular divergence. It is also necessary to maintain a low scattering chamber pressure, as well as to avoid dimer formation (for some gases more condensable than Ar). Measured velocity distributions were found to be independent of the source pressure in the 2 to 6 torr range, and of the identity of the beam gas. It should be noted that because the secondary beam gas particles used in these experiments are heavier than those of the primary beam, and so do not contribute greatly to the relative velocity distribution, the narrowness of the secondary beam velocity distribution is much less crucial than that of the primary beam.

The He-Ar scattering experiments described in this paper were performed using the optimized beam conditions presented in Table I. No primary beam velocity selection was used; the overall apparatus velocity resolution under these conditions is 11.6% FWHM. A measured primary beam attenuation of about 5%, and a scattering chamber pressure below 3×10^{-6} torr, are sufficiently low to ensure that the single-collision conditions essential for DCS measurements prevail.

The gas inlet system for the two beams have parallel needle leak valves and absolute pressure gauges.³⁷ This arrangement ensures stable regulation and accurate monitoring of beam pressures over long periods of time. The secondary beam purity is periodically checked with the mass spectrometer detector, since although we analyze scattering events specifically for He, we are unable to discriminate similarly against the identity of secondary beam particles.

Referring again to Fig. 1, we see that the detector may remotely be positioned at a variable angle in the plane of the beams by its supporting quadrant arm (QA), which rotates about a vertical axis passing through the SC. The center of this semicircular arm is coincident with the SC; the detector may also be moved along the rim of the QA, further permitting scans of scattering angles out of the plane of the beams. The force necessary to raise and lower the 120 kg bulk of the MS is transmitted through the vacuum wall via a rotary-motion feedthrough and a gear box (GB) with a 1000:1 demultiplication ratio, using a cable and pulley arrangement. The in-plane and out-of-plane angular positions θ_h and θ_v are measured by angular resolving units³⁸ geared to the vertical rotation axis of the QA, and

to the QA rim, respectively. The reproducibility of the position indicator system is 0.02° , and has a measured absolute accuracy of $\pm 0.05^\circ$. The detector angular range is restricted to $-20^\circ < \theta_h < 100^\circ$ (measured from the primary beam towards the secondary) and $-12^\circ < \theta_v < 23^\circ$ (upwards with respect to the plane of the beams).

Particles originating in the scattering region are detected by a separately enclosed quadrupole mass spectrometer (MS). As shown in Fig. 2, its entrance collimator of 1.6 mm diameter (C_3), is located 80 mm from the SC. The scattered beam passes through an entrance buffer chamber, which is separated from the remainder of the MS enclosure by a second 1.6 mm diameter collimator (C_4) located 45 mm downstream of the first. The MS penumbral cone angle³⁹ is thus 4° ; its 7 mm diameter at the SC ensures that, regardless of the detector position, the entire scattering zone is observed. Note however, that the umbral cone angle³⁹ is only 0.7° . The overall apparatus angular resolution is determined by the primary beam angular divergence and the size of the scattering volume, as well as by the detector's angular resolution. For a He primary beam, the effective overall angular resolution as determined in Section IV, has a FWHM of 1.9° .

Precise alignment of the apparatus is a prerequisite for good DCS measurements to be made. The principal alignment point, defined to be the location of the SC, is at a specific height on the cylindrical symmetry axis of the scattering chamber. A precision optical surveyor's telescope, sighting through an alignment window

(AW) set in a glass-to-metal seal at the rear of the MS enclosure (Fig. 1), is used to align the long axis of the MS. At $\theta_h = \theta_v = 0^\circ$, the MS collimators (C_3 and C_4 of Fig. 2) are aligned with the tip of a pin placed exactly at the SC. The same MS axis is simultaneously adjusted to be parallel to the plane of the QA so that out-of-plane scans may be made with a constant θ_h . The two beam axes are also optically aligned with the pin at the SC and are made to intersect at 90° .

Since the primary beam is relatively far from the SC and its location determines the zero position of the angular scattering scale, its precise alignment is especially important. With the MS at $\theta_h = \theta_v = 0^\circ$, the two MS collimators, the pin at the SC, and the three primary beam apertures are all within 0.1 mm of collinearity, corresponding to an error of less than 0.1° in either θ_h or θ_v . To check the precision of detector rotation about the SC, the distance between the entrance collimator of the MS and the pin at the SC is measured as a function of the detector position. The maximum deviation observed is 0.1 mm throughout the accessible angular range; the detector and primary beam misalignments are thus no more than 0.1° each.

The MS entrance chamber is differentially pumped (Fig. 1) by a small ion pump (IP_1 ; $S = 5 \text{ l/sec.}$); the main MS chamber is pumped by a larger one (IP_2 ; $S = 25 \text{ l/sec.}$). These are supplemented during experiments by a liquid helium cryopump (CP), which is periodically filled via a vacuum-jacketed transfer line (TL). The cryopump is surrounded by an LN_2 -cooled radiation shield; its one liter capacity is sufficient for a holding time of about one hour under operating

conditions, even though located directly above the MS ionizer. Serving as the cryogenic surface, the bottom of the dewar is an electro-polished stainless steel disc of 75 mm diameter, and at low pressure ($\lesssim 10^{-8}$ torr) it is an efficient pump for all gases, including Ne, H₂, and even He, with a conductance limit of $S = 400$ l/sec.

The pressure in the ionizer region during experiments is about 1×10^{-9} torr as measured with an uncalibrated ionization gauge (IG).

All MS components are bakeable up to 250° C to ensure attainability of the very high vacuum necessary for these experiments. During bakeouts, the MS is evacuated only by the scattering chamber diffusion pumps via a remotely operated bakeout valve (BV). When a sufficiently low pressure is reached at the end of a bakeout, this bellows-activated valve is closed; a similarly operated gate valve (GV) is then also closed over the MS entrance collimator. These two valves thus serve to isolate the MS enclosure from the rest of the system; the former remains at very high vacuum even when the bell jar is vented for periodic maintenance.

After entering the main MS chamber, particles pass through a high-efficiency electron-impact ion source (IS),^{40, 41} usually operated at 25 mA emission current. Ions thus produced are extracted and focused, then analyzed by a quadrupole mass filter (MF)⁴¹ and finally detected. Mass resolution and ion focusing parameters are adjusted to resolve adjacent mass peaks, while maintaining their symmetry and maximizing the signal at any chosen mass between 1 and 140 a.m.u.

Ion detection and signal processing may be chosen in either an analogue or digital mode by controls outside the vacuum chamber. The analogue mode utilizes a 14-stage Cu-Be dynode electron multiplier (CB), whose output is passed immediately through a bakeable low-gain DC preamplifier⁴¹ located within the MS enclosure. This signal is then processed outside the vacuum chamber by an AC tuned pre-amplifier followed by a phase-sensitive lock-in amplifier⁴² synchronized to the primary beam chopper reference signal. The modulated, in-phase component of the signal is thus extracted from a largely DC background, and is then smoothed by an RC integrator. The output is sent to an analogue-to-digital (A-D) converter, which is sampled and averaged by a laboratory minicomputer.

The digital mode of detection, which was used for these experiments, utilizes a Spiraltron³⁵ continuous dynode electron multiplier (Sp). The resulting narrow pulses ($\text{FWHM} \lesssim 1 \mu\text{sec}$) are passed through an amplifier-discriminator and are counted by a synchronous up-down counter. At the 160 Hz modulation frequency used, time-of-flight effects for a room-temperature He beam blur the edges of the modulated beam-on and beam-off time intervals by a phase-equivalent of almost 1° . To avoid these distortions, we count only in the central 90% of these intervals after suitably phase-shifting the reference signal. Care is also taken to operate the Spiraltron in the linear gain region below about 7×10^4 counts/sec with a two-terminal mode voltage of 2.8 kV. Because of this restriction, it is necessary to lower the ionizer emission current to only 1 mA in order to take low-angle scattering data (θ_h or $\theta_v \gtrsim 3.5^\circ$).

Using either the digital or analogue modes, a raw data point at a particular θ_h or θ_v is obtained by accumulating the modulated signal with the secondary beam lowered to intersect the primary, then uncrossing the beams and subtracting the modulated signal for the same length of time. The average of three successive measurements is then normalized to a repetitively measured reference scattering signal (at $\theta_h = 4.6^\circ$ or $\theta_v = 4.9^\circ$). The entire DCS versus scattering angle curve is measured at least three times, a simple average being performed to yield the experimental DCS curve. Signal-to-noise (S/N) ratios decrease from nearly 100 for low-angle scattering with total counting times of 3 min per angle, to about 10 at the widest angles used ($\sim 20^\circ$), with counting times of one hour.

The experimental error for the individual data points is determined independently of the S/N ratios quoted above, since the latter account only for statistical fluctuations of the individual measurements. Other source of error include reference signal instability (standard deviation $\approx 5\%$) and some slight uncertainty ($< 0.05^\circ$) of the MS position. In a detailed set of experiments, the standard deviation of the scattered signal was measured as a function of scattering angle, and was fitted by a quadratic polynomial increasing monotonically over the angular range of these experiments. This polynomial was used thereafter to estimate the experimental error for each data point of the DCS curve.

Data around the first minimum of the DCS (θ_h or θ_v between 6.5° and 8.5°) are also taken for the corresponding negative scattering angles. The zero positions of the angular scattering scale (θ_{0h} for in plane and θ_{0v} for out of plane) may then be determined by matching the

position of this minimum as it appears on both side of the primary beam, after making the appropriate laboratory to center-of-mass kinematic transformations. By plotting the first minimum on a scale accentuating the highly oscillatory structure of the DCS (see Section IV), we are able to locate the θ_0 to within 0.03° for both in-plane and out-of-plane scattering. Though small, these zero-angle corrections are necessary because of the great sensitivity of the DCS to the scattering angle. By comparison, the estimated accuracy of a beam centerline measurement from the intensity profile is $\approx 0.2^\circ$. Angular scale corrections obtained in the above manner are less than 0.2° relative to the scale established by the optical procedure, within the estimated accuracy of the latter. It was found however, that θ_0 shifts of the order of 0.2° produced detectable changes in the resulting interatomic potential, indicating that the higher accuracy of 0.03° in determining θ_0 is indeed necessary.

III. DATA REDUCTION

The data reduction procedure used in the course of this work has been carefully refined to distinguish between closely related inter-atomic pair potentials. This refinement required the calculation of accurate DCS's from assumed potentials, and accurate averaging over all experimental conditions.

Functionally, the procedure has three parts. First is an initialization used to set up the transformations from the center-of-mass (CM) frame to the particular laboratory frame of the experiment (scanning in the plane of the beams, or perpendicular to it with $\theta_h = 0^\circ$). The second part uses the partial wave expansion to calculate monoenergetic DCS's in the CM from an assumed interatomic potential; transformations and appropriate apparatus parameters are then used to calculate an average lab DCS. Finally, the third part optimizes the parameters of the chosen potential form to obtain a least-squares best fit to the experimental DCS.

The initialization part consists of the following steps:

1. Primary and secondary beam velocity distributions are calculated from the hypersonic expansion model³³ and the measured beam characteristics presented in Sec. II (see Table I). Between velocities corresponding to equal cut-off probabilities along these distributions, a number of gaussian integration points are chosen independently for each beam, and are designated v_{1i} ($i = 1, \dots, n_1$) and v_{2j} ($j = 1, \dots, n_2$), respectively.

2. We assume each of the beam angular divergences are described by cosine-squared distribution functions having the measured FWHM⁴³ (Table I). From these the distribution of beam intersection angles is calculated, and a third set of gaussian integration points, designated γ_k ($k = 1, \dots, n_\gamma$), is chosen along this distribution.

3. The beam intersection angle and velocity distributions are convoluted to calculate the distribution of relative collision velocities. Between relative velocities corresponding to equal cut-off probabilities, a fourth set of gauss points, designated u_p ($p = 1, \dots, n_u$), are chosen.

4. For each of an input set of CM scattering angles, θ_{CM} , we compute the corresponding laboratory scattering angles $\theta_{lab}^{ijk}(\theta_{CM})$ using the CM-to-lab coordinate transformation specified uniquely by each $(v_{1i}, v_{2j}, \gamma_k)$ combination and the plane in which the detector moves. The corresponding Jacobian factors $J_{lab}^{ijk}(\theta_{CM})$ (appropriate for a number-density detector) and relative velocities w_{ijk} are also calculated (see Appendix).

5. The peaks of the v_1 , v_2 and γ distributions are used similarly to transform the input θ_{CM} 's to the appropriate lab frame. This additional set of lab angles, denoted $\theta_{lab}^{calc}(\theta_{CM})$, is used as the set at which the laboratory averaged DCS will be calculated in step 9.

The quantities calculated in the initialization section above are stored for use throughout the second part, which follows:

6. The u_p of step 3 are used to calculate partial wave phase shifts from an assumed interaction potential (see Sec. IV for the potential forms considered). With our experimental conditions,

and for a potential close to that of He-Ar, we find that JWKB phase shifts⁴⁴ give slightly different (by about 4% or less) DCS's from those calculated using exact quantum mechanical (EQM) phase shifts. The latter were calculated by Numerov integration⁴⁵ of the Schrödinger equation, and compare satisfactorily to tabulated phase shifts.⁴⁶ Rosen-Yennie corrections⁴⁷ may be applied to the JWKB phase shifts instead, resulting in highly accurate (better than 0.5%) DCS's and substantial computational savings (see the end of this section). It is convenient to use these corrections only for smooth potentials because the numerical quadratures used require evaluations of second and third derivatives of the potential energy;^{44, 47} for any of the piecewise analytical potentials we use the EQM phase shifts.

7. The partial wave summation⁴⁸ is used to calculate DCS's at the θ_{CM} 's for each of the u_p 's. DCS's at the w_{ijk} relative velocities of step 4 are then obtained by interpolation over the u_p 's, yielding the CM cross sections $\sigma_{CM}^{ijk}(\theta_{CM})$.

8. Unlike the u_p 's, the w_{ijk} 's correspond to a particular combination of v_{1i} , v_{2j} , and γ_k , so that transformations to the lab frame may now be made. For each ijk - combination, we simply multiply the $\sigma_{CM}^{ijk}(\theta_{CM})$ by the $J_{lab}^{ijk}(\theta_{CM})$ intensity factors of step 4, to obtain the lab DCS's at the $\theta_{lab}^{ijk}(\theta_{CM})$'s. For each $(v_{1i}, v_{2j}, \gamma_k)$ - combination, this furnishes the function $\sigma_{lab}^{ijk}(\theta_{lab}^{ijk})$.

9. Since the θ_{lab}^{ijk} sets of angles are different for each $(v_{1i}, v_{2j}, \gamma_k)$ - combination, we use the functions obtained in step 8 to calculate,

by interpolation, the $\sigma_{lab}^{ijk}(\theta_{lab}^{calc})$ at the set of lab angles computed in step 5. The velocity and beam angular divergence averaged lab DCS can now be obtained by performing a gaussian integration at each of the θ_{lab}^{calc} 's to obtain the $\sigma_{lab}(\theta_{lab}^{calc})$'s.

10. At each of the θ_{lab}^{calc} 's, we perform a final averaging over the overall apparatus angular resolution. This averaging effect takes into account the divergence of the primary beam (independently of its effect on the beam intersection angle distribution of step 2 above) and the finite size of the scattering volume, in addition to the detector angular resolution. Since the correct overall resolution function would be very difficult to ascertain directly from apparatus considerations, its angular FWHM is treated as an adjustable parameter. The resolution function is assumed to have a cosine-squared shape; the suitability of this assumption is shown by noting that using a hyperbolic secant shape instead affects the fitted FWHM but not the calculated DCS.⁴³ The earlier assumption of cosine-squared angular distributions for the primary and secondary beams (step 2 above) is now seen to be justified because of their significant contributions to the overall apparatus angular resolution. The treatment of the latter's FWHM as a fitted parameter is discussed in Sec. IV.

11. The calculated scattering intensity at the experimental angles (the θ_{exp} 's) is obtained by interpolation from the averaged lab DCS's of step 10. Since the measured DCS is arbitrarily normalized (i.e., no absolute intensity calibrations are made), the calculated DCS must be scaled to it. The scaling factor α is adjusted so that the quantity,

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2, \quad (1)$$

is minimized with respect to α . At each of the n scattering angles, the I_i are the measured (relative) cross sections, while the σ_i are the calculated (absolute) cross sections. The normalized weighting factors g_i , are obtained at each data point from the associated experimental standard deviations s_i , using the expression⁴⁹

$$g_i = \frac{ns_i^{-2}}{\sum_{i=1}^n s_i^{-2}}. \quad (2)$$

Following Eq.(10) of Paper I, we define a goodness-of-fit statistical index more suitable than χ^2 ,

$$\frac{\Delta\alpha_q}{\alpha} = \frac{1}{\alpha} \cdot t_{1-q}(n-k) \left[\frac{\chi^2}{(n-k) \cdot \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}}. \quad (3)$$

Here $t_{1-q}(n-k)$ is Student's t -distribution statistic for a confidence level q of the scaling factor α , with n data points and k fitted parameters.⁴⁹

12. The final part of the data reduction procedure consists of using a weighted least-squares iterative scheme to optimize the parameters of a particular potential form. Our scheme is adapted from a general non-linear regression algorithm proposed by Marquardt.⁵⁰

We calculate the finite-difference derivatives of the DCS, with respect to each fitted potential parameter, by changing that parameter by a small amount (1%) in only one direction, rather than by calculating the numerical derivatives symmetrically about the initial value of each

parameter. This halves the computational effort and results in no loss of accuracy, because only an estimate of the first derivative is necessary.⁵⁰ In one iterative cycle, steps 6 through 11 are repeated for each potential parameter being varied, and corrections are calculated with either the linearized ($\lambda = 0$ in Marquardt's notation) or non-linearized model. As indicated in Paper I, we find it best to use $\lambda = 0.1$ or $\lambda = 0.5$ for fits to potentials with four or more adjustable parameters; otherwise $\lambda = 0$ may be used, resulting in faster convergence.¹³

Tuning of the integration and cut-off parameters to achieve computational accuracy and economy was performed. For these calculations a LJ12-6 potential, with r_m and ϵ parameters close to those of He-Ar, were used to calculate accurate DCS's in the CM frame. These were extensively averaged and transformed to the lab frame using our experimental conditions. This DCS was then used as an input set of "data" to which other DCS's, calculated using the same potential form but with less accurate integration procedures, could be compared. To successfully fit the input DCS, and obtain the original r_m and ϵ values, we found it necessary to use RY or EQM phase shifts in step 6, accurate to 0.001 radians, up to about $\ell = 50$. For higher angular momenta, the JWKB phase shifts, accurate to 0.002 radians, were sufficient; the partial wave summation was truncated at a value of ℓ (of about 150) for which the corresponding phase shift was less than 0.001 radians. The DCS's in the CM frame were calculated in step 7 at θ_{CM} 's spaced by 0.6° , at each of six gauss-point CM velocities. It was also necessary to use a total of 144

ijk-combinations along the beam velocity and intersection angle distributions to accurately simulate the CM-to-lab transformations and averagings of step 8. Recovery of the original LJ12-6 r_m and ϵ values (to within 0.02% and 0.4%, respectively) was realized, and essentially perfect fits were obtained ($\Delta\alpha_{0.95}/\alpha = 0.18\%$) with these calculational parameters. Less accurate lab DCS's gave poorer fits and/or inaccurate parameter values. These optimized calculational parameters were used for all the data reduction reported here, as well as for the fits reported in Paper I. Calculation of one fully averaged lab DCS curve requires about 30 sec. of IBM 370/158 computer time using RY phase shifts, or about 100 sec. using the EQM phase shifts.

IV. RESULTS AND DATA ANALYSIS

As indicated at the end of Sec. II, small zero-angle corrections θ_{oh} and θ_{ov} must be applied to the in-plane and out-of-plane angular scales respectively, before the potential may be fit to the experimental DCS's. After fixed-velocity kinematic transformations to the CM coordinate system, in-plane and out-of-plane data taken in the vicinity of the first minimum on both sides of the primary beam are plotted in Fig. 3 on a scale accentuating the oscillatory structure of the DCS's.⁵¹ These data are least-squares fitted to second- or third-order polynomials in the scattering angle and the minima are located. The second-order fits are shown as the curves in Fig. 3; the third-order fits are quite similar and are not displayed. The in-plane (out-of-plane) zero-angle correction θ_{oh} (θ_{ov}), is then found by iteratively adjusting the origin of the angular scale until the in-plane (out-of-plane) positions of the first minimum are the same for scattering on both sides of the primary beam. Zero-angle corrections obtained by fitting to the second- and third-order polynomials differ by $< 0.05^\circ$; their averages are $\theta_{oh} = +0.13^\circ$ and $\theta_{ov} = -0.12^\circ$ relative to the optical zero.

Preliminary fits were made to the DCS's using the LJ12-6 potential form. In these fits, the overall apparatus angular resolution function's FWHM was treated as an adjustable parameter, which was fitted simultaneously with the r_m and ϵ parameters. Best-fit values for the FWHM were 1.8_3° and 1.8_4° for the in-plane and out-of-plane fits, respectively. To preclude the possibility that these values of the

fitted FWHM might depend on the potential form used, we also employed the SPFD form [Eq. (8) below with $N = 2$, fitting r_m , ϵ , c_6 and b_0 parameters as well as the FWHM] to fit the DCS's, and obtained corresponding values 1.8_0° and 1.9_3° . For all subsequent in-plane and out-of-plane data reductions, we fixed the overall apparatus angular resolution function's FWHM at 1.9° . This value is consistent with the apparatus geometry, as discussed towards the middle of Sec. II.

The differential cross sections (DCS's) for He + Ar scattering at a most probable relative collision energy of 64.2 meV using both in-plane (with θ_v set at 0°) and out-of-plane (with θ_h set at 0°) motions of the detector were measured as described in Sec. II. Experimental DCS's were fit using the weighted least-squares data reduction procedure of Sec. III, in conjunction with the interatomic potentials described below. These potentials are written in reduced form as

$$f(\rho) = \frac{V(r)}{\epsilon}, \quad \rho = \frac{r}{r_m}; \quad (4)$$

r_m is the radius of the van der Waals attractive minimum and ϵ is its depth. The zero of the potential, occurring at $r = \sigma$, may be related to r_m and the potential shape $f(\rho)$. The potential shapes we consider are:

a) Exponential-6 (exp-6),¹⁰

$$f(\rho) = \frac{1}{\alpha - 6} [6e^{\alpha(1-\rho)} - \alpha\rho^{-6}] . \quad (5)$$

This has the single shape parameter α which governs the behavior of the exponential repulsive term; note that the coefficient of the long-range attraction term is determined by α .

b) Morse-spline-van der Waals (MSV),⁵²

$$\left. \begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } \rho \leq \rho_1 \\ f(\rho) &= (\rho_2 - \rho)[s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1)[s_2(\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_2 \end{aligned} \right\} (6)$$

The cubic spline coefficients s_i ($i = 1$ through 4) are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 , with the first one being chosen as $\rho_1 = 1 + \beta^{-1} \ln 2$ (the inflection point of the Morse function). We usually introduce the multipole expansion at $\rho_2 = 1.6$; the c_i coefficients are obtained from theoretical calculations.^{53, 54} The MSV form thus has only the Morse β parameter remaining to simultaneously control the shape of the attractive well and repulsive wall. Even the ESMSV form⁵⁵ still has only a single parameter for the well and weakly repulsive regions.

c) Morse-Morse-spline-van der Waals (M^2SV).²⁰

To avoid the inflexibility of the MSV form just mentioned, we use a second Morse function for $r < \sigma$, joined smoothly to the first one:

$$\left. \begin{aligned} f(\rho) &= \frac{1}{\omega} e^{(\beta' - \rho\beta\omega)} [e^{(\beta' - \rho\beta\omega)} - 2] && \text{for } \omega = \frac{\beta' - \ln 2}{\beta - \ln 2} \text{ and} \\ &&& \rho < 1 - \beta^{-1} \ln 2 \end{aligned} \right\}$$

$$\left. \begin{aligned}
 f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } 1 - \beta^{-1} \ln 2 \leq \rho \leq \rho_1 \\
 f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] \\
 &&& \text{for } \rho_1 < \rho < \rho_2 \\
 f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_2 .
 \end{aligned} \right\} (7)$$

Having the additional shape parameter β' , the M^2SV potential permits a description of the repulsive wall independently from the attractive well; all other parameters have the same meanings as in the corresponding MSV potential.

d) SPF-Dunham (SPFD), ^{21, 22}

$$\left. \begin{aligned}
 f(\rho) &= b_0 \lambda^2 \left(1 + \sum_{i=1}^N b_i \lambda^i \right) - 1 && \text{for } \lambda = 1 - 1/\rho \\
 &&& \text{and } \rho < \rho_f \\
 f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_f .
 \end{aligned} \right\} (8)$$

The two highest-order SPFD coefficients b_N and b_{N-1} are fixed by smoothness conditions at $\rho = \rho_f$. As for the MSV and M^2SV potentials, the multipole expansion using theoretical c_i coefficients is normally used in this paper beyond $\rho_f = 1.6$; results for the influence of other ρ_f values are presented in Sec. VI. Our usual choice of $N = 3$ ¹³ thus leaves the b_0 and b_1 parameters to determine the shape of the repulsive wall and attractive well regions of the potential.

For reduced distances below $\rho = 0.65$, the exp-6 and SPFD potentials often show spurious maxima or oscillations. These are

removed by using a Born-Mayer exponentially repulsive wall, i.e., $f(\rho) = Ae^{-b\rho}$, from some joining point ρ_i downwards. Smoothness conditions at ρ_i are used to fix A and b. Trial calculations show that values of $\rho_i < 0.75$ have no effect on the scattering results and we usually use $\rho_i = 0.70$; also see Sec. VI.

The choice of these four representations for the potential energy function was dictated by the computer simulation results of Paper I. In this investigation of the suitability of different potential energy forms $f(\rho)$ for determining an accurate He-Ar interatomic potential from regression analysis of DCS measurements,^{56,57} it was found that the most successful potentials had at least four fitted parameters. Different parameterizations for different regions of the potential were generally helpful in avoiding high statistical parameter correlations, allowing meaningful parameter values to be obtained. With fits including only the $c_6 \rho^{-6}$ term for the long-range region of the potential, up to five independent potential parameters (including c_6 , r_m and ϵ) could justifiably be determined. The M^2SV and $SPFD$ (with $N=3$) potentials of Eqs. (7) and (8), respectively, were found to be the most satisfactory in recovering the "accurate" He-Ar interatomic potentials of the simulation study.¹³ Note that since we use the theoretical⁵⁴ long-range dispersion interaction in fitting the experimental DCS's (which omits c_6 from the set of five adjusted parameters), these two potentials have the maximum number of parameters that may justifiably and reliably be determined from our DCS measurement, for the attractive well and weakly repulsive regions of the potential. The $\exp-6$ and MSV forms of Eqs. (5) and (6) respectively, were included in our analysis for a comparison with

potentials previously obtained from DCS measurements,¹⁴⁻¹⁶ although the simulation results showed that they are somewhat less satisfactory representations of the potential energy (especially the exp-6 form).¹³

The in-plane and out-of-plane experimental DCS's, with $2^\circ < \theta_h < 17^\circ$ and $2^\circ < \theta_v < 20^\circ$, respectively, are shown in Figs. 4 and 5. The curve fits of Fig. 4 were obtained by treating the in-plane and out-of-plane data sets independently of one another (i.e., using separate potentials to fit them), while those of Fig. 5 were obtained by combining these data sets (and fitting a single potential to them). For each of the four potential models considered, three different potentials are thus extracted from the data. The respective potential parameters are shown in Table II, and the corresponding M^2SV and SPFD potentials are displayed in Fig. 6. It should be noted that in combining the data sets, the in-plane scattering intensity at the reference angle (see the end of Sec. II) was measured carefully with respect to the out-of-plane reference intensity (standard deviation $\simeq 3.5\%$). This permits the same factor α of Eq. (1) to be used in scaling the in-plane and out-of-plane calculated DCS's to the corresponding experimental data (see the end of Sec. III).

It may be seen from Fig. 6 that the potential obtained by simultaneous fitting to both the in-plane and out-of-plane DCS's (termed the "combined potential") is very nearly the average of the potentials obtained by separate fits to these DCS's (termed the "in-plane potential" and the "out-of-plane potential", respectively). In view of the simulation results of Paper I, we expect the average, and therefore the combined potential, to be more accurate than either of the others.⁵⁸ The

differences between the in-plane or out-of-plane potentials and the more accurate combined potential are within the error bars quoted in Paper I for the "attractive well region" as defined in that paper. Of course, this is also true of the "attractive tail region" where the potentials are constrained to be identical.⁵⁴ However, the $\pm 40\%$ discrepancy in the "repulsive wall region" (see Fig. 6) is beyond the error bar of $\pm 30\%$ established in Paper I for $r \lesssim 3.1 \text{ \AA}$; this may be caused by several factors. Actual experimental data scatter may be larger than the error bars used in Paper I and depicted in Figs. 4 and 5. The effect may be the most severe at the larger angles where the signal level is lowest (note for example, the sharp drop in the out-of-plane DCS at $\theta = 15^\circ$); we would then expect to have a poorer determination of the potential primarily in the repulsive region. Possibly there also exists some systematic errors in the apparatus relating to the in-plane or out-of-plane detector motion; data reduction of the combined DCS's was performed to eliminate the effects of such systematic errors in determining the more accurate combined potentials. Consequently, only the combined potentials will be discussed hereafter; error bars claimed for them may be widened slightly beyond those quoted in Paper I.

V. DISCUSSION

On the basis of the computer simulation results of Paper I, we have selected the M^2SV [Eq. (7)] and third-order SPFD [$N=3$ in Eq. (8)] potentials as the most suitable ones for analyzing the present DCS data.¹³ Our best potentials (the "combined potentials" of the previous section) can now be compared with others that have been obtained from fits either entirely or primarily to DCS scattering data. These are the exponential-spline-MSV (ESMSV),¹⁴ the exp-6,¹⁶ and the Hartree-Fock-Dispersion (HFD)¹⁵ potentials. A large variety of other potentials have been obtained from fits to only transport or gas-imperfection properties (see Ref. 14 for a recent compendium of these potentials). We begin with a discussion of reasons to avoid comparing potentials obtained from these different types of experiments (see also Sec. VI).

The second virial coefficient is given classically by¹⁰

$$B(T) = 2\pi N_{AV} r_m^3 \cdot \int_0^\infty \left[1 - e^{-f(\rho) \cdot \epsilon / kT} \right] \rho^2 d\rho, \quad (9)$$

where T is the temperature, N_{AV} is Avogadro's number, k is the Boltzmann constant, and r_m , ϵ and $f(\rho)$ have the meanings introduced in Eq. (4). For He-Ar at $T \gtrsim 200K$, quantum mechanical corrections¹⁰ are small ($< 5\%$), so that the sensitivity of $B(T)$ data to different regions of the potential may be gauged by plotting the integrand of Eq. (9) as a function of ρ , as shown in Fig. 7. We may change the repulsive region without affecting the rest of the potential by altering the inner joining point ρ_i , where a Born-Mayer exponentially repulsive wall is joined smoothly to the SPFD potential (see Sec. IV). At

$T = 600$ K, the effect on the integrand of changing ρ_i from 0.80 to 0.81 (see Sec. VI) is seen to be significant (though small) for reduced distances $\rho \gtrsim 0.65$; we conclude that $B(T)$ data are sensitive to the repulsive region of the interatomic potential in the range $0.65 \lesssim \rho \lesssim 0.86$ [note that $f(\rho) = 0$ at $\rho = 0.862$]. At $T = 200$ K, a similar argument indicates sensitivity in the range $0.69 \lesssim \rho \lesssim 0.86$; in both cases the lower limit may easily be determined by noting the minimum distance for which the integrand deviates noticeably from a simple ρ^2 dependence. Consequently, in considering the relative contributions to $B(T)$ in the repulsive ($\rho \lesssim 0.86$) and attractive ($\rho \gtrsim 0.86$) regions of the potential, we are concerned only with the integrand beyond $\rho = 0.65$ at $T = 600$ K, or beyond $\rho = 0.69$ at $T = 200$ K. It is then seen from Fig. 7 that the shallowness of the He-Ar attractive well causes $B(T)$ data to be as sensitive to the attractive region as to the repulsive wall only for low temperatures ($T \lesssim 200$ K). We will therefore follow the precedent of Chen *et al.*,¹⁴ who found that they could fit the strongly repulsive region of the interatomic potential to $B(T)$ data, having already fit the weakly repulsive and attractive region to their thermal DCS measurements. They accomplished this by using the ESMSV form⁵⁵ to decouple these two regions at $\rho \simeq 0.84$ ($r = 2.97$ Å). Dilute gas transport data are in principle even less sensitive to the (shallow) attractive well region of the He-Ar potential than are $B(T)$ data when, as in the present case, $kT \gg \epsilon$;^{1c, 59} we will therefore use the repulsive wall part of the potential previously determined from these macroscopic properties, with no adjustments (see Sec. VI). The resulting potential, whose

attractive and weakly repulsive regions had been obtained from the DCS fits, will be shown in Sec. VI to be consistent with all the available microscopic and macroscopic experimental data. We emphasize that the latter type of data, being insensitive to the attractive portion of the potential, must not be used in its characterization. For example, assuming a given mathematical form for the potential (such as a LJ12-6) allows a determination of r_m and ϵ parameters by fitting to the macroscopic properties being considered. However, the validity of such a potential should not be considered to extend to the attractive region; these r_m and ϵ therefore cannot be used as physically meaningful values for the position and depth of the well minimum.^{14, 26} This is of course in strong contrast to DCS data which, at least for the present case, can be used to determine r_m and ϵ values accurately.¹³

For any direct comparison of DCS scattering results between different laboratories to be useful, a large variety of involved apparatus characteristics (see Sec. II for examples) must be taken into consideration. In view of the difficulties inherent in such a procedure, and the fact that it is the potentials extracted from the data that are ultimately to be discussed, we use the approach of comparing the various laboratories' potentials instead.^{14-16, 30} This must be performed using the same potential form to fit all of the DCS experiments, since the simulation results of Paper I clearly show that in some instances the extracted potentials may depend strongly on the potential model used.¹³ Consequently, even though the MSV form^{52, 55} previously used by others is not appropriate for obtaining accurate interatomic

potentials from the present room-temperature scattering data (cf. the M^2SV and SPFD potentials of Table II), it was used to reduce our data also, in order to compare respective scattering results.

Chen et al.'s¹⁴ experiments covered the laboratory angular range between 3° and 45° at a relative collision energy of 20.8 meV, while Smith et al.'s^{15,16} results at 18.2 meV were for scattering angles between 4° and 30° . Although these collision energies are but a third of ours, the increased sensitivity of their DCS's to the long-range region of the potential is probably compensated for by our more extensive measurements of low-angle scattering; in any case, the long-range region of the potential is taken to be a theoretically estimated one and is not fit to the data.^{14-16,30} Conversely, the higher scattering angle but lower energy results are less sensitive to repulsive interactions than our higher energy but lower scattering angle measurements.¹³ We would therefore expect all three DCS's to be sensitive to the potential for interatomic distances between about 3.0 and 6.5 Å, as determined from the simulations of Paper I. The consistency of the three experiments may thus be judged by comparing, for this range of interatomic separations, the MSV potentials extracted from fits to the respective DCS's. From Fig. 8 it is evident that these potentials are indistinguishable within our precision limits, estimated in Paper I as $\pm 30\%$ for the repulsive wall (corresponding to ± 0.04 Å in the position of the wall), $\pm 10\%$ for the attractive well, and $\pm 20\%$ for the attractive tail. Because of the greater sensitivity of our room-temperature experiments to the weakly repulsive wall of the potential ($2.8 \text{ Å} \lesssim r \lesssim 3.1 \text{ Å}$), the MSV fit to our data tends to yield a slightly deeper well

than it would if the wide-angle scattering data responsible for this sensitivity ($\theta \lesssim 15^\circ$) were neglected. However, the simulation calculations¹³ indicate that this effect is $< 10\%$, so that correcting for it would not significantly affect the agreement among the curves of Fig. 8. Further documentation of the data's consistency from the three different laboratories is furnished in Fig. 9 where the DCS's calculated from the various MSV potentials are compared. In Table III we list the corresponding r_m and ϵ parameters, and the goodness-of-fit statistical indices [Eq. 's (1) and (3)], for the three calculated DCS's scaled to our combined in- and out-of-plane data. The quality of these three fits is substantially the same. Having thus established the consistency, and from it the reliability of the three different laboratories' scattering data, we may now apply the results of Paper I in selecting the most suitable He-Ar potential. In Fig. 10 we display those He-Ar potentials extracted from DCS fits and preferred by the three different laboratories: exp-6,¹⁶ HFD,¹⁵ ESMSV,¹⁴ M²SV³⁰ and SPFD.³⁰ We now proceed to discuss them.

The simulation calculations of Paper I showed that a given mathematical model must have sufficient flexibility to decouple different regions of the potential.¹³ This is required to enable an accurate representation of the interaction energy to be obtained by iteratively inverting the kinds of DCS data under discussion here. That is, each individual parameter should be related (in the ideal case) to a specific region of the potential, and conversely.¹² The consequent unsuitability of the exp-6 potential [Eq. (5)] for fitting DCS data is substantiated by the results of Paper I. The single reduced form parameter α has the onus of determining the

shape of the entire potential, including the long-range dispersion interaction for which it is known to be inappropriate at the distances sampled by the DCS experiments.^{16, 54} On the other hand, the HFD formulation has a large number of parameters, each with a fairly clear physical interpretation.^{60, 61} The resulting potential combines the convenience of being represented by a single analytical expression with the advantage of having ranges of interatomic distances in which the potential is sensitive to individual parameters. This pleasing combination is attained through use of exponential damping factors. We note that the HFD parameterization is a generalization of the Buckingham-Corner (BC) potential,¹⁰ and is somewhat akin to the Barker-Pompe form,⁶² both of which were investigated in detail in Paper I. In fitting the potential to their DCS data, Smith *et al.*¹⁵ varied only the r_m and ϵ parameters of the HFD model; they relied on recent theoretically determined dispersion coefficients C_6 , C_8 , and C_{10} ⁵⁴ and on repulsion parameters fitted to SCF-HF calculations.⁶¹ We shall hereafter refer to the HFD potential they obtained as "constrained" in the sense that the full flexibility of the HFD model was not exploited in the fits to their data. We note that the exponential repulsion parameters strongly influence the HFD potential^{15, 60, 61} at its attractive minimum and beyond, even though the HF calculations are unreliable at these large interatomic distances.⁶¹ For example, even at the minimum the contribution of this repulsion is +2.4 meV, whereas that of the remaining attractive terms is -5.0 meV. It is apparent from these caveats that although the HFD form itself should indeed be highly flexible,¹⁵ the approximate nature of the data used in fixing the repulsion

parameters of the constrained HFD potential restricts its flexibility to that of a two-parameter potential, and limits its ability to provide reliable r_m and ϵ parameters.¹³ This is especially true because the repulsion parameters are responsible for determining not only the repulsive wall, but also the attractive well region of the potential, to which the DCS data are highly sensitive. As shown in paper I and in Sec. IV of the present paper, a greater degree of flexibility is needed for an appropriate description of these regions of the potential. In particular, the simulation results of Paper I showed that the BC parameterization, having about the same flexibility as the unconstrained HFD form,¹⁵ does not yield an accurate long-range potential when fitted to the DCS data. By fixing this region of the potential with known values for the dispersion constants,⁵⁴ as was done with the constrained HFD potential, the weakly repulsive wall and attractive minimum regions have no remaining flexibility. It is therefore not surprising that the He-Ar constrained HFD¹⁵ potential is quite similar in shape to the rather inflexible¹³ exp-6 potential¹⁶ (Fig. 10). Nor is it surprising that both are quite different from the ESMSV potential,¹⁴ as well as from the present SPFD and M²SV potentials. The SPFD potential form is fully able to mimic the HFD potential in direct numerical fits to the latter's shape¹³ [i.e., fitting only the b_0 and b_1 parameters of Eq.(8)], within the range of interatomic distances probed by the DCS experiments. Consequently, if the constrained HFD potential provides a description of the He-Ar interaction within the accuracy obtainable from the scattering measurements, the present SPFD potential should be identical to it within that accuracy.¹³ However, as seen from Fig.

10, it is not. This is in spite of the equivalence of the scattering data used to obtain these respective potentials, as demonstrated earlier in this section (see also Figs. 8 and 9). From these considerations, we conclude that the constrained HFD potential does not provide an accurate representation of the He-Ar potential (see also Sec. VI. B).

In fitting the ESMSV potential to their scattering data, Chen et al.¹⁴ did not adjust its exponential or spline components; since these are used only for the strongly repulsive wall of the potential, their effect on the DCS fits are minimal.⁵⁵ We can therefore use the simulation results of Paper I, as applied to the MSV potential form,⁵² to assess the suitability of the ESMSV form to provide a potential accurate in the van der Waals minimum region. The (ES)MSV potential is clearly superior to the exp-6 one,¹³ especially since it can be made to have the correct long-range behavior. With the availability of its Morse β parameter to describe weakly repulsive interactions, the (ES)MSV potential may also be preferred over the constrained HFD one. However, as demonstrated in Paper I, the (ES)MSV parameterization is unable, for room-temperature experiments, to describe the attractive well region as adequately as some other potentials that have an additional parameter available to describe the weakly repulsive wall independently of the well region. This particular parametric independence does not appear to be required for the lower collision energy experiments. However, their increased sensitivity to the long-range region of the potential suggests that accurate values for the dispersion coefficients are particularly important.¹³ Thus, the use of a C_8 coefficient too weak by a factor of two,⁵⁴ and the

neglect of the C_{10} contribution altogether, may induce a slight bias into the ESMSV potentials extracted from the low collision energy experiments. In addition, the dispersion series was used for distances that may be too close to the attractive minimum¹⁴ (see also Sec. VI.B).

We may use the above discussion to justify our preference for the shallower wells of our M^2SV and SPFD potentials. However, because of the relatively small difference between those potentials and the ESMSV one,¹⁴ we cannot discriminate completely against the latter. Nevertheless, it must be stressed that the DCS data of the various laboratories, which are equivalent, should be reduced with more flexible potentials, or with potentials whose known parameters are more accurate than heretofore used. Otherwise, the analysis introduces a systematic bias into the potentials extracted from the data,¹³ a bias which may not be circumvented by claiming good fits of the calculated to the experimental DCS's. It is on this basis that we reject the $\exp^{-6}$ ¹⁶ and the constrained HFD¹⁵ potentials as having attractive wells that are apparently too deep.

VI. APPROPRIATENESS OF THE M^2SV AND SPFD POTENTIALS FOR THE DESCRIPTION OF OTHER PROPERTIES

In this section, we compare the predictions of the SPFD or M^2SV potentials, which are nearly equivalent (see Fig. 6), with experimental measurements of microscopic and macroscopic properties. We also refer to similar comparisons using the previously proposed scattering potentials.¹⁴⁻¹⁶

A. Microscopic properties

Integral cross sections Q , measured in arbitrary units as a function of the relative collision velocity v , provide data sensitive to the "area" of the attractive well. This "area" is usually expressed as a product of the ϵ and r_m parameters,^{1b} but is of course dependent upon the model chosen to describe the potential. The $\epsilon \cdot r_m$ product for an LJ12-6 model of the He-Ar interaction has been obtained from $Q(v)$ data as 7.7 ± 0.8^{18} or 7.5 ± 0.8^{63} meV·Å. To provide a first indication of the consistency of our DCS measurements with these results, both of which are sensitive to the attractive well region, we fitted the LJ12-6 model to our scattering data. We obtained an $\epsilon \cdot r_m$ product of 7.6 meV·Å, which is very close to the value obtained from the $Q(v)$ results. However, this value is no more reliable than is the rather crude LJ12-6 model, and is presented here only as a rough estimate of the compatibility of the (arbitrarily normalized) $Q(v)$ and DCS results. A more accurate value for the $\epsilon \cdot r_m$ product, obtained from the third-order SPFD and M^2SV potentials (see Table III), is 6.4 ± 0.7 meV·Å. A comparison of absolute $Q(v)$ values calculated directly from the

respective SPFD and LJ12-6 potentials¹⁸ is given below.

More recent $Q(v)$ data have been obtained with absolute normalization, and have been used to determine the r_m and ϵ parameters of an (ES)MSV potential.¹⁷ The potential obtained is identical to the (ES)MSV potential of Smith et al.,¹⁵ and very close to our MSV potential; it is therefore significantly different from the more accurate third-order SPFD or M^2SV potentials (see Figs. 8 and 10 and Table III). This equivalence of the several (ES)MSV potentials demonstrates the consistency of the (absolute) $Q(v)$ data with the DCS results. In Fig. 12, we compare $Q(v)$ curves calculated from the (ES)MSV potential as well as from the more accurate third-order SPFD and M^2SV potentials [the $Q(v)$ curves for the M^2SV and SPFD potentials are indistinguishable in the figure]. It can be seen that the curves are within the estimated systematic error of $\pm 2\%$ in the absolute calibration of the Q . In addition, there seems to be an additional random experimental error not shown in the figure of about $\pm 2\%$.¹⁷ The $Q(v)$ curve calculated from Helbing et al.'s LJ12-6 potential lies an average of $\sim 3\%$ below that of the SPFD potential.¹⁸ These experiments are thus unable to discriminate between the potentials [i.e., the $Q(v)$ data are consistent with all of them], despite their sensitivity to the attractive well region¹⁷ and the 30% greater well depth of the (ES)MSV potential. This is probably due to the $Q(v)$ data's insensitivity to the shape of the potential well; we emphasize again that the third-order SPFD or M^2SV potentials are more accurate than is the (ES)MSV one, as demonstrated in Sec. V and Paper I.

By studying the vacuum ultraviolet absorption spectra of rare gases and their binary mixtures, the energy levels of many weakly

bound van der Waals molecules have been obtained.¹⁹ Unfortunately, even a very recent study was unsuccessful in determining the dissociation energy for the $v = 0$ vibrational level D_0 of either He-Kr or He-Xe,¹⁹ which probably supports only the $v = 0$ level.⁶⁴ To the best of our knowledge, no such studies are yet available for He-Ar. In anticipation of the future availability of such D_0 measurements, we compare below the calculated values for D_0 of the different He-Ar potentials being considered. In Table IV we display these predictions for the SPFD and M^2SV potentials, as well as those obtained from several previously proposed He-Ar potentials.¹⁴⁻¹⁶ We also show the well depth ϵ and zero-point energy $G(0)$ for each of these potentials; none supports more than one vibrational level. Although the value of ϵ for the ESMSV potential is $\sim 17\%$ greater than that for the SPFD or M^2SV potentials, the respective D_0 values are all very close. Since $D_0 = \epsilon - G(0)$, such fortuitous agreement is due to the larger curvature of the ESMSV minimum (listed as κ in Table IV), which gives it a larger value of $G(0)$ than those of the SPFD and M^2SV potentials (note that the latter two have similar values of κ). The D_0 values of the exp-6 and HFD potentials are closer to those of the SPFD and M^2SV potentials than are the respective well depths. Here, however, the compensatory effect of the greater curvature at the minima for the former two potentials than for the latter two is insufficient to produce a fortuitous agreement between these D_0 values.

Calculating D_0 for each of the third-order SPFD "experimental" potentials of paper I,¹³ we estimate the accuracy with which this quantity may be predicted for He-Ar from DCS measurements to be about $\pm 5\%$. The predicted dissociation energy determined from the potentials of this

work is thus $D_0 = (0.72 \pm 0.04)$ meV. The anticipated spectroscopic measurements of D_0 may eventually provide a very direct means of discriminating between some of the proposed potentials, at least in their respective attractive well regions. It should be noted, however, that such measurements cannot be used to obtain the well depth ϵ (equivalent to the dissociation energy D_e) of He-containing pairs, because the zero-point energy may be estimated only if several vibrational states are observed.^{19, 66, 67} The implication is that for very weak attractive wells (those which support no more than two bound states), the DCS measurements contain more information about the shape of the well than do the spectroscopic measurements.

B. Macroscopic properties

In a preliminary comparison of experimental macroscopic dilute gas properties²³⁻²⁹ with those calculated from our M^2SV or $SPFD$ scattering potentials, we encountered a problem similar to that of Chen et al.¹⁴ They were unable to satisfactorily reproduce second virial coefficient $B(T)$ data with an MSV potential⁵² fitted solely to their He + Ar scattering results, and chose to overcome this difficulty by using the $ESMSV$ form⁵⁵ instead (see the beginning of Sec. V). This is quite reasonable insofar as the $B(T)$ data are more sensitive to the repulsive wall than are the scattering results; the former are sensitive primarily to the attractive portion of the potential only at low temperature (see Fig. 7 and Ref. 10). Viscosity and diffusion coefficients $\eta(T)$ and $D(T)$, respectively, are even less sensitive to the attractive portion of the potential^{1c, 59} in the relatively high temperature regime to which the experiments²³⁻²⁹ are inherently limited (by the condensability of

the Ar); it is therefore to be anticipated that these properties may also not be described adequately by a potential fit solely to DCS measurements. The usefulness of the He-Ar $B(T)$, $\eta(T)$, and $D(T)$ data therefore is not necessarily in distinguishing between potential curves or parameters characteristic of the attractive well and adjacent regions of the potential, but rather lies primarily in describing more strongly repulsive interactions. In this regard, these data provide a means of obtaining the potential for interatomic separations not probed by the thermal DCS measurements.

Dilute gas transport properties have been used to obtain the He-Ar potential for repulsive interactions between 25 and 100 meV.²⁶ The lower distance limit of ~ 2.4 Å to which these data are sensitive is governed by the availability of high-temperature diffusion data, while the upper distance limit is dictated by the failure of the fitting procedure for distances beyond ~ 2.7 Å. The potential obtained was displayed graphically.²⁶ We have been able to represent it accurately and conveniently by the Born-Mayer form

$$V_{BM}(r) = Ce^{-\alpha r} \quad \text{for} \quad 2.4 < r < 2.7 \text{ Å}, \quad (10)$$

with the nonreduced values of $C = 1.23 \times 10^5$ eV and $\alpha = 5.69$ Å⁻¹. The range of validity of this repulsive potential does not overlap that of the potentials obtained from fits to the scattering data (see Sec. V). Consequently, it should be possible to combine the potentials by "switching" between them. The "switch-over" should, of course, occur for interatomic separations at which neither the DCS nor the $\eta(T)$ and $D(T)$ data are highly sensitive to the potential. Halfway between the upper limit for Eq.(10) of $\rho \simeq 0.75$ and the lower reduced distance limit of sensitivity

for DCS data ($\rho \simeq 0.81$)¹³ is therefore an appropriate central "switch-over" distance ρ_0 .

We choose a convenient switching function as

$$h(\rho) = \frac{1}{1 + e^{\tau(\rho - \rho_0)}} \quad (11)$$

This function rises from 0 to 1 as ρ is decreased; the rapidity of the rise is governed by τ . The switching function has a value $h(\rho) = 0.5$ at $\rho = \rho_0$, so that we specify $\rho_0 = 0.78$. By requiring $h(\rho) = 0.95$ at the upper limit for Eq.(1) of $\rho = 0.75$, thus dampening the influence of one region of the potential on properties depending on another, we specify $\tau = 100$. The switching function is thus completely specified by the sensitivity of the DCS and gas transport properties to the potential, without adjustment of either of its parameters. It is used to combine the V_{BM} potential of Eq.(10) with the M^2SV or SPFD potentials obtained by fits to the DCS measurements. Denoting the latter collectively as V_{DCS} , the "modified" M^2SV or SPFD potentials are given by

$$V(r) = h(r/r_m) \times V_{BM}(r) + [1 - h(r/r_m)] \times V_{DCS}(r) \quad (12)$$

The r_m reduction parameter is 3.659 Å or 3.573 Å for V_{DCS} being the M^2SV or SPFD potential, respectively (see Table II). In order to test the validity of the above procedure for combining scattering and macroscopic data, the modified M^2SV and SPFD potentials are used to calculate values for DCS, transport, and equilibrium properties for comparison with experimental results.

The virial coefficients were calculated by numerically integrating Eq. (9); first and second quantum corrections¹⁰ were calculated and

applied to the classical $B(T)$, amounting to a total of 4.6% at $T = 200$ K and 1.0% at $T = 600$ K. Transport coefficients were calculated in the first approximation¹⁰ by the method of Smith and Munn,⁶⁸ but using quantum mechanical cross sections (see Sec. III). The experimental "interaction coefficients" B_{12} , η_{12} and D_{12} , were calculated from measurements of the corresponding pure component and mixture virial and transport properties, with the exception of Brewer and Vaughn's B_{12} coefficients.²³ These were calculated using experimental literature values for the pure component $B(T)$.

The M^2SV and SPFD potentials, whose parameters are listed in Table II, were modified using Eqs. (11) and (12), and then used for the bulk property calculations. Results are presented in Table V, showing the standard deviations of the various calculated properties from the corresponding experimental ones. Also shown in this table (see the last row) is the effect of modifying the M^2SV and SPFD potentials on the standard deviations for the fits to our DCS data. These standard deviations correspond to values of the $\Delta\alpha_{0.95}/\alpha$ statistical index [Eq.(3)] of 2.16% and 2.15% for the modified M^2SV and SPFD potentials, respectively. In comparing these $\Delta\alpha_{0.95}/\alpha$ to the values of 2.08% and 2.07% obtained in the absence of the modifications (see Table II), their effect on the DCS is seen to be rather minimal. The standard deviations for our DCS fits may be scaled to those of other experiments by the signal intensities at our out-of-plane reference angle of 4.9° . Using the normalization appropriate for Smith et al.'s data, our standard deviation then becomes about 1.0, which is of the same quality of their best fits to their data¹⁵ (Chen et al. do not report their fitting quality¹⁴).

Both the modified M^2SV and SPFD potentials are seen to describe the experimental macroscopic data rather well (Table V). This is very encouraging, especially since the $B(T)$ data are reproduced, even though they were not used at all in choosing the modified potentials of Eq. (12). We also note from the table that the modified M^2SV potential is slightly better able to describe the bulk property data than is the SPFD one.

The modified M^2SV potential is shown in Fig. 13, which has a logarithmic energy scale above 1.0 meV. Also shown for comparison are the corresponding curves for the ESMSV potential,¹⁴ and for the HFD one.¹⁵ On the scale used, the modified SPFD potential is very close to the M^2SV one and is not plotted. Let us first consider the three potentials in the repulsive region between 2.4 Å and 3.0 Å, where we can see that they are all quite similar. Both the modified M^2SV and SPFD potentials describe $B(T)$ data as well as does the ESMSV one; this was the only bulk property considered by Chen *et al.*¹⁴ These two modified potentials also describe all the macroscopic data about as well as does the HFD potential¹⁵ (Table V). High energy integral collision cross section results are also shown in Fig. 13 for extremely repulsive interactions.⁶⁹ Unfortunately, there is a gap between 1.8 Å and 2.4 Å where the potential is poorly characterized by this method (or by any other); however, it is rather tempting to interpolate smoothly between the high-energy scattering and bulk property results. If such an interpolation is valid, the repulsive He-Ar potential can now be regarded as reasonably well known for $r \gtrsim 1.4$ Å.

The comparison among the three potentials in the attractive region is much less satisfactory. The discrepancies seen in Fig. 13, especially

between the HFD and (modified) M^2SV potentials, is beyond the 10% error bar established by independent computer simulation studies¹³ for the sensitivity of the potentials in the attractive well region. These discrepancies are not caused by differences in the data, which have been shown to be equivalent (Sec. V). Nor can the discrepancies be resolved by appealing to macroscopic properties, which are described equivalently by our modified potentials and by Smith *et al.*'s HFD one (Table V and Ref. 16). Rather, the discrepancies are caused entirely by inadequacies in the potentials previously used to fit the scattering data. We have independently shown that the present M^2SV and SPFD ones do have the flexibility required for an accurate potential to be obtained from iterative fits to the DCS data.^{13, 30}

As mentioned towards the middle of Sec. IV, we now discuss the choice of the reduced distance ρ_f beyond which the theoretical multipole expansion is used⁵⁴ for the SPFD potential [Eq.(8)].

For an early statistical model of interactions between closed-shell atoms and ions, it was found^{5a} that the leading term of the multipole expansion mimics well the calculated potential for reduced distances beyond $\rho = 1.1$ for Ar_2 and $\rho = 1.7$ for He_2 . Although the results of these calculations were not very reliable for the repulsive and for the attractive well regions of the potential, the relative contributions of the short-range, induction, and dispersion components to the potential at large interatomic separations is probably realistic. Our adoption of $\rho_f = 1.6$ for switching to the first three terms of the multipole expansion is predicated upon these semi-empirical results.^{5a, 72} Lacking sufficiently detailed accurate theoretical calculations, we also seek to justify this choice empirically.

To this effect, we fit the SPFD potential [r_m , ϵ , b_0 , and b_1 parameters of Eqs. (4) and (8)] to our DCS data for values of ρ_f held fixed at 1.4, 1.8, and 2.0, in addition to the original value of 1.6. Now, the computer simulation results of paper I showed that up to five statistically independent potential parameters may justifiably be fit to our DCS data,¹³ and that ρ_f is one such parameter. We therefore use ρ_f as the fifth fitted parameter in place of the c_6 dispersion coefficient,⁵³ which is held constant by using a fixed long-range potential (see Sec. IV), and fit the SPFD potential to the DCS data with the least-squares optimization of ρ_f included. The parameters obtained for all these fits are shown in Table VI, and some of the resulting potentials are displayed in Fig. 14. Within the range of distances of the potential to which the DCS are sensitive, the effect of increasing ρ_f is primarily to deepen the attractive well of the potential; the position of the repulsive wall is changed only slightly over the range of ρ_f values considered. The shallow potential obtained from the $\rho_f = 1.4$ fit is considered unrealistic because of its uneven shape in the interatomic distance region between 3.5 Å and 4.5 Å (see the inset of Fig. 14); moreover, least-squares convergence was unusually difficult to attain. Both problems are caused by the small b_0 parameter value obtained, leading to inappropriately large⁷³ b_2 and b_3 coefficients. This empirical evidence that ρ_f must be greater than 1.4 may indicate that the lower limit of interatomic distances for which the multipole expansion is valid is ~ 5 Å for He-Ar. For $\rho_f = 2.0$, the increase in ϵ is seen to be beyond the error bar estimated to reflect the accuracy with which this part of the potential may be determined.¹³ A stronger indication that the most

appropriate among the fixed ρ_f values is $\rho_f = 1.6$ is provided by the least-squares fitting of ρ_f to the DCS data. As shown in Table VI, this results in a value of 1.64; the resulting potential is almost indistinguishable from the $\rho_f = 1.6$ one and is therefore not plotted in Fig. 14.

In this section we have shown that the repulsive wall region of the potential, obtained exclusively from measurements of bulk properties, may be combined with the weakly repulsive and attractive regions of the potential, as determined exclusively by differential scattering experiments. Microscopic and macroscopic properties are simultaneously well described by this combined potential, which has thus been determined over a wider range of interatomic separations than would be possible by consideration of either microscopic or macroscopic properties alone. This is largely due to non-overlapping regions of sensitivity of such properties to the He-Ar potential.

VII. SUMMARY AND CONCLUSIONS

The computer simulation results of Paper I and the thermal DCS scattering measurements presented here have been used to construct two equivalent, accurate potentials, having different mathematical parameterizations, for the attractive well and adjacent regions of the important heteronuclear rare gas diatom He-Ar. These potentials have been modified for strongly repulsive interactions, to which the DCS data are insensitive, by "switching over" to a potential determined exclusively from dilute gas transport properties.²⁶ This modification has virtually no effect on the DCS scattering results, while a very good description of gas-phase bulk properties²³⁻²⁹ is obtained without further variation of any parameters. Both potentials are most conveniently written in reduced form,

$$f(\rho) = V(r)/\epsilon \quad ; \quad \rho = r/r_m . \quad (4)$$

The first of these is the modified SPFD,^{21, 22} written as

$$\left. \begin{aligned} f(\rho) &= h(\rho)Ae^{-b\rho} + [1 - h(\rho)] \cdot \left[b_0\lambda^2 \left(1 + \sum_{i=1}^N b_i\lambda^i \right) - 1 \right] , \\ \text{with } h(\rho) &= \frac{1}{1 + e^{\tau(\rho-\rho_0)}} \quad ; \quad \lambda = 1 - 1/\rho \text{ and } \rho < \rho_f \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho \geq \rho_f . \end{aligned} \right\} (13)$$

We have used the results of Paper I to select $N = 3$.¹³ The DCS data presented in Sec. IV and shown in Sec. V to be equivalent to those of two

other laboratories,^{14, 16, 30} were used to determine the r_m , ϵ , b_0 , and b_1 parameters in the above equations. The value of the long-range joining point ρ_f was chosen on the basis of semi-empirical calculations,^{5a, 72} and was justified in Sec. VI by goodness-of-fit criteria. For $\rho > \rho_f$, theoretical⁵⁴ dispersion coefficients c_6 , c_8 , and c_{10} were used; smoothness conditions at $\rho = \rho_f$ then determined b_2 and b_3 . We obtained the Born-Mayer parameters A and b from a repulsive potential which resulted solely from gas transport properties.²⁶ The "switching function" parameters ρ_0 and τ [see also Eq.(11)] were chosen to minimize the effect of one region of the potential on properties depending on the other. Integral cross section^{17, 18, 63} and virial coefficient²³⁻²⁵ data were reproduced successfully by the modified SPFD potential, and were not considered further in its determination. Although our modified SPFD potential is characterized by a total of 15 parameters, only the five parameters r_m , ϵ , b_0 , b_1 , and ρ_f were obtained from the fits presented here. The final modified SPFD parameters are listed in Table VII.

The r_m and ϵ parameters of course retain their familiar physical significance as the position and depth, respectively, of the attractive minimum, as do the dispersion coefficients⁵³ and the Born-Mayer repulsive parameters A and b . The b_0 parameter governs the curvature of the attractive minimum (i.e., $\left[\frac{d^2f}{d\rho^2}\right]_{\rho=1} = 2b_0$), and ρ_f may be regarded as the reduced distance beyond which the multipole expansion is appropriate. Unfortunately, the physical significance of the remaining parameters is more obscure.

The second of our accurate He-Ar potentials is the modified M^2SV ,²⁰ written as:

$$\left. \begin{aligned}
 f(\rho) &= h(\rho) A e^{-b\rho} + [1 - h(\rho)] \cdot \frac{e^{(\beta' - \rho\beta\omega)}}{\omega} \left[e^{(\beta' - \rho\beta\omega)} - 2 \right], \\
 \text{where} \\
 h(\rho) &= \frac{1}{1 + e^{\tau(\rho - \rho_0)}}; \quad \omega = \frac{\beta' - \ln 2}{\beta - \ln 2} \quad \text{and} \quad \rho < 1 - \beta^{-1} \ln 2 \\
 f(\rho) &= e^{\beta(1-\rho)} \left[e^{\beta(1-\rho)} - 2 \right] \quad \text{for} \quad 1 - \beta^{-1} \ln 2 \leq \rho \leq \rho_1 \\
 f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] \\
 &\quad \text{for} \quad \rho_1 < \rho < \rho_2 \\
 f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for} \quad \rho \geq \rho_2.
 \end{aligned} \right\} (14)$$

The modified M^2SV potential for He-Ar is characterized by the 17 parameters listed in Table VIII.

As for the modified SPFD potential [Eq. (13) and Table VII], only five of these parameters were adjusted to fit the DCS data: r_m , ϵ , β , β' , and ρ_2 . Four of the remaining parameters are fixed by smoothness conditions (s_1 through s_4), and a fifth is otherwise completely determined (ρ_1). The remaining long- and short-range parameters were obtained in the same fashion as were the corresponding modified SPFD parameters.

The large number of parameters required to adequately describe all the He-Ar data discussed here indicates that it is highly unlikely that the principle of corresponding states¹⁰ can be used to predict an accurate interatomic potential for this system from those of others. It is therefore also unlikely that combination rules can be found having a predictive accuracy comparable to that with which interaction potentials for simple van der Waals systems may be experimentally determined.

Independent computer simulation studies¹³ indicated that the range of sensitivity of the present DCS data is 2.8 Å to 6.5 Å. Consequently, we consider this to be the minimum range of validity of the M²SV and SPFD potentials. However, in view of the supplementary information discussed here, the validity of the modified M²SV and SPFD potentials extends to all separations larger than 2.4 Å. If one furthermore interpolates these potentials over the 1.8 Å to 2.4 Å gap for which no accurate information is available, the range of interatomic distances for which the He-Ar potential can be assumed known is $r \lesssim 1.4$ Å. For such interatomic separations, these two potentials are identical within experimental error, and have been shown to provide an accurate representation of the He-Ar interaction. For distances $2.8 \text{ Å} \lesssim r \lesssim 6.5 \text{ Å}$, the potentials obtained here are free of any significant biases arising either from the experimental data or from the parameterizations used to model the interaction.

ACKNOWLEDGMENTS

We wish to thank Messrs. W. W. Schuelke, A. W. Stark, and I. Moskovitz of the Instrument and Electronics Shops of the Division of Chemistry and Chemical Engineering at Caltech for their talented technical support of the apparatus. We also wish to thank Ambassador College for generous use of its computing facilities.

APPENDIX: CM TO LAB COORDINATE TRANSFORMATION

We present here a brief description of the center-of-mass (CM) to laboratory (lab) coordinate transformation equations, for an arbitrary beam intersection angle and for arbitrary polar scattering angles. The quantities used in this derivation are defined in the velocity vector diagram of Fig. 15, which is restricted to elastic scattering, i.e.,

$$|\underline{u}| = u = u_1 . \quad (\text{A1})$$

The Oz velocity-space lab coordinate axis is chosen to be coincident with the primary beam velocity vector, and the $x \geq 0$ xz half-plane contains the secondary beam velocity vector. The GZ velocity-space CM axis similarly coincides with the primary particle CM velocity vector with the GX axis being in the $x \geq 0$ xz half-plane. Orthogonal unit vectors in the lab frame are $\hat{i}$, $\hat{j}$ and $\hat{k}$; in the CM frame they are $\hat{\underline{i}}$, $\hat{\underline{j}}$ and $\hat{\underline{k}}$. These unit vectors are related by:

$$\left. \begin{aligned} \hat{\underline{i}} &= \hat{i} \cos \alpha + \hat{k} \sin \alpha & (\text{i}) \\ \hat{\underline{j}} &= \hat{j} & (\text{ii}) \\ \hat{\underline{k}} &= -\hat{i} \sin \alpha + \hat{k} \cos \alpha & (\text{iii}) \end{aligned} \right\} , \quad (\text{A2})$$

where α is easily expressed in terms of v_1 , v_2 and γ . The relative collision velocity vector $\underline{u}_r$ is given by

$$\underline{u}_r = \underline{u}_1 - \underline{u}_2 = \underline{v}_1 - \underline{v}_2 . \quad (\text{A3})$$

The scattered velocity vectors $\underline{v}$ and $\underline{u}$ are related by

$$\underline{v} = \underline{v}_g + \underline{u} , \quad (\text{A4})$$

where

$$\underline{v}_g = \frac{1}{M} [\hat{k} (m_1 v_1 + m_2 v_2 \cos \gamma) + \hat{j} m_2 v_2 \sin \gamma] ; \quad (A5)$$

M is the sum of the primary and secondary beam particle masses m_1 and m_2 , respectively. The lab and CM scattered velocity vectors are given by

$$\left. \begin{aligned} \underline{v} &= v(\hat{i} \sin \theta \cos \phi + \hat{j} \sin \theta \sin \phi + \hat{k} \cos \theta) & (i) \\ \underline{u} &= u(\hat{I} \sin \Theta \cos \Phi + \hat{J} \sin \Theta \sin \Phi + \hat{K} \cos \Theta) & (ii) \end{aligned} \right\} \quad (A6)$$

From Eqs. (A2), (A4), (A5), and (A6) we obtain

$$\left. \begin{aligned} Mv \sin \theta \cos \phi &= m_2 [v_2 \sin \gamma + u_r (\sin \Theta \cos \Phi \cos \alpha - \cos \Theta \sin \alpha)] & (i) \\ Mv \sin \theta \sin \phi &= m_2 u_r \sin \Theta \sin \Phi & (ii) \\ Mv \cos \theta &= m_1 v_1 + m_2 [v_2 \cos \gamma + u_r (\sin \Theta \cos \Phi \sin \alpha + \cos \Theta \cos \alpha)] & (iii) \end{aligned} \right\} \quad (A7)$$

It is now useful to express θ , Φ and v in terms of Θ , ϕ and u .

Eqs. (A7i) and (A7ii) furnish

$$\left. \begin{aligned} \Phi &= 0 & \text{for } \phi = 0 & (i) \\ \Phi &= \cos^{-1} \left[\frac{r_2 \sin \gamma (\cos \Theta - 1)}{u_r \sin \Theta \cos \alpha} \right] & \text{for } \phi = \frac{\pi}{2} & (ii) \\ \Phi &= \cos^{-1} \left[\frac{C_\phi (B_\phi^2 + C_\phi^2 - A_\phi^2)^{\frac{1}{2}} - A_\phi B_\phi}{B_\phi^2 + C_\phi^2} \right] & \text{for } \phi \neq 0, \neq \frac{\pi}{2} & (iii) \end{aligned} \right\} \quad (A8)$$

where

$$A_\phi = v_2 \sin \gamma \tan \phi (1 - \cos \Theta)$$

$$B_\phi = u_r \sin \Theta \tan \phi \cos \alpha$$

$$C_\phi = u_r \sin \theta .$$

The special cases $\phi = 0$ and $\phi = \frac{\pi}{2}$ correspond to in-plane and out-of-plane scattering respectively, as defined in Sec. II. We may similarly obtain θ (in the range 0 to π) from Eqs. (A7):

$$\left. \begin{aligned} \theta &= \tan^{-1} \left[\frac{m_2 [v_2 \sin \gamma (1 - \cos \Theta) + u_r \sin \Theta \cos \alpha]}{P_k} \right] & \text{for } \phi = 0 & \text{(i)} \\ \theta &= \tan^{-1} \left[\frac{m_2 u_r \sin \Theta (1 - \cos \phi)^{\frac{1}{2}}}{P_k \sin \phi} \right] & \text{for } \phi \neq 0 & \text{(ii)} \end{aligned} \right\} \quad (A9)$$

where

$$P_k = m_1 v_1 + m_2 [v_2 (\cos \gamma + \sin \Theta \sin \gamma) + u_r \cos \Theta \cos \alpha]. \quad (A10)$$

Finally, Eq. (A7iii) yields

$$v = \frac{P_k}{M \cos \theta} \quad (A11)$$

This quantity is useful in calculating the Jacobian of the $(\Theta, \Phi) \rightarrow (\theta, \phi)$ coordinate transformation. Requiring the conservation of flux upon performing this transformation, and relating differential surface elements in the two coordinate frames, the ratio of the lab to CM DCS gives⁷⁴

$$\frac{\sigma_{\text{lab}}}{\sigma_{\text{CM}}} = \frac{v^2}{u^2 |\cos \delta|} \quad . \quad (\text{A12})$$

The angle δ may be obtained from triangle OGD of Fig.15 as

$$\delta = \cos^{-1} \left[\frac{u^2 + v^2 - v_g^2}{2uv} \right] . \quad (\text{A13})$$

The output signals of our electron-bombardment detector are proportional to number densities. To obtain quantities proportional instead to fluxes, and hence to DCS's, we must multiply those signals by the corresponding lab velocities. Therefore,

$$\sigma_{\text{lab}} = C \cdot \frac{I_{\text{sc}} v}{I_{\text{inc}} v_1} , \quad (\text{A14})$$

where I_{sc} and I_{inc} are the scattered and incident signals, respectively. C is independent of scattering direction, and includes the secondary beam number density and the detector acceptance angle. From Eqs. (A12) and (A14) we get

$$I_{\text{sc}} = \frac{C}{I_{\text{inc}}} \cdot \sigma_{\text{CM}} \cdot \frac{vv_1}{u^2 |\cos \delta|} , \quad (\text{A15})$$

where C/I_{inc} is independent not only of the scattering direction, but also of v and v_1 .

After specifying the variables v_1 , v_2 , γ , ϕ and Θ , as well as the constants m_1 and m_2 , the $(\Theta, \phi) \rightarrow (\theta, \Phi)$ angular transformation is performed using Eqs. (A8) and (A9). The detected signal intensity I_{sc} is then obtained (in arbitrary units) from Eqs. (A11) and (A15).

Table I. Beam operating conditions

Characteristic	Primary beam	Secondary beam
beam gas	He	Ar
inlet pressure/torr	1300	3.2
inlet temperature/K	298	298
angular FWHM ^a /deg.	1	3
most probable velocity/(km/sec)	1.757	0.502
velocity FWHM ^a , $\Delta v/v$	0.10	0.75
Mach number	18	1.5

^a Full width at half-maximum.

Table II. Interatomic potential fits to the experimental DCS's

Potential type ^a	scattering frame ^b	$r_m/\text{\AA}$	ϵ/meV	shape parameters ^c	χ^2 ^{d,e}	$\Delta\alpha_{0.95/\alpha}$ ^e (%)
exp-6	in-plane	3.51	1.92	$\alpha = 11.2$	1300 (3)	2.89
	out-of-plane	3.55	2.27	12.3	650 (3)	1.97
	combined	3.53 ₀	2.06	11.6	3900 (3)	2.40
MSV	in-plane	3.57	2.01	$\beta = 5.01$	930 (3)	2.46
	out-of-plane	3.58	2.36	5.61	460 (3)	1.65
	combined	3.57 ₂	2.16	5.26	3300 (3)	2.19
M ² SV	in-plane	3.67	1.66	$\beta = 4.20; \beta' = 7.70$	740 (4)	2.22
	out-of-plane	3.64	2.01	4.73 9.78	270 (4)	1.29
	combined ^f	3.65 ₉	1.80	4.41; 8.54	2900 (4)	2.08
SPFD (N=3)	in-plane	3.63	1.53	$b_0 = 11.5; b_1 = -3.91$	700 (4)	2.17
	out-of-plane	3.55	2.00	24.0; -5.33	270 (4)	1.29
	combined ^f	3.57 ₃	1.76	17.8; -4.69	2900 (4)	2.07

^a Defined in Eqs. (5) through (8) of the text.

^b See Sec. II. Potential parameters are fit to 38 in-plane data points, or 39 out-of-plane data points; the combined potentials are fit to all 77 data points.

^c Symbols have the same meaning as in Eqs. (5) through (8) of the text. The MSV and M²SV potentials also have $\rho_2 = 1.60$; the SPFD potential has $\rho_f = 1.60$. These three potentials use the theoretical dispersion constants^{53,54} $C_6 = 5.867 \text{ eV} \cdot \text{\AA}^6$; $C_8 = 25.68 \text{ eV} \cdot \text{\AA}^8$; $C_{10} = 152.1 \text{ eV} \cdot \text{\AA}^{10}$.

^d Scattering intensity normalized to 500 at $\theta_h = 0.0^\circ$, $\theta_v = 4.9^\circ$, and to 465 at $\theta_h = 4.6^\circ$, $\theta_v = 0.0^\circ$ for the in-plane fits; the number of parameters varied is given in parentheses.

^e See Eqs. (1) and (3).

^f Best potentials.

TABLE III. Fitted parameters for various MSV potentials.^a

$r_m/\text{\AA}$	ϵ/meV	χ^2 ^{b, c, d}	$\Delta\alpha_{0.95/\alpha}$ ^c (%)	Ref.
3.54 ± 0.01	2.09 ± 0.15	4100 (3)	2.44	14
3.55	2.30	3900 (2)	2.36	16
3.55	2.25	3900 (2)	2.36	this work

^aDefined in Eq. (6) of the text, with $\beta = 5.45$, $\rho_2 = 1.40$,

$C_6 = 5.889 \text{ eV} \cdot \text{\AA}^6$; $C_8 = 11.12 \text{ eV} \cdot \text{\AA}^8$; $C_{10} = 0.0$.¹⁴

^b Scattering intensity normalized to 500 at $\theta_h = 0.0^\circ$, $\theta_v = 4.9^\circ$ for the combined data fits; the number of parameters varied is given in parentheses.

^cSee Eqs. (1) and (3).

^dThe fitted parameters were β , r_m and ϵ for reference 14. For reference 15 and the present work they were r_m and ϵ only, with β fixed at the value obtained in reference 14.

TABLE IV. Calculated spectroscopic quantities for He-Ar from several proposed potentials.^a

Potential	ϵ/meV	$G(0)/\text{meV}$	D_0/meV	$\kappa/(\text{meV}/\text{\AA}^2)^b$	Ref.
SPFD	1.76	1.05	0.71	4.9	this work
M ² SV	1.80	1.08	0.72	5.2	this work
ESMSV	2.09	1.39	0.70	9.9	14
HFD	2.60	1.77	0.83	17.5	15
exp-6	2.72	1.81	0.91	18.2	16

^aSee footnote 65.

^b κ is defined as the curvature of the potential at the minimum of the attractive well.

TABLE V. Standard deviations σ for dilute gas properties.

Property	Temperature range/°K	data range ^{a-d}	σ		Experimental error	Reference
			modified M^2SV^e, f	modified SPFD ^{e, f}		
B(T) ^b	123-323	10.6-18.4 (9)	0.65	0.73	0.12	23
B(T)	223-323	16.1-18.4 (3)	0.27	0.15	0.05	24
B(T)	303-773	18.8-20.5 (6)	0.72	0.93	0.20	25
$\eta(T)^c$	122-311	88-160 (8)	2.5	4.1	2.5	26
$\eta(T)$	295-1553	160-470 (11)	6.0	6.0	6.0	27
D(T) ^d	90-400	0.09-1.2 (4)	0.034	0.031	0.003	28
D(T)	300-1400	0.73-9.5 (23)	0.038	0.038	0.10	29
B(T) ^b -total ^g	123-773	10.6-20.5 (18)	0.60	0.71	-	-
$\eta(T)^c$ -total	122-1553	88-470 (19)	4.7	5.2	-	-
D(T) ^d -total	90-1400	0.09-9.5 (27)	0.036	0.037	-	-
DCS ^h	-	9.8-4500 (77)	6.6	6.6	1.5-100	this work

^a The number of data points that is compared with calculated values is given in parentheses; the data of Ref. 29 were "smoothed".

^b Second virial coefficients, units of cm^3/mole .

^c Viscosity coefficients, units of micro-poise.

^d Diffusion coefficients at 1 atm, units of cm^2/sec .

^e Mathematical forms defined in Eqs. (7) and (8); potential parameters are given in Table II.

^f The potentials are "switched over" to a Born-Mayer short-range repulsive wall as shown in Eqs. (11) and (12). Parameters of Eq. (11) are $\tau = 100$ and $\rho_0 = 0.78$; the nonreduced Born-Mayer parameters of Eq. (10) are $C = 1.23 \times 10^5 \text{ eV}$ and $\alpha = 5.69 \text{ \AA}^{-1}$.

^g "total" applies to the combined data of the several references given for each particular property.

^h Differential cross sections in arbitrary units. Values of the $\Delta\alpha_{0.95}/\alpha$ statistical index of Eq. (3), corresponding to the absolute standard deviations quoted here, are 2.16% and 2.15% for the modified M^2SV and SPFD potentials, respectively;

cf. Table II. The DCS scattering intensities and experimental errors are normalized to 500 at the out-of-plane reference angle of 4.9° .

TABLE VI. Fitted parameters for SPFD potentials with different values of ρ_f .^a

$\rho_f^{a,b}$	$r_m/\text{\AA}$	ϵ/meV	b_0	b_1	$\chi^2_{b,c,d}$	$\Delta\alpha_{0.95}/\alpha\text{ (\%)}^d$
1.4	3.72 ₃	1.62	3.15	5.15	3100 (4)	2.12
1.6	3.57 ₃	1.76	17.8	-4.69	2900 (4)	2.07
1.8	3.59 ₁	1.87	22.1	-3.51	3000 (4)	2.11
2.0	3.59 ₀	2.05	24.7	-3.19	3200 (4)	2.17
1.64	3.58 ₉	1.76	18.2	-4.28	2900 (5)	2.07

^aReduced distance beyond which the potential assumes its theoretical⁵⁴ asymptotic form [see Eq. (8)].^bFor $\rho_f = 1.4, 1.6, 1.8$ and 2.0 , the fitted parameters were r_m, ϵ, b_0 and b_1 of Eqs. (4) and (8);the $\rho_f = 1.64$ value was obtained by optimizing it simultaneously with the other four parameters.^cScattering intensity normalized to 500 at $\theta_h = 0.0^\circ$, $\theta_v = 4.9^\circ$; the number of parameters varied is given in parentheses for the fits to the "combined" data sets.^dSee Eqs. (1) and (3).

TABLE VII. Modified SPFD potential parameters for He-Ar.^a

Parameter	Value ^b	Method of Determination
N	3	computer simulation ^c
r_m	$3.57_3 \text{ \AA}$	DCS measurements ^d
ϵ	1.76 meV	DCS measurements ^d
b_0	17.75	DCS measurements ^d
b_1	-4.685	DCS measurements ^d
ρ_f	1.60	semi-empirically; DCS measurements ^d
c_6^e	1.602	theoretically ^f
c_8^e	0.549	theoretically ^f
c_{10}^e	0.255	theoretically ^f
b_2	15.13	smoothness at $\rho = \rho_f$
b_3	-19.23	smoothness at $\rho = \rho_f$
A^g	6.972×10^7	viscosity; ^h diffusion ⁱ data
b^g	20.33	viscosity; ^h diffusion ⁱ data
ρ_0	0.78	switching function [Eq. (11)]
τ	100	switching function [Eq. (11)]

^a Modified SPFD form of Eq. (13), parameter symbols are used there and in Eq. (4). $\sigma = 3.08_1 \text{ \AA}$ for this potential.

^b Those values quoted to four digits (except r_m) are not actually significant in the last place; we display them only to avoid round-off errors which might otherwise result in apparent discontinuities of the potential at ρ_f .

^c Reference 13.

^d This work.

^e Nonreduced dispersion coefficients are^{53, 54} $C_6 = 5.867 \text{ eV} \cdot \text{\AA}^6$; $C_8 = 25.68 \text{ eV} \cdot \text{\AA}^8$; $C_{10} = 152.1 \text{ eV} \cdot \text{\AA}^{10}$.

^f Reference 54.

^g Nonreduced Born-Mayer parameters are $C = 1.23 \times 10^5 \text{ eV}$; $\alpha = 5.69 \text{ \AA}^{-1}$.

^h References 26 and 27.

ⁱ References 28 and 29.

TABLE VIII. Modified M²SV potential parameters for He-Ar.^a

Parameter	Value ^b	Method of Determination
r_m	3.65 ₉	DCS measurements ^c
ϵ	1.80	DCS measurements ^c
β	4.41	DCS measurements ^c
β'	8.54	DCS measurements ^c
ρ_2	1.60	semi-empirically; DCS measurements ^c
c_6^d	1.358	theoretically ^e
c_8^d	0.444	theoretically ^e
c_{10}^d	0.196	theoretically ^e
ρ_1	1.157	Morse β parameter
s_1	-0.552	smoothness at $\rho = \rho_1$ and ρ_2
s_2	-2.573	smoothness at $\rho = \rho_1$ and ρ_2
s_3	-1.586	smoothness at $\rho = \rho_1$ and ρ_2
s_4	0.294	smoothness at $\rho = \rho_1$ and ρ_2
A^f	6.834×10^7	viscosity; ^g diffusion ^h data
b^f	20.82	viscosity; ^g diffusion ^h data
ρ_0	0.78	switching function [Eq. (11)]
τ	100	switching function [Eq. (11)]

^a Modified M²SV form of Eq. (14), parameter symbols are used there and in Eq. (4). $\sigma = 3.08_4$ Å for this potential.

^b Those values quoted to four digits (except r_m) are not actually significant in the last place; we display them only to avoid round-off errors which might otherwise result in apparent discontinuities of the potential at $\rho = \rho_1$, ρ_2 , or at σ/r_m .

^c This work.

^d Nonreduced dispersion coefficients are^{53, 54} $C_6 = 5.867 \text{ eV} \cdot \text{Å}^6$; $C_8 = 25.68 \text{ eV} \cdot \text{Å}^8$; $C_{10} = 152.1 \text{ eV} \cdot \text{Å}^{10}$.

^e Reference 54.

^f Nonreduced Born-Mayer parameters are $C = 1.23 \times 10^5 \text{ eV}$; $\alpha = 5.69 \text{ Å}^{-1}$.

^g References 26 and 27.

^h References 28 and 29.

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$$c_{2i+4} = \frac{C_{2i+4}}{\epsilon \cdot r_m^{2i+4}} \quad (i = 1, 2, 3) .$$

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FIGURE CAPTIONS

Fig. 1. Vertical cross section of the molecular beam apparatus, drawn approximately to scale. FT - copper gasket feedthroughs, DP_{1-5} - oil diffusion pumps, DP_6 - mercury diffusion pump, PB - primary beam source, Nz - nozzle, Sk - skimmer, Ch - beam chopper, VS - velocity selector, Fl - beam flag, SB - secondary beam source, CA - capillary array, SCh - scattering chamber, QA - mass spectrometer quadrant arm, GB - gear box and pulleys, MS - mass spectrometer detector, AW - alignment window, IP_1 - 5 ℓ /sec ion pump, IP_2 - 25 ℓ /sec ion pump, CP - liquid He cryopump, TL - transfer line, IG - ionization gauge, BV - bakeout valve, GV - gate valve, IS - electron bombardment ion source and ion optics, MF - quadrupole mass filter, CB - Cu-Be dynode electron multiplier, Sp - Spiraltron electron multiplier, θ_h - in-plane scattering angle, θ_v - out-of-plane scattering angle.

Fig. 2. Schematic of the crossed beam scattering zone, viewed from above and drawn to scale. SC - scattering center, PB - primary beam angular divergence cone, SB - secondary beam angular divergence cone, MS - detector penumbral³⁹ viewing cone (umbral viewing cone angle = 0.7°), C_1 - primary beam collimator, C_2 - secondary beam collimator, C_3 - detector entrance collimator, C_4 - detector buffer chamber collimator, Nz - primary beam nozzle, Sk - primary beam skimmer, IS - mass spectrometer ion source.

Fig. 3. He + Ar experimental cross sections in the vicinity of the first diffraction oscillation. $I_{CM}(\theta_{CM})$ is the DCS in arbitrary units, transformed to the CM coordinate frame at the scattering angle θ_{CM} . In-plane measurements on the left panel and out-of-plane measurements on the right panel are shown as points with error bars; open circles are for measurements at positive scattering angles and full circles are for negative scattering angles (in the sense defined in Sec. II). The lines are curve fits, quadratic in θ_{CM} , used to locate the minimum position; solid lines are for positive scattering angles and dashed lines are for negative scattering angles.

Fig. 4. Laboratory differential cross sections for in-plane and out-of-plane scattering; the latter are shifted downwards by one decade for clarity of display. Points with error bars are experimental measurements of the He+Ar differential scattering cross sections $I_{lab}(\theta_{lab}) \cdot \sin\theta_{lab}$ vs. θ_{lab} at an average relative collision energy of 64.2 meV. Curves are DCS's calculated from potentials fit separately to the two sets of experimental data. Solid line: SPFD potential; dotted line: M^2SV potential; dashed line: MSV potential; dash-dotted line: exp-6 potential. The potential parameters are given in Table II.

Fig. 5. Laboratory differential cross sections for in-plane and out-of-plane scattering. Curves are DCS's calculated from potentials fit to the combined sets of experimental data (parameters given in Table II); other symbols as in Fig. 4.

Fig. 6. Interatomic potentials for He-Ar as a function of interatomic distance. The inset magnifies the vertical scale of the potential energy minimum region by a factor of 2.5. Curves with dots are M^2SV potentials; those without are SPFD potentials. Solid curves: fits to the combined in-plane and out-of-plane data sets (best potentials); short dashed curves: fits to the in-plane data only; long dashed curves: fits to the out-of-plane data only. The vertical error bar in the inset indicates the estimated inaccuracy of $\pm 10\%$ in our determination at the minimum, while the horizontal error bar at 7.5 meV on the repulsive wall indicates the distance equivalent to the $\pm 30\%$ uncertainty of the potential there. The arrows on the abscissa at interatomic distances of 2.8 Å and 6.5 Å delineate the range of sensitivity of the room-temperature experiments to the DCS.¹³

Fig. 7. Differential contribution to the classical second virial coefficient as a function of the reduced interatomic distance ρ . $I(\rho)$ is the integrand of the second virial coefficient expression [see Eq. (9) of the text]. Curves are calculated from the SPFD potential whose parameters are listed in Table II. Solid line: $T = 600$ K and $\rho_i = 0.80$; dashed line: $T = 200$ K and $\rho_i = 0.80$; dotted line: $T = 600$ K and $\rho_i = 0.81$; ρ_i is the point below which a Born-Mayer repulsive wall is used as discussed in Sec. IV.

Fig. 8. Interatomic potentials of the MSV shape for He-Ar as a function of interatomic distance; inset as in Fig. 6. Solid curve: this work; dashed curve: ref. 14; dotted curve: ref. 15. The potential parameters are given in Table III. Error bars and arrows along the abscissa are placed as in Fig. 6.

Fig. 9. Laboratory-averaged differential cross sections for in-plane and out-of-plane scattering calculated from the corresponding MSV potentials of Fig. 8.

Fig. 10. Interatomic potentials proposed for He-Ar as a function of interatomic distance; inset as in Fig. 6. Solid curve: SPFD potential of this work; dashed curve: MSV potential from ref. 14; dotted curve: HFD potential of ref. 16; dash-dotted curve: exp-6 potential of ref. 15. The M^2SV potential is not shown here as it is very close to the SPFD one (see the solid curves of Fig. 6). Error bars and arrows along the abscissa are placed as in Fig. 6.

Fig. 11. Laboratory differential cross sections for in-plane and out-of-plane scattering. Points as in Fig. 4; curves are calculated from the corresponding potentials of Fig. 10.

Fig. 12. He-Ar integral cross sections Q as a function of the relative collision velocity v (lower abscissa scale) and corresponding relative energy E (upper abscissa scale). All scales are logarithmic. Solid curve: calculated from the SPFD potential of this work; dotted curve: calculated from the (ES)MSV potential of Ref. 17. The error bar at $v = 2.5$ km/sec represents a constant calibration error of $\pm 2\%$ in the experimental data of Ref. 17.

Fig. 13. He-Ar potentials, plotted semilogarithmically for energies above 1 meV, and linearly below 1 meV. Solid curve at the upper left is obtained from the high-energy integral collision cross section measurements of Ref. 69. Other curves are constructed from an amalgam of DCS and bulk property measurements. Solid curve: modified M^2SV

potential of this work (the modified SPFD potential is very similar and is not plotted); dashed curve: ESMSV potential of Ref. 14; dotted curve: HFD potential of Ref. 15. The horizontal error at $r = 2.6 \text{ \AA}$ is $\pm 0.01 \text{ \AA}$ and is about the same as the horizontal displacements among the three potentials there;²⁶ at the attractive minimum, the error bar is $\pm 10\%$ of the potential energy.¹³

Fig. 14. Interatomic potentials of the SPFD shape for He-Ar as a function of interatomic distance; inset as in Fig. 6. Different curves are obtained by fixing $\rho_f = 1.6$ (solid); $\rho_f = 1.8$ (dashed); $\rho_f = 2.0$ (dash-dotted); $\rho_f = 1.4$ (dotted), while fitting the four remaining SPFD parameters to DCS data. The corresponding curve with ρ_f fitted along with the other SPFD parameters is almost indistinguishable from the $\rho_f = 1.6$ curve and is not plotted. The potential parameters are given in Table VI. Error bars and arrows along the abscissa are placed as in Fig. 6.

Fig. 15. Velocity vector diagram for He-Ar collisions at an arbitrary beam intersection angle γ . O and G are the origins (in velocity space) of the lab (Oxyz) and CM (GXYZ) coordinate axes, respectively, as defined in the text. The detector position D has spherical polar angles θ , ϕ and Θ , Φ in these respective frames. In configuration space, the CM moves at a velocity $\underline{v}_g$ with respect to the lab origin; the Oz and GZ coordinate axes intersect at an angle α . Velocity vectors are denoted ' $\underline{v}$ ' in the lab and ' $\underline{u}$ ' in the CM frames; those with a subscript '1' refer to the primary beam, while a '2' refers to the secondary beam. The scattered velocity vectors $\underline{v}$ and $\underline{u}$ (no subscripts) intersect at an angle δ . Symbols in the figure with overhead arrows are vector quantities, corresponding to bold-face symbols in the text.

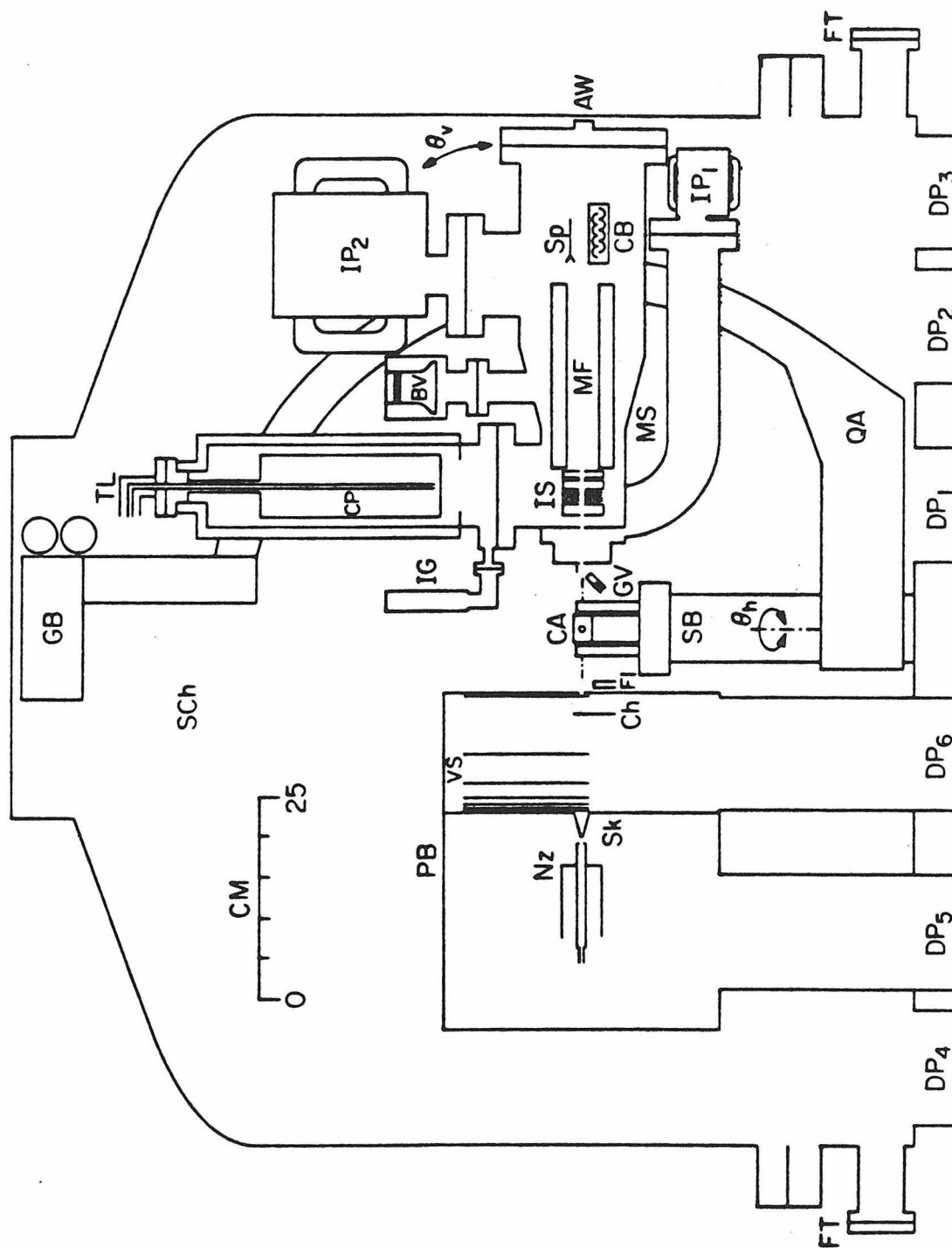


Figure 1.

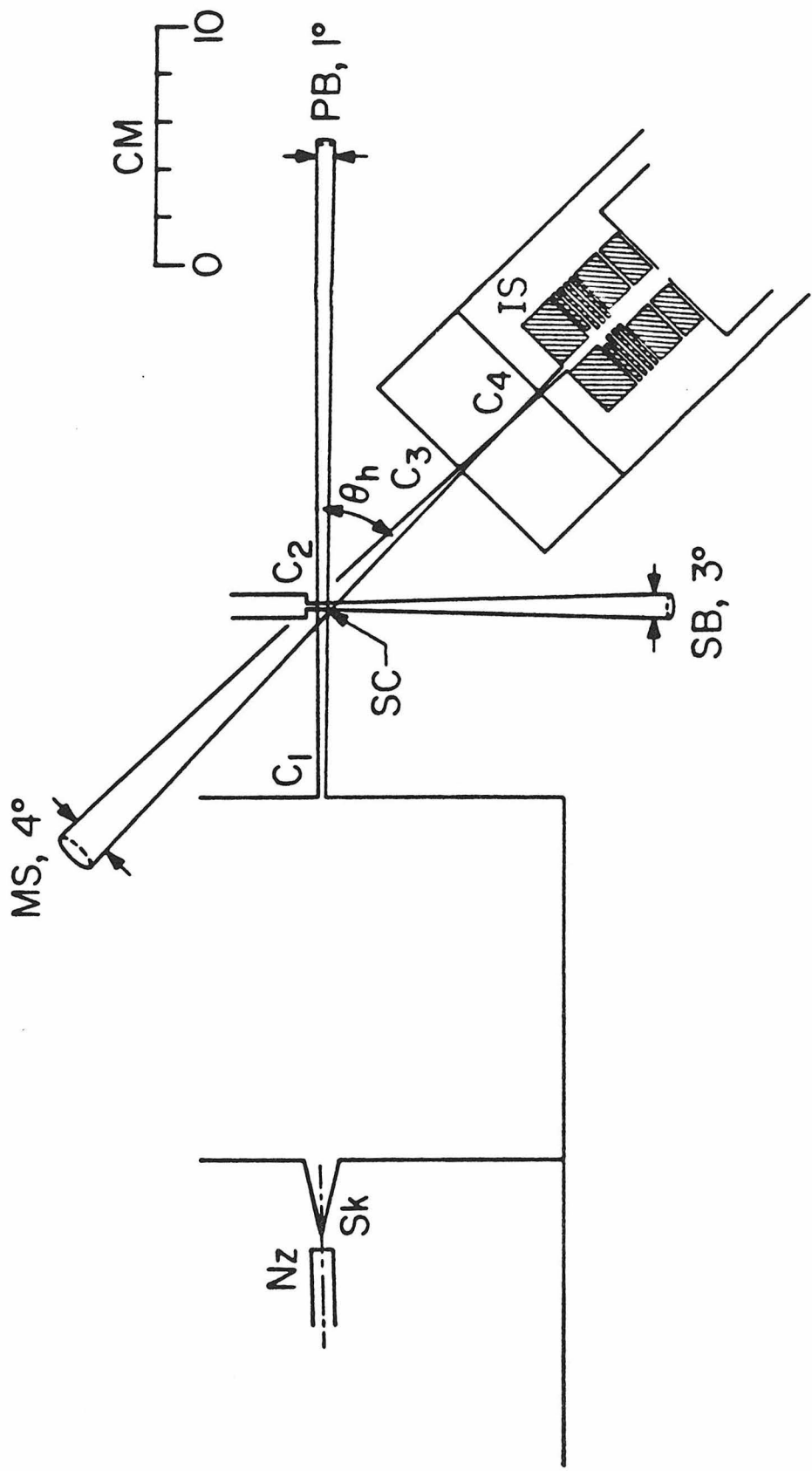


Figure 2.

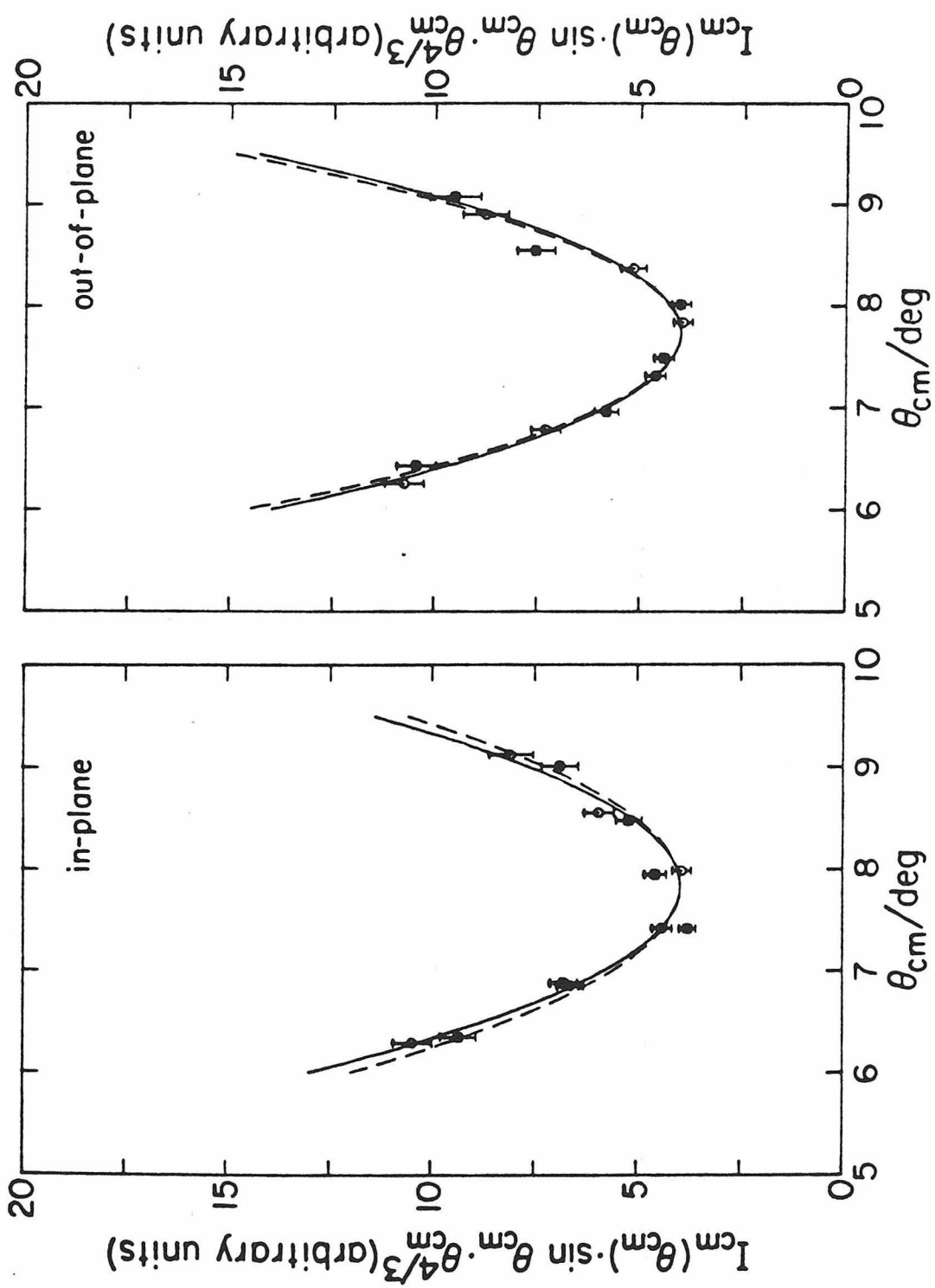


Figure 3.

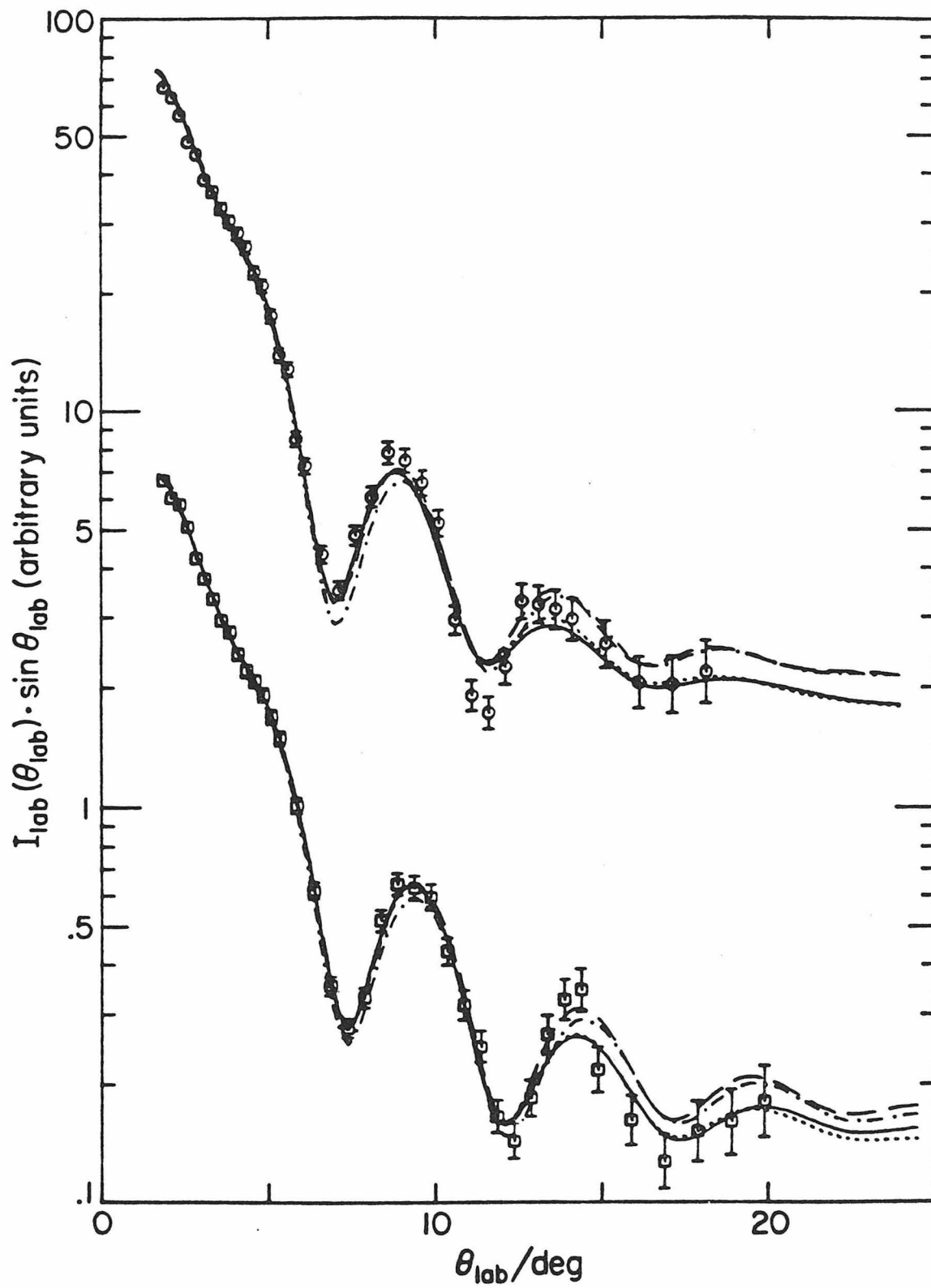


Figure 4.

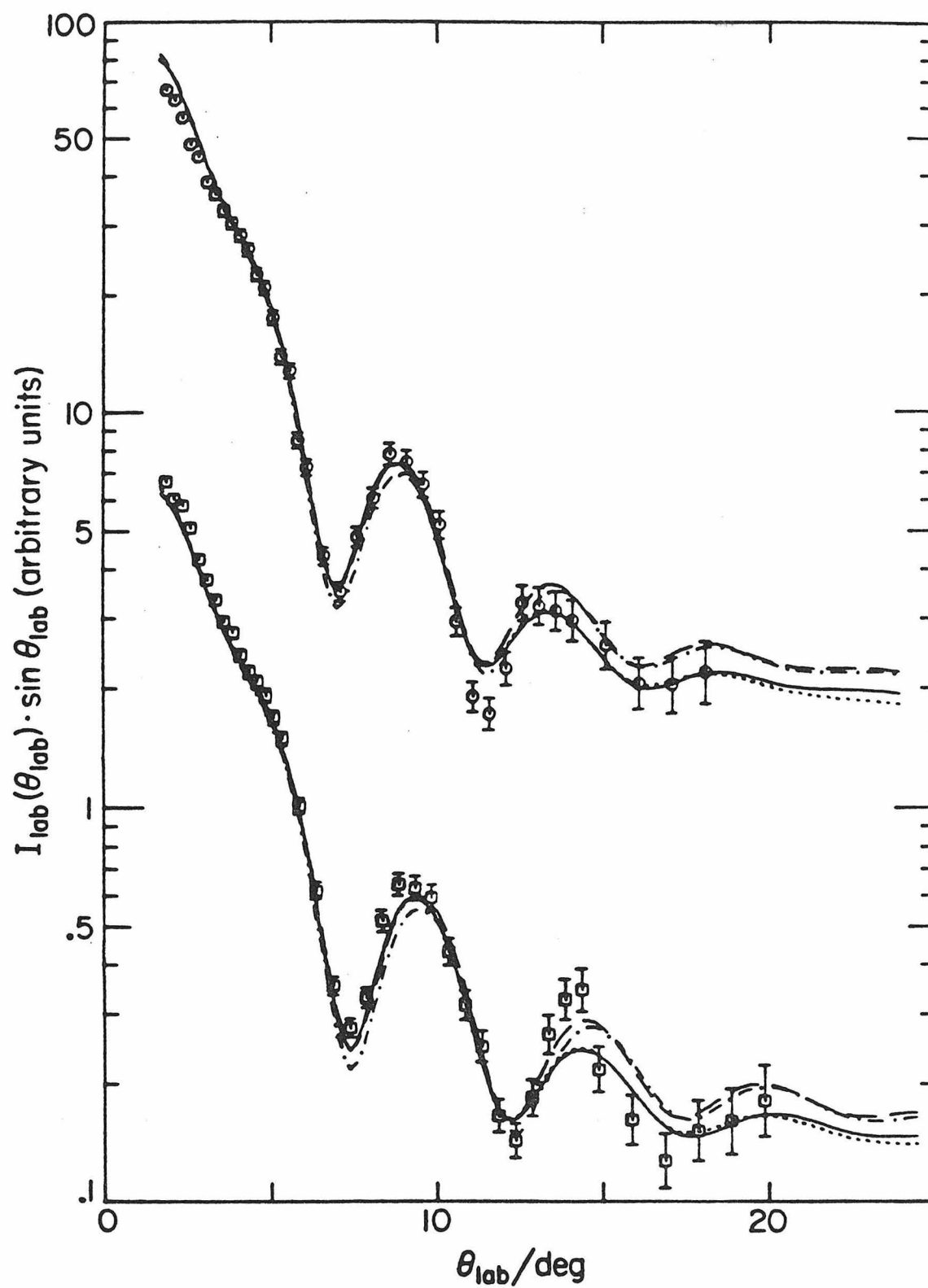


Figure 5.

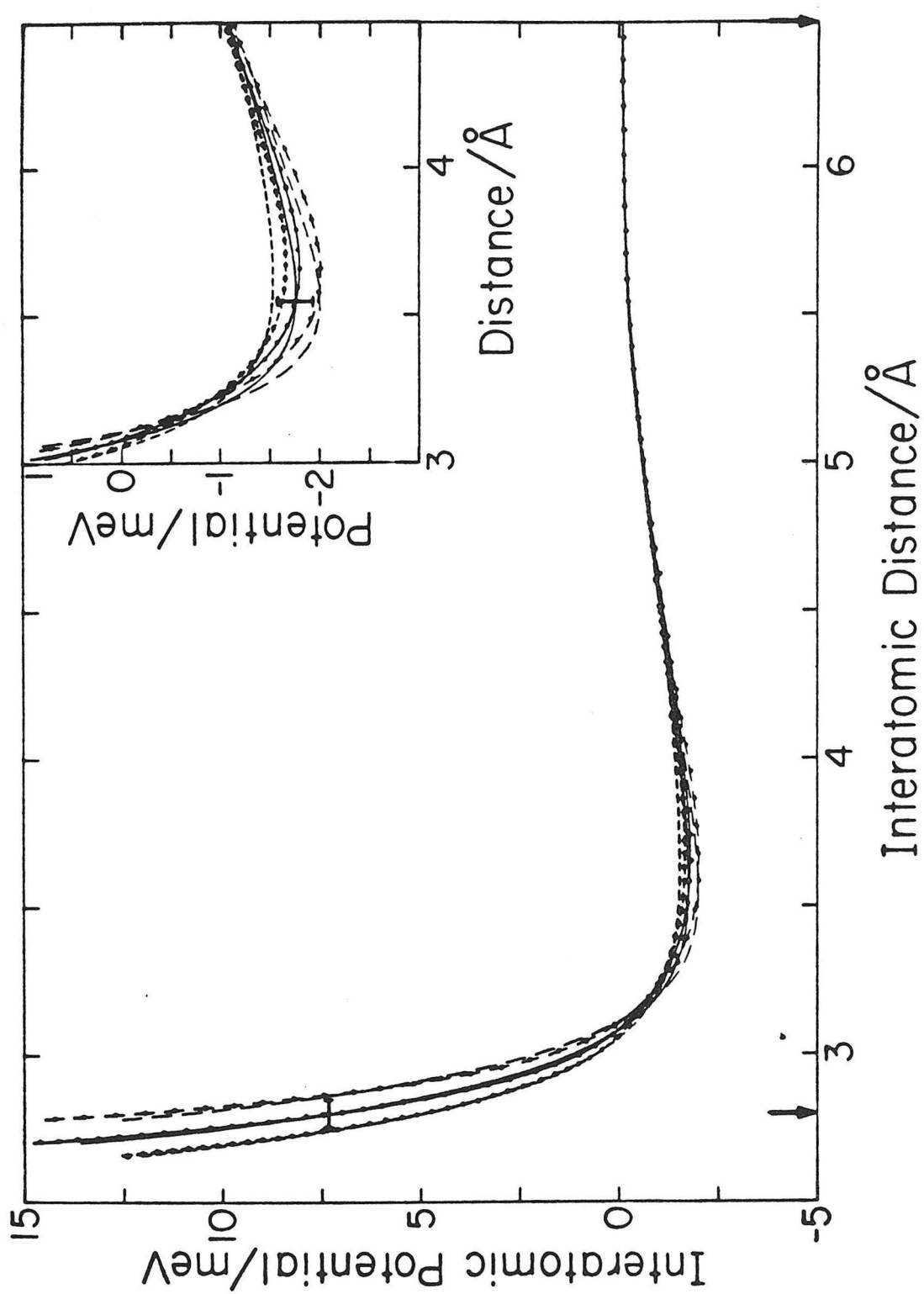


Figure 6.

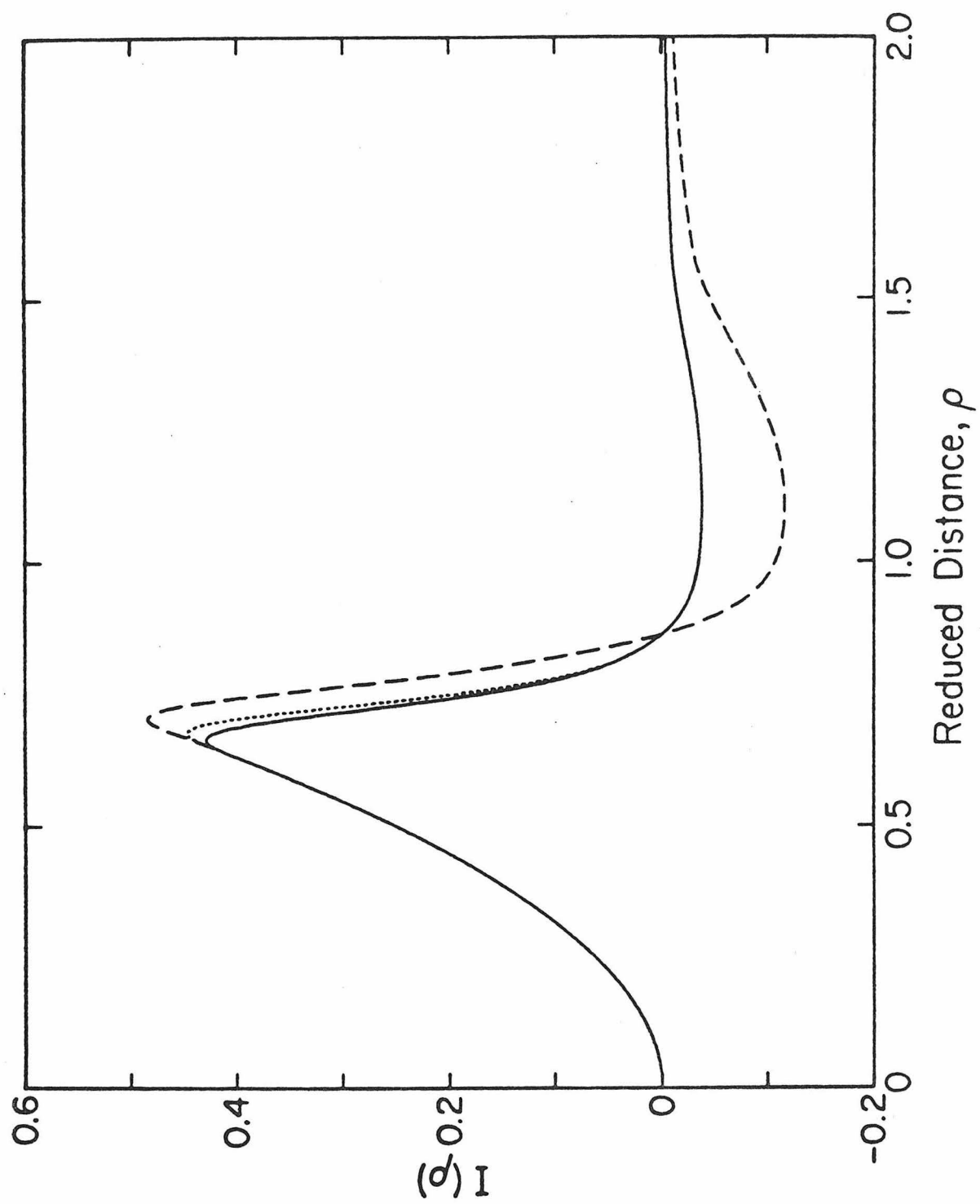


Figure 7.

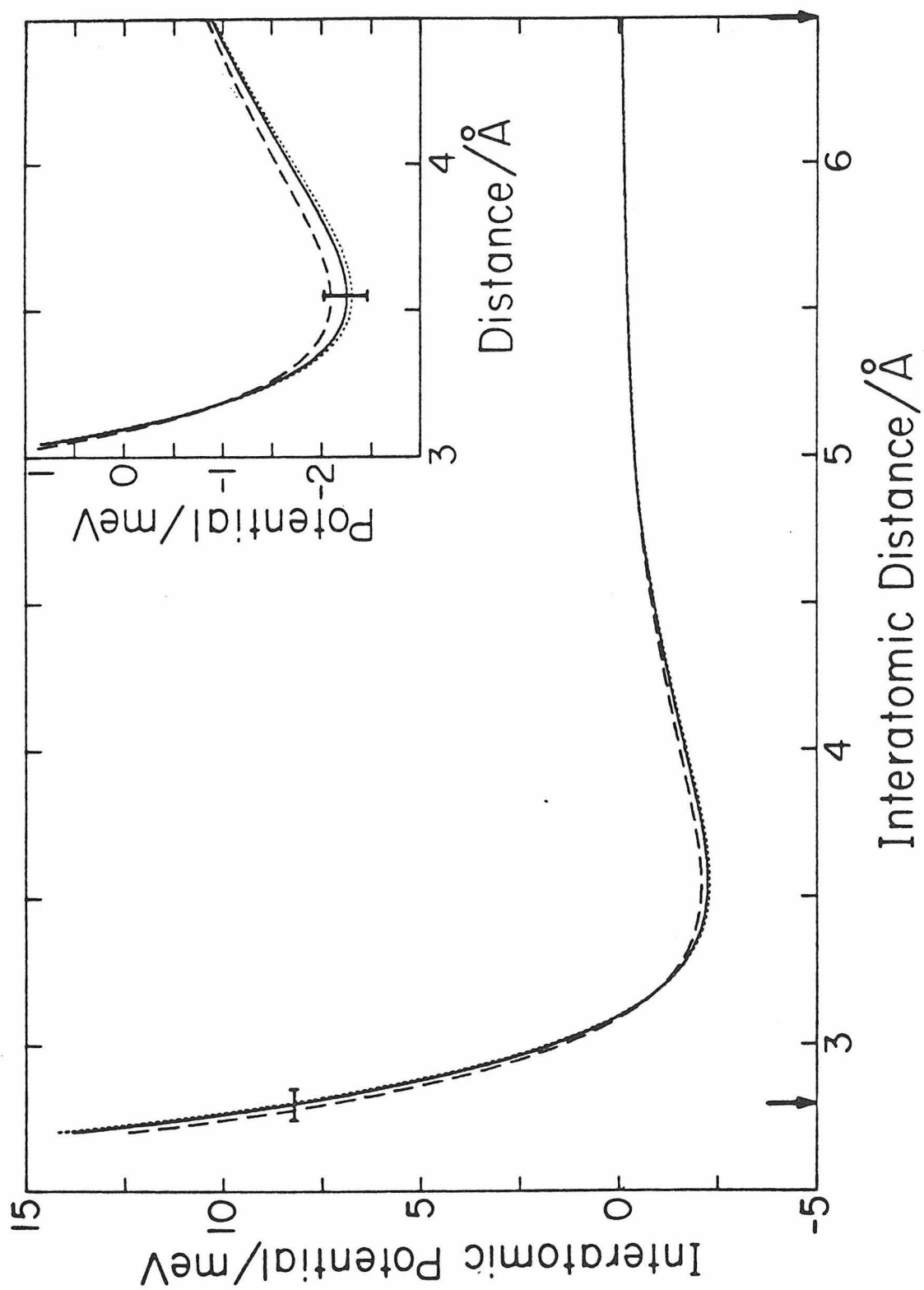


Figure 8.

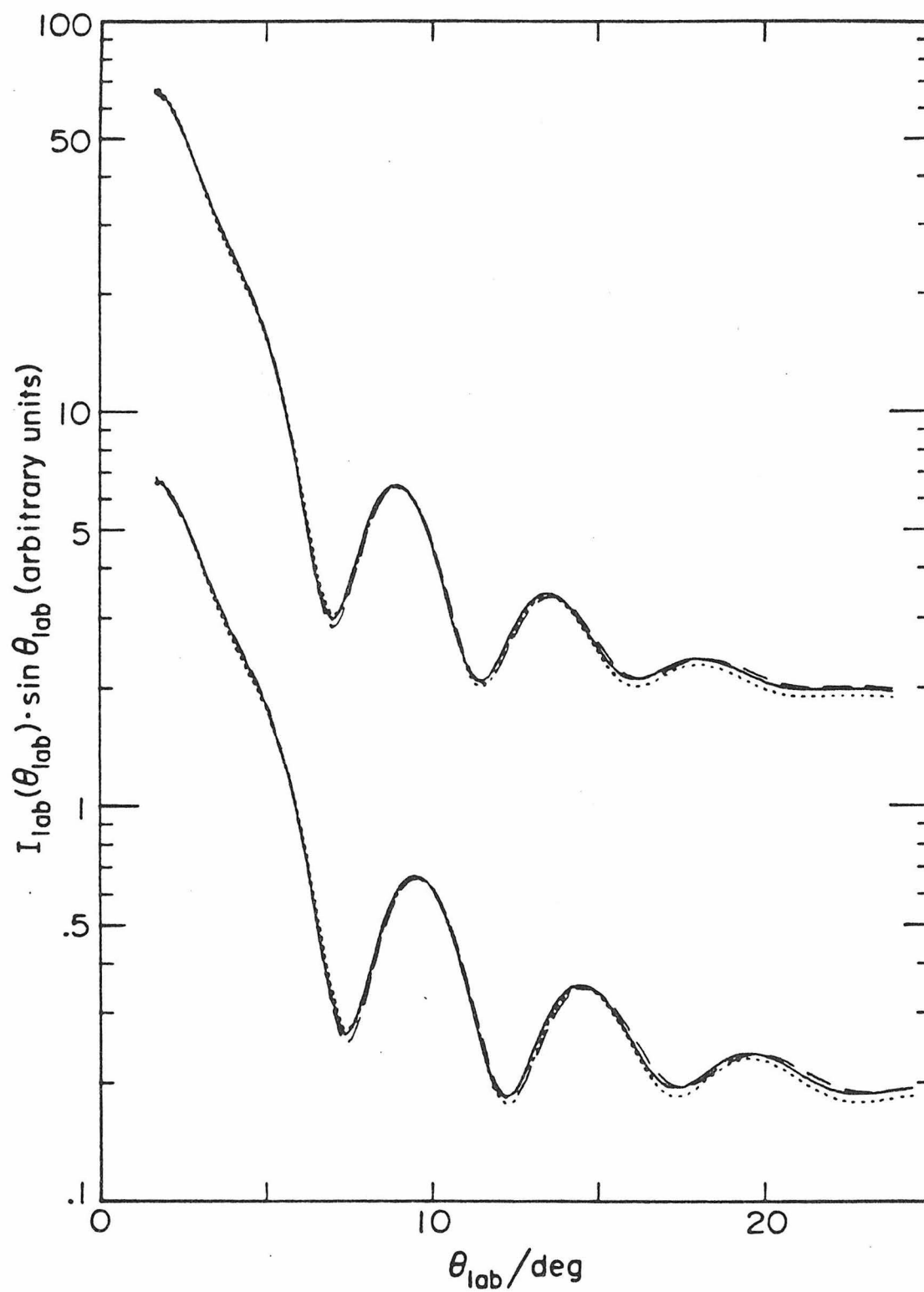


Figure 9.

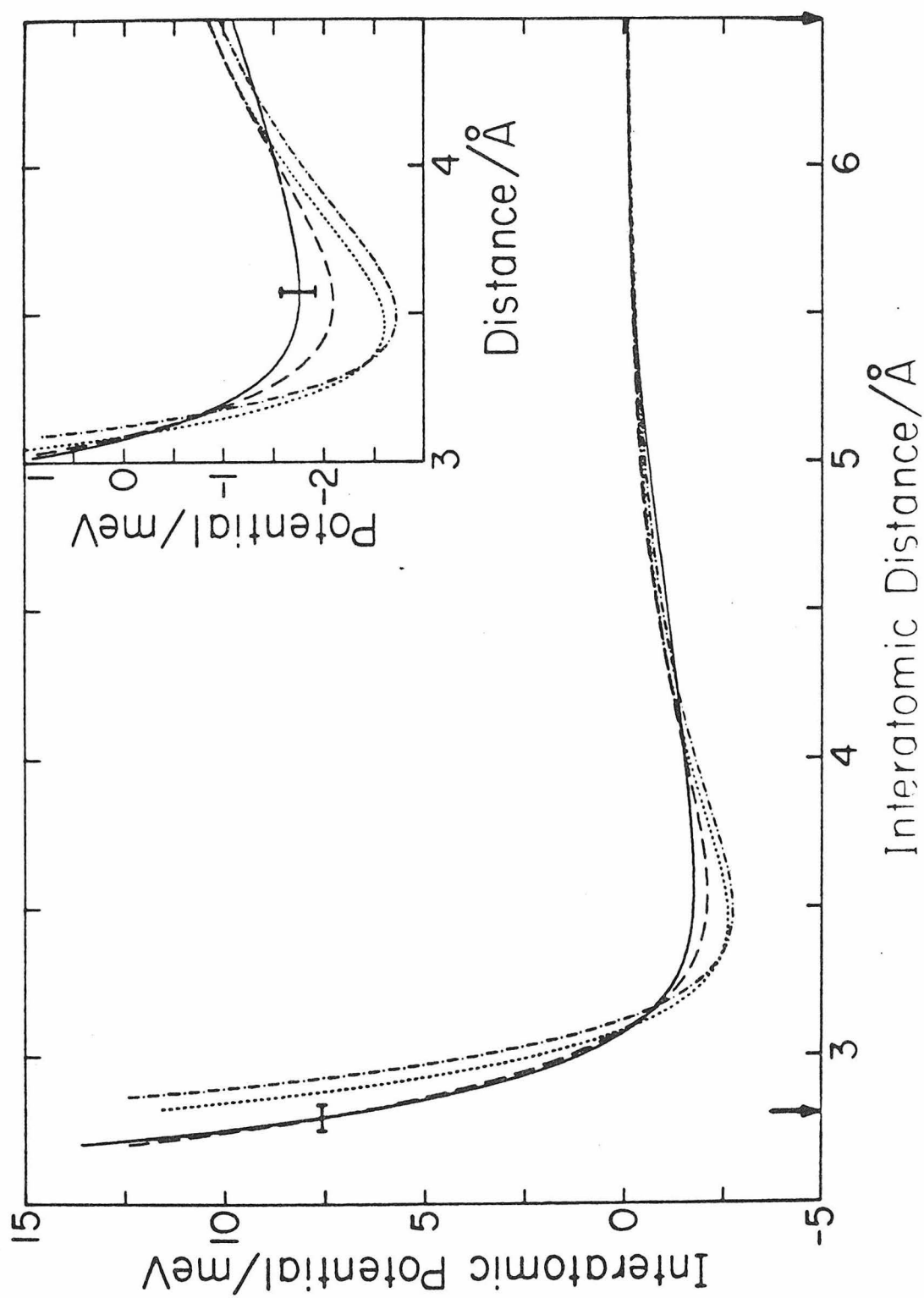


Figure 10.

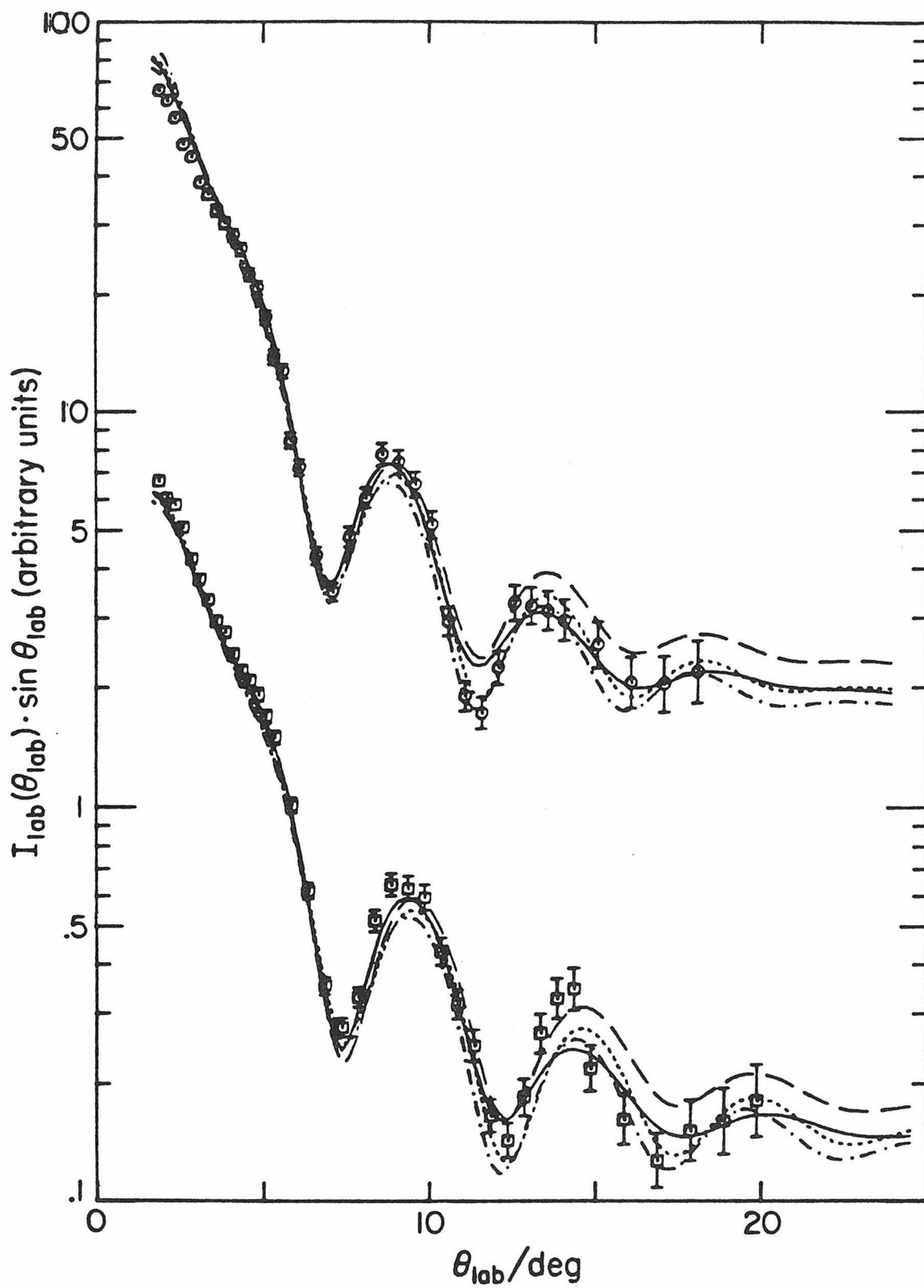


Figure 11.

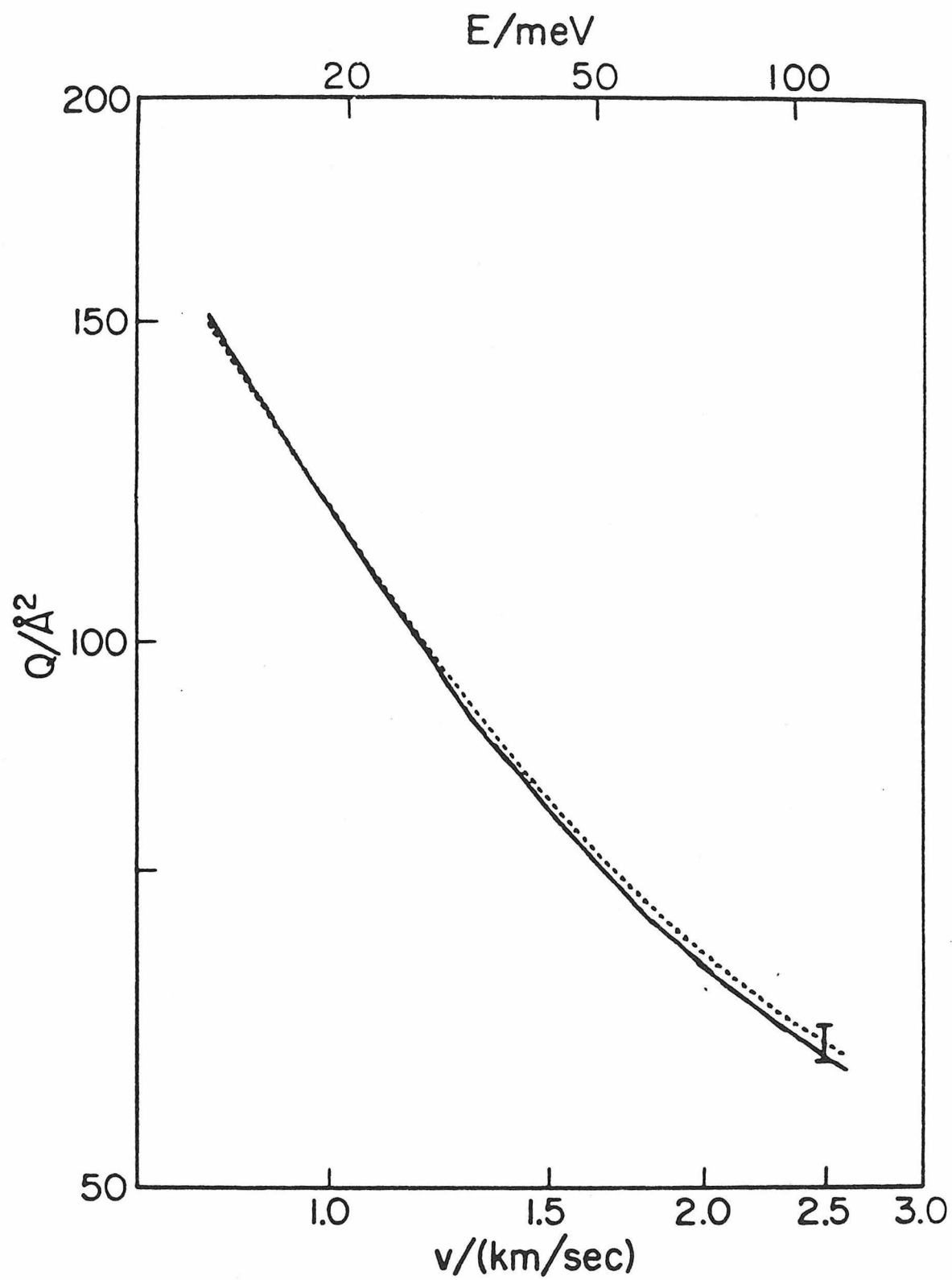


Figure 12.

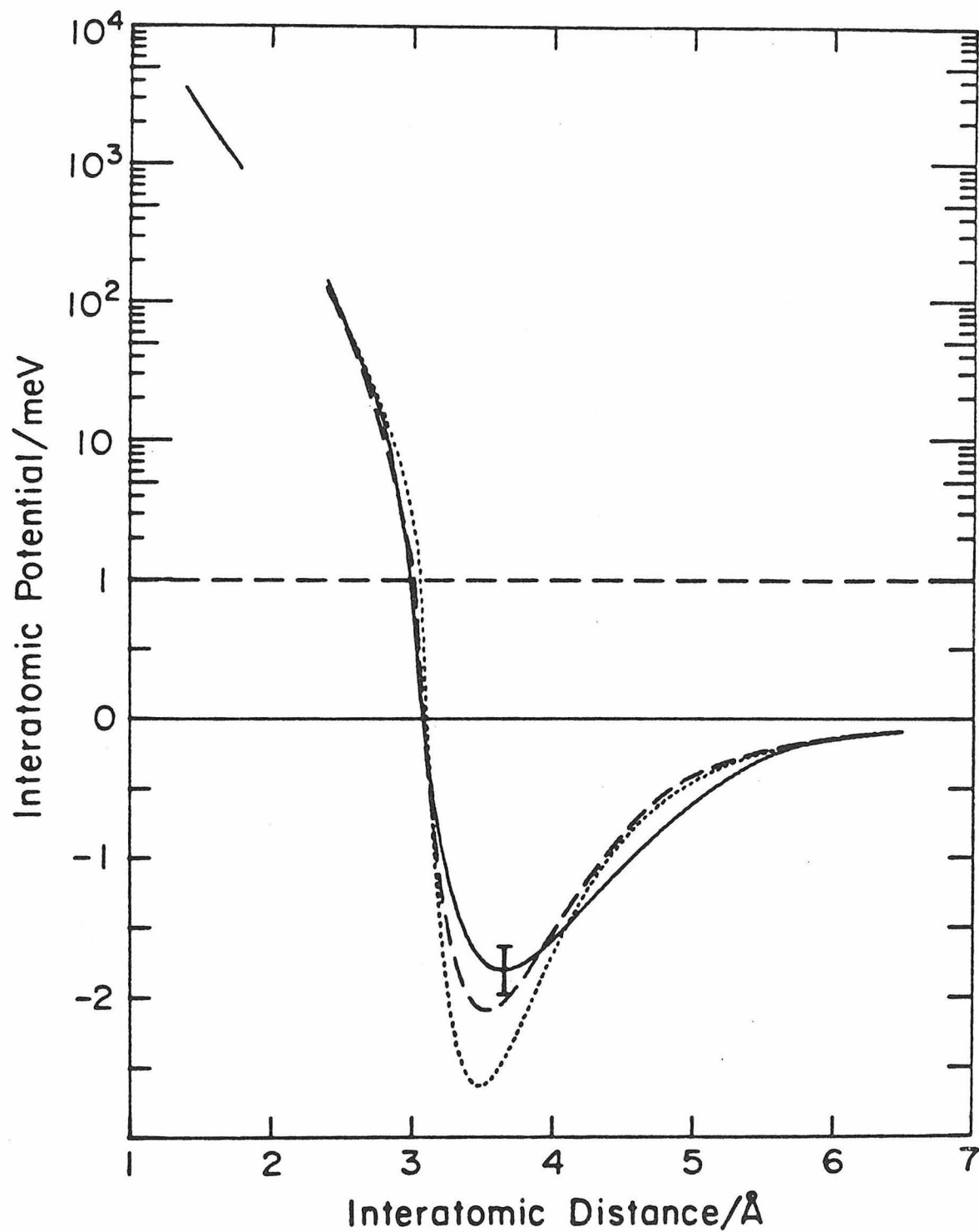


Figure 13.

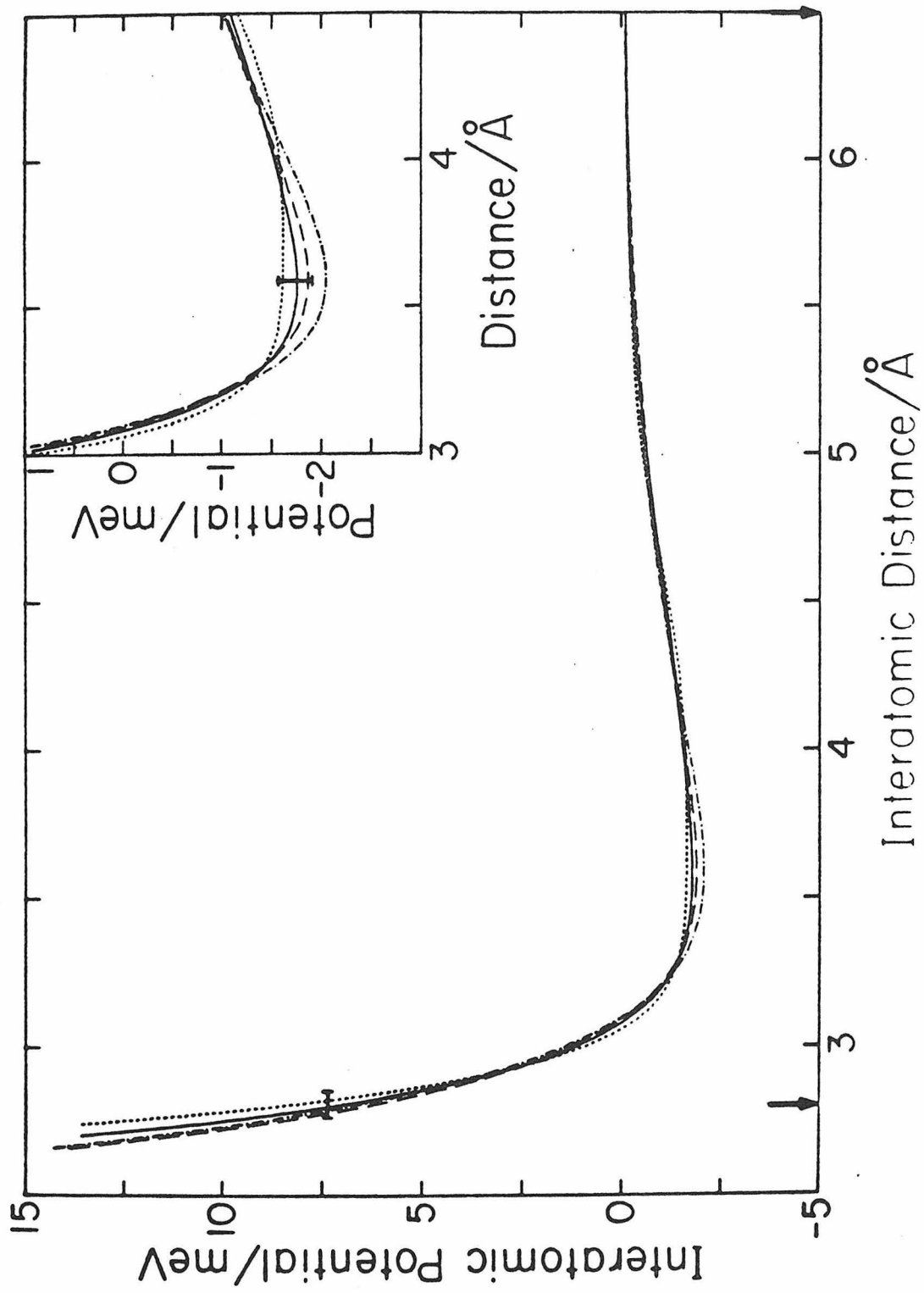


Figure 14.

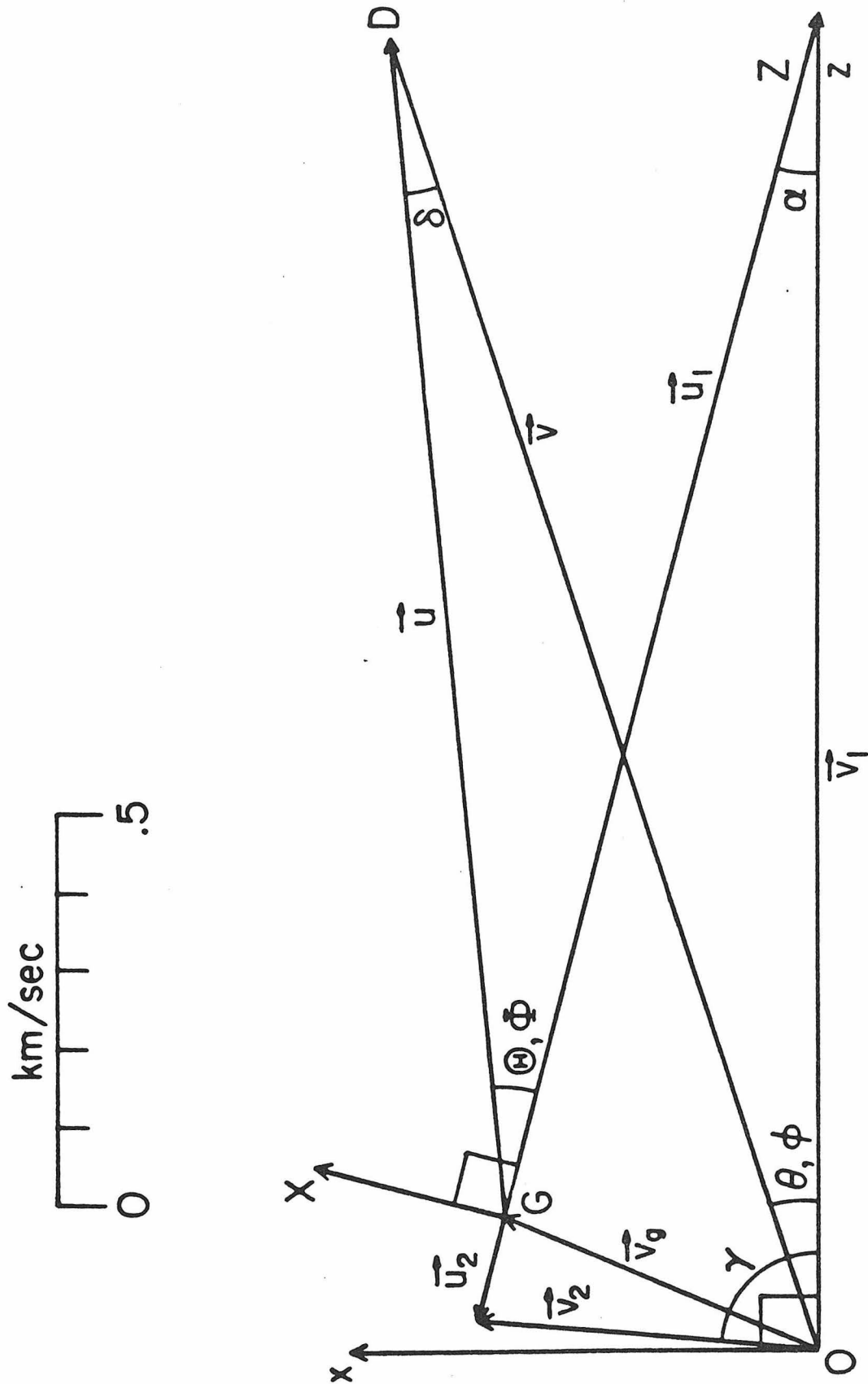


Figure 15.

APPENDIX F

Anisotropic intermolecular potentials
for He + N₂, O₂, CO, and NO

Scattering of thermal He beams by crossed atomic and molecular beams. III. Anisotropic intermolecular potentials for He + N₂, O₂, CO, and NO^{a)}

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ABSTRACT

Differential scattering cross sections are measured for He + N₂, O₂, CO, and NO, using the crossed molecular beams technique. These data, which are sensitive to the van der Waals attractive minima and adjacent regions of the intermolecular potentials, are analyzed in terms of both central-field and anisotropic models. Little evidence is found for quenching of the observed diffraction oscillations, and anisotropic contributions are determined to be small: the spherical averages of these anisotropic potentials are indistinguishable, within experimental error, from the potentials obtained by a central-field analysis. This study thus provides a quantitative, empirical validation of the central-field assumption for molecular scattering in weakly anisotropic systems.

^{a)}This work was supported in part by a Contract (EY-76-S-03-767) from the Department of Energy. Report Code: CALT-767P4-174.

^{b)}Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

^{c)}Contribution No. 5776.

I. INTRODUCTION

Van der Waals interaction potentials, which are responsible for a wide variety of gas-phase, ^{1,2} as well as condensed-phase properties, ^{2,3} have been rather well characterized for rare gas atom-atom pairwise interactions. These potentials, determined by a combination of experimental⁴ and theoretical⁵ techniques, may now be used to correlate experimental data of many different kinds.⁶⁻⁸ This success in determining such a detailed microscopic property as the weak van der Waals interatomic potential has been due to a concerted and sustained effort to obtain such information over the past several years.

Many of the techniques so successfully applied to the determination of atom-atom potentials have also been directed towards atom-molecule and molecule-molecule systems.⁹ Because of the additional degrees of freedom, it may be possible to gain more information from studies of van der Waals interactions in molecular systems than in atomic ones: the potentials depend not only on the intermolecular separation, but also on the molecular orientation and intramolecular configuration.^{10,11} Very often however, the internal structure of the molecular partner(s) is neglected; a central-field analysis is then used to determine what is hoped to be the spherically symmetric component of the full (anisotropic) potential.⁹ This central-field analysis has until recently^{10,11} been necessitated by the complexities inherent in analyzing anisotropic interactions. The validity of the central-field analyses are thus predicated upon a combination of orientational averaging of the potentials, which would result in "effective" spherically

symmetric potentials, and upon negligibly small anisotropies in the intermolecular potentials of the systems considered.

Anisotropic effects for molecular scattering have been investigated both experimentally and theoretically. Quenching of the oscillatory structure both for semiclassical and quantal systems has been predicted,^{12,13} and has been verified experimentally.^{11,14} However, with most systems studied to date, the observed effects have been rather small.¹⁴ In such cases, the lack of strong quenching has been taken as indicative of small anisotropies, and the central-field analysis has been applied, usually without any further justification.⁹ Recently however, it has become clear that anisotropic effects for the scattering of atoms by highly non-spherical molecules yield central-field potentials which are quite different from the spherically symmetric components of the actual anisotropic potentials.¹¹ Consequently, the validity of central-field analyses of scattering in less highly anisotropic systems must be verified quantitatively. Phrasing the problem somewhat differently, we need to know just how nearly isotropic the system must be in order to validate the central-field analysis. It is only when the central field analysis is incapable of fitting the data that information about the anisotropy of the potential can be deduced from measurements that do not distinguish between elastic and concurrent inelastic processes.

In the present paper, we analyze experimental measurements of the differential cross sections (DCS) for the highly quantum systems He + N₂, O₂, CO, and NO, obtained using room-temperature crossed beams.

These systems were chosen as representative of non-hydride molecules which should be weakly anisotropic. This is expected on the basis that the diatomic bond lengths are significantly smaller (by a factor of ~ 2.5) than the smallest intermolecular separations to which the present DCS data are sensitive. In Sec. II, we briefly describe the apparatus used to measure the DCS's, and the data reduction procedures used to interpret them. The DCS measurements, and the central-field and anisotropic intermolecular potentials extracted from them, are presented in Sec. III. In Sec. IV, we discuss the appropriateness of the central-field analysis for these systems and compare our potentials to those obtained from other experiments. Systematic trends in the potentials for the four systems studied herein are also discussed. Finally, we summarize our findings in Sec. V.

II. EXPERIMENTAL AND DATA REDUCTION

The crossed molecular beam apparatus used in this study has been described previously,^{8,15} and is discussed below only very succinctly. The modulated He primary beam is formed in a supersonic expansion, and is angularly well collimated in two stages of differential pumping. Secondary beams of the various gases studied emerge from a glass capillary array, directly into the scattering chamber, and are intense but only slightly supersonic. The secondary beam source may be tilted upwards, thus uncrossing the beams, to allow measurements of the modulated primary beam scattered by background gas. Beam operating characteristics are summarized in Table I. Due to the slightly supersonic nature of the secondary beam, its internal temperature (particularly its rotational temperature) may not be the ambient one (298 K). We note that its velocity distribution is best described by a Mach number of 1.5 (Table I) as well as an effective specific heat ratio of 1.64,¹⁶ the latter indicating only a very slight cooling of internal states.

A quadrupole mass spectrometer detector having an electron bombardment ion source may be positioned at a variable angle in, or out of, the plane of the beams. These experiments were performed with out-of-plane detection (fixing the in-plane angle at 0°) of scattered He atoms. This selection of scattering geometry increases the laboratory angular spacings between the observed diffraction oscillations, enabling a better characterization.¹⁷ In addition, experiments with He + Ar using this geometry yielded potentials whose

fits to the DCS were of consistently higher quality than were those of the in-plane detection geometry.⁸ Ion detection and signal processing in these experiments utilized a 14-stage Cu-Be dynode electron multiplier, followed by several stages of analogue preamplification, and a lock-in amplifier whose reference signal input was synchronized with the primary beam chopper. The output signal was digitized for sampling and averaging by a laboratory minicomputer, which also performed background signal subtraction by uncrossing the beams and remeasuring the modulated signal.

Differential pumping in the mass spectrometer is provided by a small (5 l/sec) ion pump in the detector's entrance buffer chamber, followed by a larger (25 l/sec) ion pump in the ionizer region. The latter is supplemented during experiments by a liquid helium cryopump (400 l/sec). In a very clean environment, such as provided by baking out the detector at $\sim 200^{\circ}\text{C}$ for ~ 20 hours, the electropolished stainless steel surface of the liquid helium dewar provides an effective pump for all gases, including Ne, H₂, and even He!⁸ The pressure in the ion source region was about 5×10^{10} Torr during the course of these experiments.

Maintaining the scattering chamber pressure below 3×10^{-6} torr, and keeping the primary beam attenuation due to scattering by the secondary beam at $\sim 5\%$, ensures that the single-collision conditions essential for DCS measurements prevail. The slight cryopumping of NO on liquid-nitrogen cooled surfaces in the scattering chamber allowed use of a somewhat higher secondary beam pressure for this gas which, however, increased this beam's angular divergence slightly

(see Table I). Periodic mass spectrometric checks of the secondary beams revealed their high purity for all the scattering experiments, with no discernible dimerization.

Scattered primary beam signals were measured between $\sim 2.7^\circ$ and $\sim 16.5^\circ$ above the plane of the beams, at a relative collision energy of ~ 64 meV (the exact values depend on the identity of the secondary beam gas). Measurements were also made for out-of-plane scattering below the plane of the beams, in order to locate accurately the zero position of the angular scattering scale (to within 0.03°).⁸ Long-term drifts in beam intensities and detection efficiency were compensated for by periodic measurements of the scattering signal at a reference angle near 5° . The experimental DCS's are shown in Fig. 1 for He + N₂, He + O₂, He + CO and He + NO.¹⁸ Data points represent the average of two or three independent angular scans performed in several days' experimentation for each scattering pair; total integration times at each angle ranged from ~ 2 min near 3° , to ~ 30 min at the widest angles. Signal-to-noise ratios over the same angular range were between about 40 and 6, respectively.

The data reduction procedure used to obtain the fits shown in Fig. 1 has been described previously.⁸ Using Marquardt's weighted least-squares prescription,¹⁹ we fit the parameters of mathematical functions chosen to represent the intermolecular potential, as discussed in Sec. III. DCS's in the center-of-mass coordinate frame are calculated from partial wave phase shifts of high accuracy, and are averaged extensively over the angular and velocity spreads of both beams at the time the transformation to the out-of-plane laboratory

coordinate frame is performed. The overall apparatus velocity resolution is $\sim 12\%$ FWHM for the systems studied here. Additional angular averaging is also used to account for the overall apparatus angular resolution, of 1.9° FWHM.⁸

The functional to be minimized in the least-squares fits is given by

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2 . \quad (1)$$

Following Paper II, we define a goodness-of-fit statistical index more suitable than χ^2 for describing the quality of the fits to the DCS,

$$\frac{\Delta\alpha_{0.95}}{\alpha} = \frac{1}{\alpha} \cdot t_{0.05}(n-k) \left[\frac{\chi^2}{(n-k) \cdot \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}} . \quad (2)$$

In these equations, I_i and σ_i are the measured (arbitrarily normalized) and calculated (absolute) cross sections¹⁸ at each of n scattering angles, respectively, with the normalized weights g_i . For n data points and k parameters, $t_{0.05}(n-k)$ is the appropriate Student t -distribution statistic for a 95% confidence level of the scaling factor α .²⁰ Note that the $\Delta\alpha_{0.95}/\alpha$ statistical index is independent of the arbitrary normalization used in the experiment, and furthermore is statistically adjusted for the number of data points. This should allow a more straightforward comparison between the results from different laboratories.

III. DATA ANALYSIS AND INTERMOLECULAR POTENTIALS

The experimental DCS's obtained as described in Sec. II and displayed in Fig. 1 were fitted by weighted least-squares optimization of the parameters of the intermolecular potentials described below. These potentials are written in the reduced form

$$f(\rho) = \frac{V(r)}{\epsilon}, \quad \rho = \frac{r}{r_m}, \quad (3)$$

where r_m is the radius of the attractive minimum and ϵ is its depth. The zero of the potential, occurring at $r = \sigma$, is related to r_m and the potential shape $f(\rho)$, and is not an independent parameter.

The mathematical shape functions $f(\rho)$ used in the present study include the familiar LJ12-6 potential form,² in order to allow a comparison with results from measurements of integral scattering cross sections.^{21,22} More flexible potential shape functions are however, required to accurately describe the weak van der Waals interactions analyzed here.^{8,23,24} One such potential function²³ is the Morse-spline-van der Waals (MSV) parameterization,²⁵ given by

$$\left. \begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } \rho < \rho_1 \\ f(\rho) &= (\rho_2 - \rho)[s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1)[s_2(\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= -\sum_{i=1}^3 t_{2i+4} \rho^{-(2i+4)} && \text{for } \rho > \rho_2. \end{aligned} \right\} \quad (4)$$

The cubic spline coefficients s_i ($i = 1$ through 4) are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 , with the first one being chosen as the inflection point of the Morse function,²³ $\rho_1 = 1 + \beta^{-1} \ln 2$. The second spline point is fixed at $\rho_2 = 1.6$.⁸

It has recently been shown that room-temperature DCS measurements of the type considered here enable up to five independent potential parameters to be determined, providing that the parameterization in which they are used has the appropriate flexibility.²³ In particular, the MSV form of Eq. (4) necessarily couples the weakly repulsive wall region of the potential with the attractive minimum, since the Morse β parameter is used to describe both these regions simultaneously.

The present room-temperature data, in addition to being sensitive to the attractive well region of the potential, are also somewhat sensitive to the weakly repulsive wall (down to $\rho \simeq 0.8$) and to the long-range attraction (up to $\rho \simeq 1.7$), and the coupling between these two regions inherent in the MSV form tends to yield attractive minima which are systematically too deep.^{8, 23}

Consequently, we also analyzed the data using a modified MSV potential, which has a second Morse function joined to the first at $r = \sigma$.²⁶ This M^2SV form uses the β' parameter to describe the potential for $r < \sigma$, but is otherwise identical to the MSV potential of Eq. (4). Another parameterization that successfully decouples the attractive minimum region from adjacent regions of the potential is the third-order Simons-Parr-Finlan Dunham (SPFD) potential,²⁷ given by

$$\left. \begin{aligned} f(\rho) &= b_0 \lambda^2 \left(1 + \sum_{i=1}^3 b_i \lambda^i \right) - 1 && \text{for } \lambda = 1 - \frac{1}{\rho} \text{ and } \rho < \rho_f \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho \geq \rho_f . \end{aligned} \right\} (5)$$

The two highest-order coefficients of the SPFD expansion (b_2 and b_3) are fixed by smoothness conditions²⁸ at $\rho_f = 1.6$.⁸

For reduced distances below $\rho = 0.65$ (to which our DCS data are not sensitive²³), the SPFD potential often shows spurious maxima or oscillations. For numerical convenience in the phase shift calculation, these irregularities are removed by using a Born-Mayer exponentially repulsive wall, i.e., $f(\rho) = A e^{-b\rho}$, from some joining point ρ_i downwards. A and b are fixed by smoothness conditions at $\rho = \rho_i$; trial calculations show that values of $\rho_i < 0.75$ have no effect on the scattering results, and we usually use $\rho_i = 0.70$.²³

Although nonreduced C_6 dispersion constants (not to be confused with their reduced counterparts c_6 , where $C_6 = \epsilon r_m^6 \cdot c_6$) have been calculated for all four systems considered here,²⁹⁻³¹ we felt it best to fit this region of the potential, for reasons discussed below. Thus, by fixing $c_8 = c_{10} = 0$ in Eqs. (4) and (5), we obtain "effective" dispersion constants, termed C'_6 for each interaction pair. These are expected to be somewhat greater than the corresponding actual C_6 constants, because of our neglect of higher-order dispersion terms, which have not yet been calculated. The c_6 parameter obtained bears significance only in

describing the scattering data, and in describing the region of the potential to which these data are sensitive. This region probably does not extend as far as the 6.5 Å upper limit attained for the He-Ar potentials of Paper II, because the present experiments include low-angle scattering data down to $\sim 2.7^\circ$, instead of 1.9° .⁸ As a further consequence, our accuracy is probably less than 20% in the "attractive tail" region beyond $\sim 5\text{Å}$.²³ For these reasons, the C_6 parameter is optimized in these fits instead of being held fixed at its theoretical value. The MSV potential thus has four adjustable parameters (r_m , ϵ , β , and c_6), while the M^2SV and SPFD potentials each have five (r_m , ϵ , β , β' , and c_6 ; r_m , ϵ , b_0 , b_1 , and c_6 , respectively).

A prerequisite for Eq. (3), together with the reduced potential forms of Eqs. (4) and (5), to provide an accurate description of the intermolecular interactions of the systems studied here, is that anisotropic contributions to the potential must be small over the intermolecular distance range to which the DCS data are sensitive ($2.8\text{Å} \lesssim r \lesssim 6\text{Å}$).²³ It is only in such a case that the potential is independent of the molecular orientation. Although this central-field assumption may not be made a priori for the analysis of atom-molecule scattering experiments, we nevertheless base a "first-order" extraction of intermolecular potentials on it.

A possible procedure for more appropriately modeling the systems studied here is to incorporate anisotropic contributions to the intermolecular potentials in the r_m and ϵ parameters of Eq. (3), using an elliptical modification to central-field types of potentials:¹¹

$$\left. \begin{aligned} V(r, \gamma) &= \epsilon(\gamma) \cdot f[\rho(r, \gamma)], \quad \text{where } \rho(r, \gamma) = \frac{r}{r_m(\gamma)}, \text{ and} \\ r_m(\gamma) &= r_{m\perp} \cdot \left(\frac{1 + r_q \sin^2 \gamma}{1 + r_q} \right)^{\frac{1}{2}}; \quad \epsilon(\gamma) = \epsilon_0 + \epsilon_2 P_2(\cos \gamma). \end{aligned} \right\} \quad (6)$$

In this expression r is the length of the position vector $\underline{r}$ of the He atom with respect to the molecular center-of-mass, and γ is the angle between $\underline{r}$ and the molecular axis. For arbitrary γ , $r_m(\gamma)$ is the value of r at the potential minimum, and $-\epsilon(\gamma)$ is the corresponding potential energy. The parameters r_q and ϵ_2 are measures of the anisotropy of the intermolecular potential. Any central-field reduced potential energy function $f(\rho)$ may be used, since Eq. (6) introduces anisotropy into the potential through the elliptically shaped $r_m(\gamma)$ and the Legendre polynomial representation for $\epsilon(\gamma)$. Scattering calculations for the anisotropic potential model of Eq. (6) are performed using the infinite-order sudden approximation,^{13a} as discussed in Sec. IV. Because the MSV potential form for $f(\rho)$ is known to provide a reasonably good representation for spherically symmetric interactions without requiring too many adjustable parameters,²³ we use this form in Eq. (6) for the present anisotropic potential fits.

Since the central-field MSV potential already has four adjustable parameters, we may adjust only one of the anisotropy parameters of Eq. (6) to the data.²³ We choose to fix the ϵ_2/ϵ_0 ratio (see Sec. IV.A),

while adjusting r_q because of its greater influence on the rapid quantum oscillatory structure of the DCS.^{13b} The five adjustable parameters of the anisotropic potential model of Eqs. (4) and (6) are thus $r_{m\perp}$, ϵ_0 , r_q , β , and c_6 . Unfortunately, the $D_{\infty h}$ symmetry of our "cigar-shaped" model potential of Eq. (6) is inappropriate for the He-CO and He-NO interactions. A "pear-shaped" model having the appropriate $C_{\infty v}$ symmetry would, however, require at least one additional parameter. This further refinement should have a rather small effect; we note for example that the dipole moments of CO and NO are -0.112 D^{32} and $\pm 0.158 \text{ D}$,³³ respectively (the sign has not yet been determined for NO). These dipole moments are too small to produce the large distortions in the overall electronic cloud distribution that presumably would necessitate a model with $C_{\infty v}$ symmetry. By comparing the goodness-of-fit [to the DCS data, as measured by the $\Delta\alpha_{0.95}/\alpha$ statistical index of Eq. (2)] of the anisotropic potential with those of the central-field M^2SV and SPFD potentials, all of which have five adjustable parameters, it may be possible to gauge the appropriateness of the model potential of Eq. (6).

Potential parameters for the He + N₂, O₂, CO, and NO van der Waals interactions are given in Table II for the fits to the central-field MSV, M^2SV , and SPFD potentials of Eqs. (4) and (5). The $\Delta\alpha_{0.95}/\alpha$ goodness of fit index [Eq. (2)] displayed in this table statistically accounts for the number of fitted parameters.^{8,20} It may immediately be seen that the five-parameter M^2SV and SPFD potentials are better

able to fit the DCS data than is the MSV model. Although the size parameters r_m and σ are seen to be largely model-independent ($\pm 0.04 \text{ \AA}$ for r_m and $\pm 0.01 \text{ \AA}$ for σ), the MSV potentials give attractive minima consistently deeper than those of the M^2SV or SPFD potentials, by $\sim 15\%$. The latter two potentials' ϵ values are however, within 5% of one another for each interaction pair. Under conditions of validity of the central-field assumption, the M^2SV and SPFD parameterizations yield potentials which are accurate, when fitted to room-temperature DCS data for the present highly quantum systems, to about $\pm 10\%$ in the van der Waals attractive minimum region.²³ The DCS data are fitted about equally well by either the M^2SV or SPFD potentials, with the quality-of-fit being quite good except possibly for the He+NO system. We also display in Table II the integral cross sections Q at a relative collision energy of 64 meV, calculated for each system studied using the partial wave expansion. Because of the consistently greater well depths of the MSV potential, their Q are almost 10% larger than those of the corresponding M^2SV or SPFD potentials.

In Table III we list the parameters obtained by fitting the anisotropic MSV potential model of Eqs. (4) and (6) to the DCS data. In the last three columns of this table, we also list the position and depth parameters for the spherical averages of these anisotropic potentials; we note that these are in quite close agreement with the corresponding parameters of the central-field M^2SV and SPFD potentials as listed in Table II. In Figs. 2-5 we plot these three spherically symmetric potentials for the He + N₂, O₂, CO and NO systems, respectively. For each of the four systems studied, the central-field potentials are seen to be substantially the same as the spherical average of the anisotropic potentials (see also the following discussion).

IV. DISCUSSION

A. Central-field and anisotropic potential analysis

The van der Waals interactions for the atom-molecule systems considered here are anisotropic. As such, the central-field potentials generically represented by Eq. (3) provide at best an approximate description of these interactions. Consequently, the first problem to be addressed is the validity of the central-field assumption. In the discussion that follows, we shall present a quantitative assessment of this assumption.

Even if the central-field assumption were invalid within the range of intermolecular distances sampled, Eq. (3) could still be expected to provide an "effective" description of processes which occur on a time scale much slower than molecular rotations, since any such process would sample only the spherical average of the anisotropic potential. Such processes do not, however, include the present scattering experiment. For a thermal rigid rotor at 300 K, representative of the secondary beams used in the present studies (Sec. II), a typical rotation frequency is $\sim 10^{12}$ Hz (for N_2). Under our experimental conditions, the collision interaction time (to traverse $\sim 8 \text{ \AA}$) is $\sim 5 \times 10^{-13}$ sec, permitting the molecule only about half a revolution during the collision.

Interpretations of scattering results for anisotropic interactions have been based for some time on semiclassical calculations.¹² These showed that the effect of anisotropic potential scattering on integral elastic cross sections is primarily to dampen, or quench, the glory undulations.³⁴ Similar results were obtained for the supernumary rainbow and rapid quantum oscillatory structure of elastic DCS's.³⁴

On this basis, "total" (elastic plus inelastic) DCS's not exhibiting the quenching effect relative to corresponding DCS's from spherically symmetric potentials have usually been interpreted as sensitive only to the spherical average of the intermolecular potential.⁹ Such a straightforward application of the semiclassical theory for DCS's is however, inappropriate for the highly quantum systems under discussion here. As an example of the differences between semiclassical and quantum scattering, we note that the present DCS's exhibit strong undulations well beyond the classical rainbow angle (at $\sim 4^\circ$ for these systems); semiclassical oscillations should not appear on the dark (wide-angle) side of the rainbow,^{9c,34} unless the effect of complex trajectories is included.³⁵

More recently, quantum mechanical calculations have been performed for scattering from anisotropic potentials. These calculations are extremely involved, and are expensive to perform exactly by close-coupling techniques;³⁶ "routine" calculations more wieldy for data reduction require the use of various approximation schemes.³⁷ One of the most successful of these is the infinite-order sudden approximation (IOSA),^{13a} which should be accurate when the collision energy is substantially greater than the rotational spacings of the molecular partner.^{13b} This condition is satisfied in the present case: the most probable rotational levels at 298 K are separated by ~ 3 meV, whereas the collision energy is ~ 64 meV (Sec. II). Computationally, the IOSA involves taking cuts along the potential energy surface for various angles γ between the molecular axis and the position vector of the approaching He atom with respect to the diatom center of mass.

The resulting potentials depend only parametrically on γ , allowing central-field scattering calculations to be performed at each such γ . The DCS's obtained in this manner are then simply spherically averaged^{13a} by an 8-point Gauss-Legendre quadrature to yield the IOSA scattering pattern resulting from the assumed anisotropic potential. Although this procedure appears to be tantamount to assuming that the angle γ remains fixed during the collision (which would be incorrect, as mentioned at the beginning of this section), it has been shown that the IOSA formulation need assume only that the rotational energy level spacing, and the differences in centrifugal potentials for adjacent orbital angular momentum channels, are small.^{13a} We note that the IOSA DCS's calculated in the above fashion are degeneracy-averaged over initial, and summed over final, rotational states. This is also true of our experimental measurements, which were performed with a nearly thermal distribution of internal rotational states (Sec. II), and without detection of rotational inelasticities. We may therefore directly compare the IOSA DCS's with the experimental measurements, after suitable coordinate transformations and instrumental averaging effects are included in the calculations (Sec. II).

In fitting the anisotropic MSV potential model of Eqs. (4) and (6) to the DCS data, it was necessary to keep the number of adjustable parameters limited to five.²³ Consequently, we fix the ϵ_2/ϵ_0 ratio, but fit the r_q anisotropy parameter of Eq. (6). We predicate this choice on the demonstrated sensitivity of the rapid quantum oscillatory structure on the attractive well position anisotropy, and on its relative

lack of sensitivity to the well depth anisotropy.^{13b} A suitable estimate for the well depth anisotropy was taken as $\epsilon_2/\epsilon_0 = -0.2$, mimicking the behavior of an electron-gas calculation for the He+CO potential with angles $\gamma = 0$ or π and $\gamma = \pi/2$.^{36b} Note that $\epsilon_2/\epsilon_0 < 0$ implies that the absolute minimum of the van der Waals potential energy surface is along $\gamma = \pi/2$. The resulting fitted potentials, whose parameters are given in Table III, are seen to be only weakly anisotropic. For example, for the He + NO system, which exhibits the largest absolute value of the anisotropy parameter r_q , the ratio of r_m at $\gamma = 0$ to that at $\gamma = \pi/2$ is only 1.2. Referring to the $\Delta\alpha_{0.95}/\alpha$ columns of Tables II and III, we see that for the He+N₂ system, the anisotropic model does not fit the data any better than do the central-field models having the same number of parameters (M²SV and SPFD potentials of Table II). The r_q parameters obtained from the fits to the He+O₂ and He+CO DCS data indicate that radial anisotropies for these systems are more pronounced than for He+N₂. Despite this, the DCS data are not fit strikingly better by the anisotropic potential model than by the central-field one. In contrast to these three systems, the anisotropic potential fit to the He+NO DCS does yield a substantial improvement over any of the central-field fits. In addition, we note that the r_q radial anisotropy parameter is more substantial for He+NO than for any of the other systems considered in these studies (Table III). Because of the ²Π electronic symmetry of the NO molecule, He+NO collisions at thermal energies involve two potential energy surfaces.³⁰ However, since these experiments were performed using randomly oriented NO molecules, these closely-related³⁸ potentials may be averaged, yielding a single effective potential having axial symmetry.

We note that, for all four of these systems, the r_q parameter is negative, implying that the major axis of the fitted elliptical potential is parallel to the molecular axis, as would be expected.

We must regard with some caution however, the relative sizes of the r_q anisotropy parameters presented in Table III.³⁹ From the He+N₂ fit, it is apparent that the present DCS data can be accurately described, and well fit, by a central-field potential when the r_q parameter is smaller in magnitude than ~ 0.15 . In addition, quenching of the oscillatory structure or other obvious manifestations of anisotropy are not present in our DCS data. Indeed, the experimental DCS's presented in Fig. 1 are quite similar in overall appearance to the He+Ar DCS of Paper II.⁸ This is shown in Fig. 6, which displays the latter DCS (also for scattering at a relative collision energy of 64 meV), for a similar range of scattering angles as used in this study, as well as the present He+NO DCS. Both these DCS's, as well as the He+N₂, O₂, and CO DCS's (Fig. 1), exhibit a vestige of rainbow scattering at $\sim 4^\circ$, and all show the highly oscillatory structure at the wider angles that is characteristic of systems with relatively long de Broglie wavelengths and shallow attractive wells.^{7-9,24} In addition, the present scattering results may be fitted reasonably well with potential models that are spherically symmetric (Table II). This is so despite the fact that some of the experimental DCS's, and those calculated from the anisotropic potentials [Eq. (6) and Table III], show a slight loss of undulatory amplitude as compared to the best-fit (central-field) calculations (Fig. 1). The potential parameters for the molecular partners are all quite similar to those of the He+Ar pair (Paper II). This is quite reasonable, based on the empirical observation

that the well depth value ϵ depends primarily on the polarizability of the least polarizable partner,²⁴ which in all these cases is He.

The above similarities between the present slightly anisotropic potentials and the central-field He+Ar one suggest that the DCS's presented in this paper may be interpreted with a fair degree of confidence as due primarily to central-field scattering. Similar arguments have been used in the past to justify the central-field potentials obtained from the analysis of scattering for anisotropic interactions.^{9, 14} However, as has recently been suggested theoretically^{13a} and confirmed experimentally,¹¹ this justification is invalid for highly anisotropic interactions such as He+CO₂. More quantitative evidence is therefore required to justify the central-field potentials' validity for the somewhat less anisotropic systems considered herein and elsewhere.⁹ Evidence of this kind is provided by comparing the spherical averages of the anisotropic potentials with the central-field potentials, as extracted from the present DCS data (Tables II and III, and Figs. 2-5). We see that the central-field potentials are apparently indistinguishable from the spherical average of the anisotropic potentials. Thus, for the present systems, which are only slightly anisotropic and which show little evidence for quenching of the rapid quantum oscillatory structure in the DCS (Fig. 6), the central-field analysis may be used to obtain intermolecular potentials which closely approximate the spherical averages of the actual anisotropic interactions.

B. Comparisons with other potentials

We now compare the present spherically symmetric potentials with earlier proposed ones. We do not, however, consider results from bulk property measurements (e.g., virial coefficients, viscosity data, etc.). This is because the bulk properties of highly quantum systems are usually sensitive only to a part of the repulsive wall to which the DCS data are insensitive.⁸ All four of the systems studied here have been investigated by measuring arbitrarily-normalized integral scattering cross sections Q as a function of the relative collision velocity v ;²¹ absolute $Q(v)$ measurements have also been reported for He-O₂.²² The arbitrarily-normalized $Q(v)$ provide data sensitive to the "area" of the attractive well, which is usually expressed as the product $\epsilon \cdot r_m$,^{1b} and is dependent upon the model chosen to describe the interaction. The $\epsilon \cdot r_m$ products for a LJ12-6 model are presented for the $Q(v)$ results in Table IV. To provide an indication of the consistency of our DCS measurements with these results, both of which are sensitive to the attractive well region, we fitted the LJ12-6 model to our scattering data (Sec. III). We list the corresponding $\epsilon \cdot r_m$ products in the same table, where we see that the DCS values are in reasonable agreement with the parameters obtained from the $Q(v)$ results. We note however, that these values are no more reliable than is the rather crude LJ12-6 model, and are presented here only as a rough estimate of the compatibility of the $Q(v)$ and DCS results.⁸ More reliable values for the $\epsilon \cdot r_m$ products may be obtained from the more accurate five-parameter potentials, and are presented in Table IV.

Also in Table IV, we compare our fitted "effective" C'_6 dispersion coefficients (Sec. III) with those obtained theoretically. The experimentally determined coefficients for He + O₂, CO, and NO are seen to be $\sim 20\%$ higher than the corresponding calculated ones.²⁹⁻³¹ This is expected from our neglect of dispersion interaction contributions of higher order than C_6 (Sec. III). However, the discrepancy for He+N₂ is almost a factor of two,³¹ with our experimental value appearing to be anomalously high with respect to the other experimental values. This difference may be related to our lack of very low angle measurements. We therefore place less confidence in our He + N₂ long-range potential than in our long-range potentials for He + O₂, CO, and NO. We also compare the present He + CO potential to that calculated from the electron-gas formulation.^{36b} The latter's spherically symmetric component has $r_m = 3.30 \text{ \AA}$, $\sigma = 2.98 \text{ \AA}$, and $\epsilon = 2.8 \text{ meV}$. The theoretical distance parameters appear to be too small by $\sim 0.4 \text{ \AA}$, while the well is too deep by perhaps $\sim 25\%$. This is not too surprising, since it is known that the electron-gas method does not yield very good results for attractive interactions of He-containing systems.^{5c,d} This may also be responsible for the observation that the theoretical anisotropies^{36b} for the well region of the He+CO potential appear to be somewhat larger than indicated by the r_q parameter obtained from the present analysis of DCS scattering results.

Finally, we compare in Fig. 7 the spherically averaged anisotropic potentials of the four scattering systems described in the present

paper. As is already evident from Tables II and III, and is more graphically seen in the figure, the He+O₂ potential's attractive minimum occurs at a significantly shorter intermolecular separation than do those of He + N₂, CO, and NO; the attractive minimum is also somewhat deeper for He + O₂. We also note that the repulsive walls of the systems studied generally have the same steepness (except for He + NO), but that the intermolecular distance at which they occur (as indicated by the value of σ , for example) appear to be somewhat different. These differences are not correlated with the equilibrium bond lengths of the diatomic molecules (O₂ > NO > CO > N₂). In determining the potentials for these systems, it was hoped that some such simple correlation could be found between the electronic or molecular structures of these molecules and their van der Waals interactions with He atoms. Thus, N₂ and CO were naively expected to yield closely related spherically averaged potentials. Similarly, NO (with one unpaired electron) was expected to show some of the characteristics apparently peculiar to O₂ (with two unpaired electrons), such as those mentioned above. The lack of any such simple correlations is testimony to the complexity of van der Waals interactions in the weakly repulsive and attractive minimum regions; only the long-range potentials are as yet well understood.

SUMMARY AND CONCLUSIONS

By measuring the differential cross sections (DCS) for scattering of a room-temperature hypersonic beam of He by crossed beams of N_2 , O_2 , CO, and NO, we have determined intermolecular potentials describing their van der Waals interactions in the attractive minimum and adjacent regions of the potential.²³ The extraction of these intermolecular potentials were based initially on the central-field assumption, since there was little evidence for quenching of the experimental DCS's, which have been predicted,^{12,13} and observed,^{11,14} for scattering from highly anisotropic potentials.

A more detailed analysis, using a convenient and realistic anisotropic intermolecular potential model, together with the infinite-order sudden approximation,^{13a} was used to show that anisotropy contributions are appreciable only for He+NO, being negligible for He+ N_2 , and small for He+ O_2 and He+CO. The present study provides examples of anisotropic interactions which are too weak to significantly distort the DCS scattering patterns from those expected from central-field interactions. Indeed, the central-field potentials are indistinguishable, within experimental error, from the spherical averages of the present anisotropic potentials. This finding is in strong contrast to scattering results for more highly anisotropic interactions, such as He+CO₂.¹¹ For weakly anisotropic interactions in highly quantum systems, the central-field assumption thus provides a valid framework for the extraction of intermolecular potentials from thermal scattering data lacking discrimination between elastic and inelastic contributions.

Consequently, of course, more detailed experimental information, such as the measurement of inelastic cross sections, will be required for determining anisotropic contributions to the intermolecular potentials for such systems from DCS scattering data.^{40, 41}

ACKNOWLEDGMENTS

We wish to thank Dr. Gregory Parker for many useful discussions concerning the infinite-order sudden approximation, and for much help with its use. We also thank Ambassador College for generous use of its computing facilities.

Table I. Beam operating conditions

Characteristic	Primary beam		Secondary beams		
Beam gas	He		N ₂	O ₂	CO
Inlet pressure/torr	1300		3.8	3.8	3.8
Inlet temperature/K	298		298	298	298
Angular FWHM ^a /deg.	1		4	4	4
Most probable velocity/(km/sec)	1.757		0.599	0.561	0.599
Velocity FWHM, ^a $\Delta v/v$	0.10		0.75	0.75	0.75
Mach number ¹⁶	18		1.5	1.5	1.5

^a Full width at half-maximum.

TABLE II. Central field intermolecular potentials fit to the experimental DCS's.

System ^a	potential type ^b	$r_m/\text{\AA}$	$\sigma/\text{\AA}$	ϵ/meV	shape parameters ^c	$Q^d/\text{\AA}^2$	$\chi^2 e, f$	$\Delta\alpha_{0.95}/\alpha^f$ (%)
He + N ₂ (29)	MSV	3.67	3.24	2.50	$\beta = 5.82; c_e = 2.15$	87	130 (4)	1.74
	M ² SV	3.72	3.24	2.15	$\beta = 5.30; \beta' = 9.09; c_e = 1.88$	82	100 (5)	1.58
	SPFD	3.65	3.22	2.27	$b_0 = 31.9; b_1 = -4.72; c_e = 2.10$	83	110 (5)	1.64
He + O ₂ (31)	MSV	3.44	3.05	3.05	$\beta = 6.03; c_e = 1.95$	83	200 (4)	2.22
	M ² SV	3.49	3.04	2.52	$\beta = 5.35; \beta' = 12.1; c_e = 1.50$	76	160 (5)	2.01
	SPFD	3.40	3.03	2.73	$b_0 = 36.3; b_1 = -5.45; c_e = 1.85$	77	160 (5)	2.02
He + CO (27)	MSV	3.73	3.32	2.43	$\beta = 6.27; c_e = 1.62$	84	190 (4)	1.91
	M ² SV	3.77	3.32	2.09	$\beta = 5.77; \beta' = 10.3; c_e = 1.29$	79	160 (5)	1.78
	SPFD	3.70	3.31	2.28	$b_0 = 39.2; b_1 = -5.10; c_e = 1.52$	81	160 (5)	1.81
He + NO (26)	MSV	3.69	3.18	2.56	$\beta = 5.03; c_e = 1.78$	90	320 (4)	2.55
	M ² SV	3.73	3.17	2.12	$\beta = 4.66; \beta' = 9.33; c_e = 1.15$	79	240 (5)	2.23
	SPFD	3.67	3.16	2.16	$b_0 = 19.1; b_1 = -3.98; c_e = 1.56$	82	250 (5)	2.31

^aExperimental conditions given in Table I; the number of experimental data points is given in parentheses.^bDefined in Eqs. (3-5).^cSymbols have the same meanings as in Eqs. (3-5) of the text. The MSV and M²SV potentials have $\rho_2 = 1.60$; the SPFD potential similarly has $\rho_f = 1.60$. The dispersion constant C'_e is obtained from the fitted reduced dispersion coefficient c_e , where $C'_e = \epsilon r_m^6 c_e$. The prime denotes an "effective" dispersion coefficient, obtained by neglecting higher-order contributions.^dIntegral cross sections at a relative collision energy of 64 meV calculated from the partial wave expansion and the potentials given.^eScattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.^fSee Eqs. (1) and (2).

TABLE III. Intermolecular potential parameters from anisotropic fits to the experimental DCS's.

System ^a	anisotropic potential parameters ^b					χ^2 c, d	$\Delta\alpha_{0.95}/\alpha$ (%)	spherically averaged anisotropic potential parameters		
	$r_{m_1}/\text{\AA}$	r_q	ϵ_0/meV	ϵ_2/meV	β	c_6		$r_m/\text{\AA}$	$\sigma/\text{\AA}$	ϵ/meV
He + N ₂ (29)	3.60	-0.13	2.43	-0.49	5.75	2.24	1.77	3.69	3.25	2.39
He + O ₂ (31)	3.29	-0.24	2.94	-0.59	5.90	2.13	1.92	3.48	3.07	2.76
He + CO (27)	3.58	-0.22	2.35	-0.47	6.25	1.75	1.59	3.76	3.35	2.20
He + NO (26)	3.45	-0.30	2.45	-0.49	4.98	1.98	1.46	3.73	3.21	2.27

^aExperimental conditions given in Table I; the number of experimental data points is given in parentheses.^bPotential form defined by Eqs. (4) and (6); symbols have the same meanings as in these equations. The MSV potential of Eq. (4) has $\rho_2 = 1.60$; the ϵ_2/ϵ_0 ratio is fixed at -0.2 as discussed in Sec. IV.^cScattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.^dSee Eqs. (1) and (2).

TABLE IV. Potential parameters obtained from DCS results, integral cross section measurements and calculated dispersion coefficients.

Potential quantity	system					Method of determination	Ref.
	He + N ₂	He + O ₂	He + CO	He + NO	error		
$\epsilon \cdot r_m / (\text{meV} \cdot \text{\AA})$	8.3	9.1	8.3	8.8	0.6	$Q(v)^a$	21
	-	8.6	-	-	-	$Q(v)^a$	22
	8.8	10.0	8.5	10.4	-	DCS ^a	this work
	8.4	9.2	8.2	8.1	0.4 ^b	DCS ^b	this work
$C_6 / (\text{eV} \cdot \text{\AA}^6)$	-	-	6.7	-	0.8	calculated ^c	29
	-	-	-	5.8	0.5	calculated ^c	30
	6.1	5.6	-	6.0	-	calculated ^c	31
$C'_6 / (\text{eV} \cdot \text{\AA}^6)$	11	7	8	7	$\gtrsim 2$	DCS ^d	this work

^aUsing the LJ12-6 potential.

^bUsing the central-field M³SV and SPFD potentials, as well as the spherically averaged anisotropic MSV potential. Error reflects the discrepancies among the $\epsilon \cdot r_m$ products for these three potential forms.

^cSpherically symmetric contributions to C_6 .

^dUsing the central-field M²SV and SPFD potentials, and neglecting contributions higher than C_6 to the dispersion interaction. The error reflects the $\pm 20\%$ or poorer accuracy with which the "attractive tail" portion of the potential ($r \gtrsim 5 \text{\AA}$) is determined.²³ (Sec. III).

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FIGURE CAPTIONS

Figure 1. Laboratory differential cross sections for out-of-plane scattering of He by N₂, O₂, CO, and NO, with ordinates shifted downwards by one decade for each system in this sequence. Points with error bars are the experimental measurements of the scattering cross sections $^{18} I(\theta) \cdot \sin\theta$ vs. the scattering angle θ at a relative collision energy of 64 meV. Curves are DCS's calculated using potentials extracted from the data. Solid lines: anisotropic MSV potential; dashed lines: central-field SPFD potential; dotted lines: spherical average of the anisotropic MSV potential. The potential models are presented in Eqs. (3-6); their parameters are given in Tables II and III.

Figure 2. Spherically symmetric intermolecular potentials for He+N₂ as a function of intermolecular distance. Solid curve: central-field SPFD potential; dashed curve: central-field M²SV potential; dotted curve: spherical average of the anisotropic MSV potential. The error bars on the SPFD potential represent the accuracy with which it has been determined, $\pm 10\%$ of the potential energy at the attractive minimum, $\pm 0.04\text{\AA}$ in the position of the repulsive wall at ~ 7.5 meV.

Figure 3. Spherically symmetric intermolecular potentials for He+O₂; symbols as in Fig. 2.

Figure 4. Spherically symmetric intermolecular potentials for He+CO; symbols as in Fig. 2.

Figure 5. Spherically symmetric intermolecular potentials for He+NO. Symbols as in Fig. 2.

Figure 6. Laboratory differential cross sections¹⁸ for out-of-plane scattering of He by NO and by Ar; the latter are shifted downwards by one decade for clarity of display. The He+Ar DCS is reproduced from Paper II⁸ for comparison with the He+NO DCS. Points with error bars are as in Fig. 1. The curves are DCS's calculated from the fitted central-field SPFD potentials. Note the overall similarity between the two cross sections, but compare this to the slight dampening of the rapid quantum oscillatory structure in He+NO at $\theta = 7^\circ$, 9° and 12° , relative to the best-fit central-field calculation; the He+Ar DCS shows no analogous effect.

Figure 7. Spherical averages of the anisotropic MSV potential model of Eqs. (4) and (6), as a function of the intermolecular separation. Solid curve: He+N₂; dashed curve: He+O₂; dotted curve: He+CO; dash-dotted curve: He+NO. The error bars on the He+N₂ potential have the same meanings as in Fig. 2.

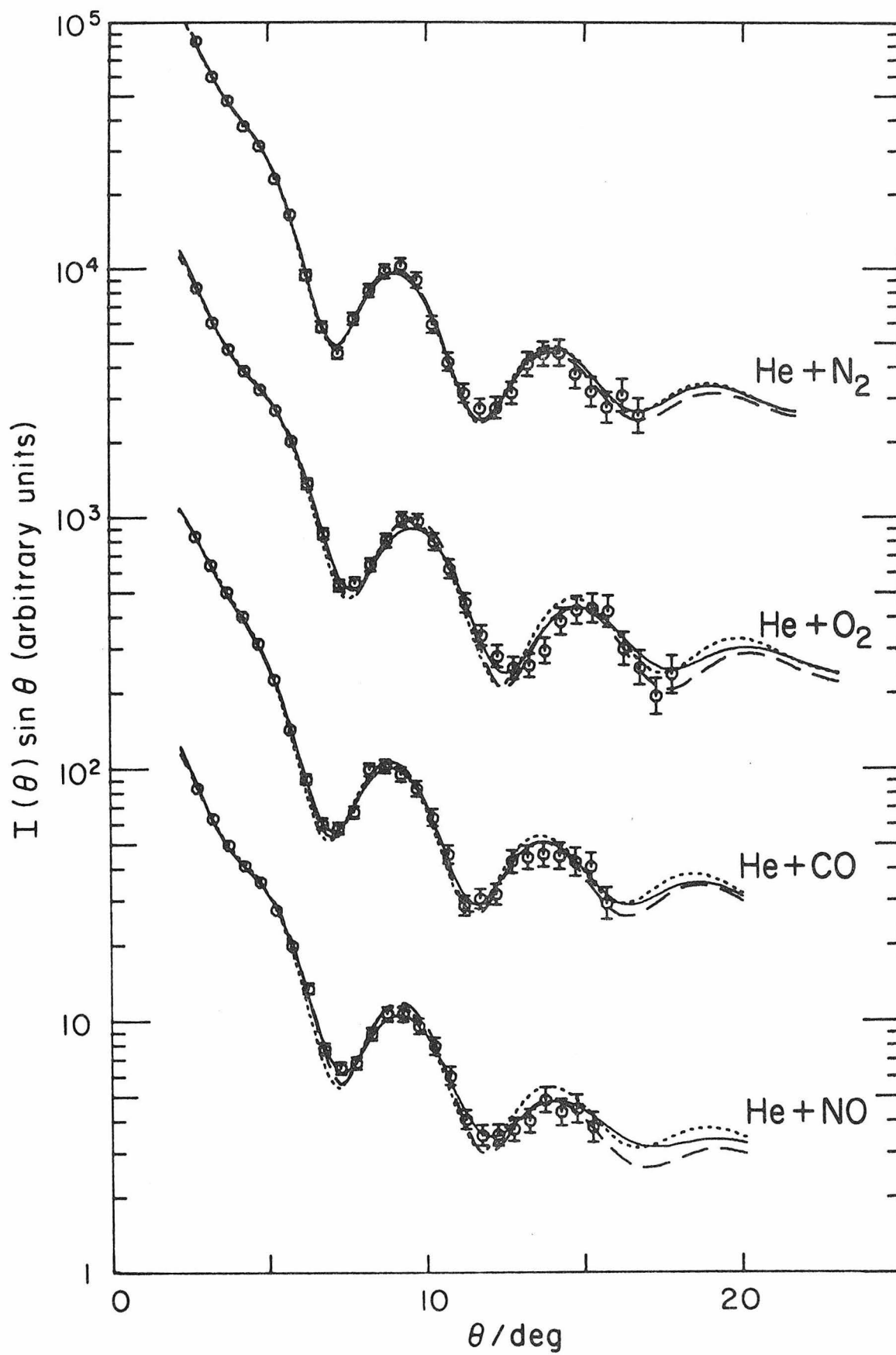


Figure 1

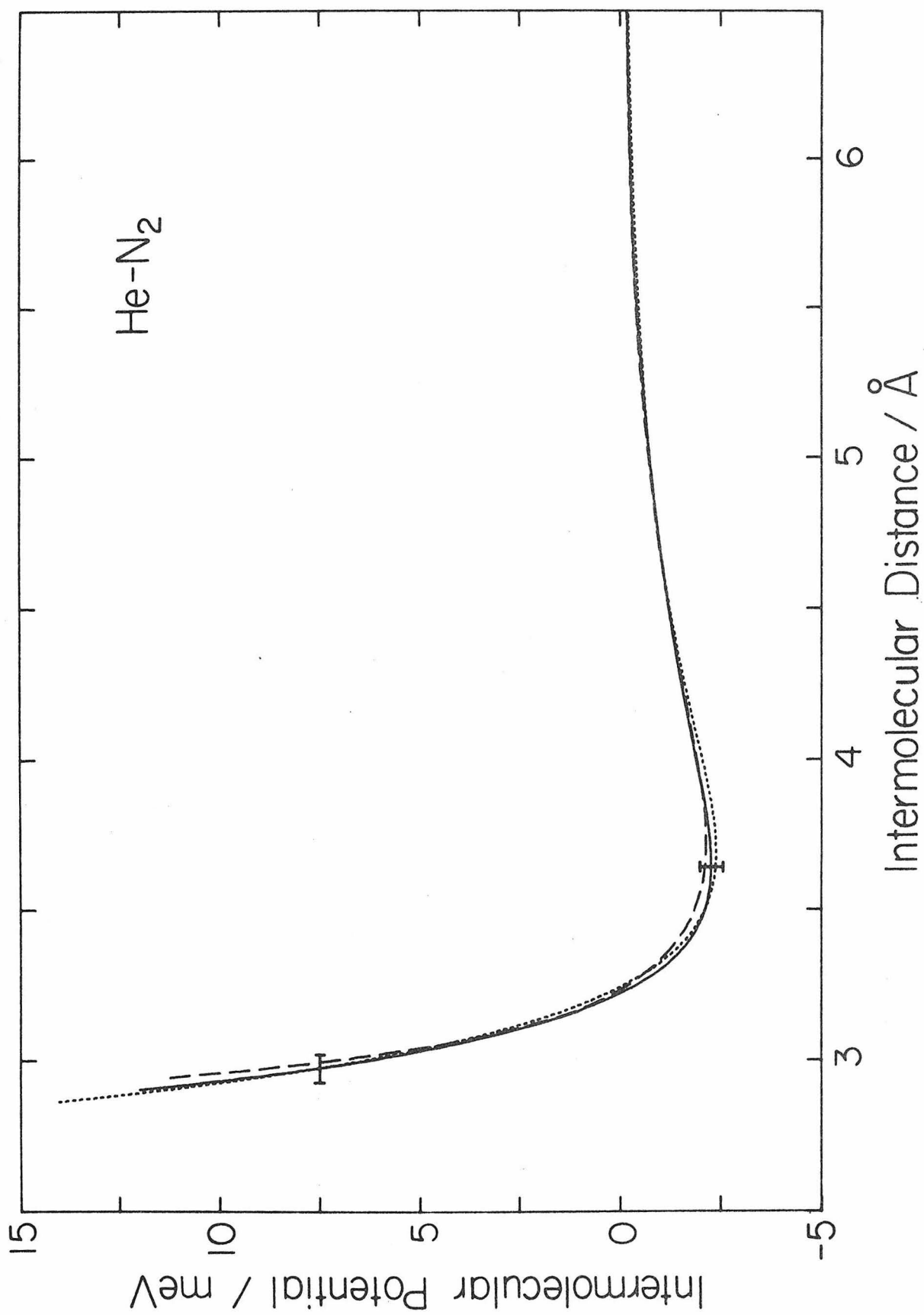


Figure 2

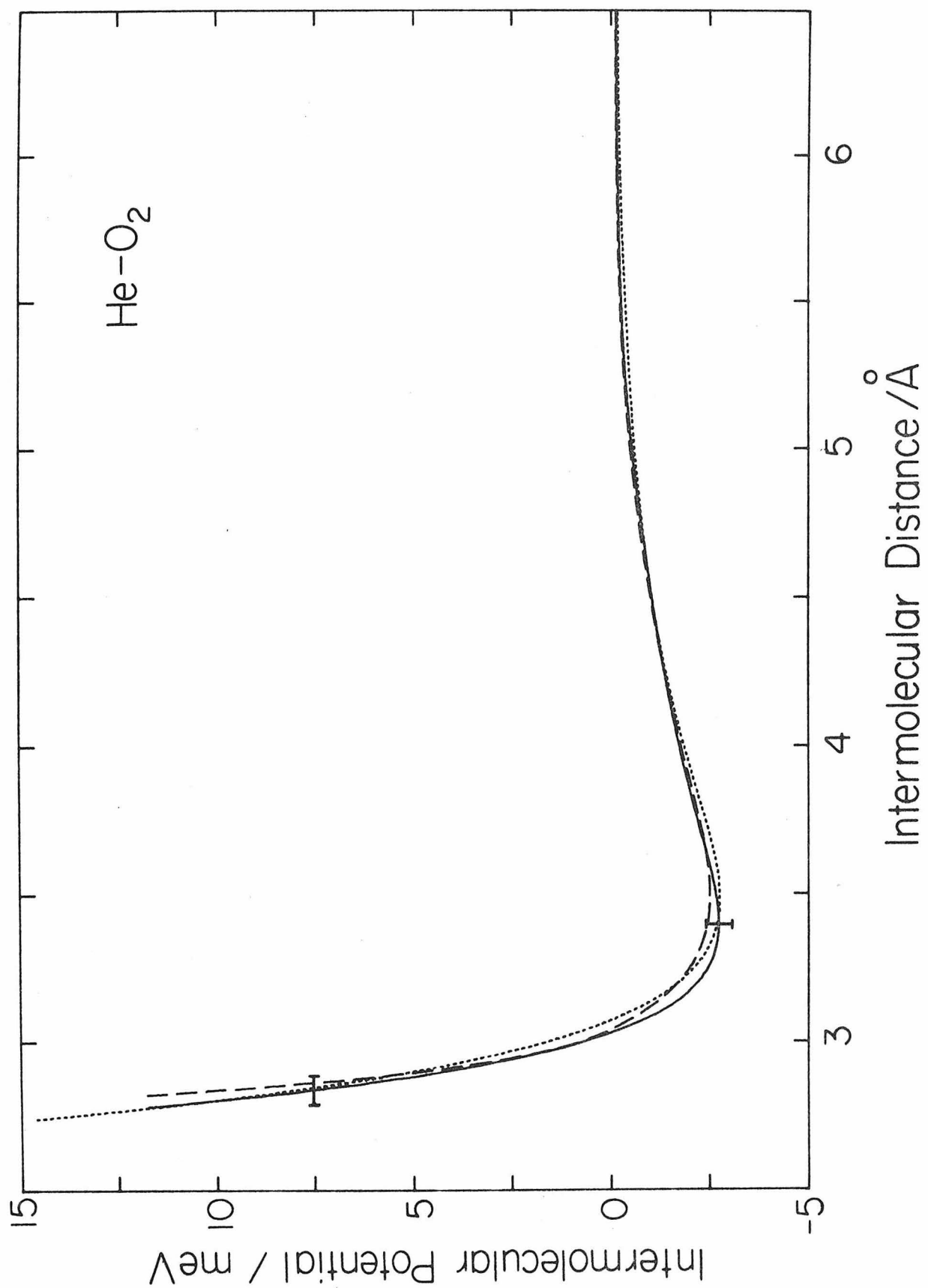


Figure 3

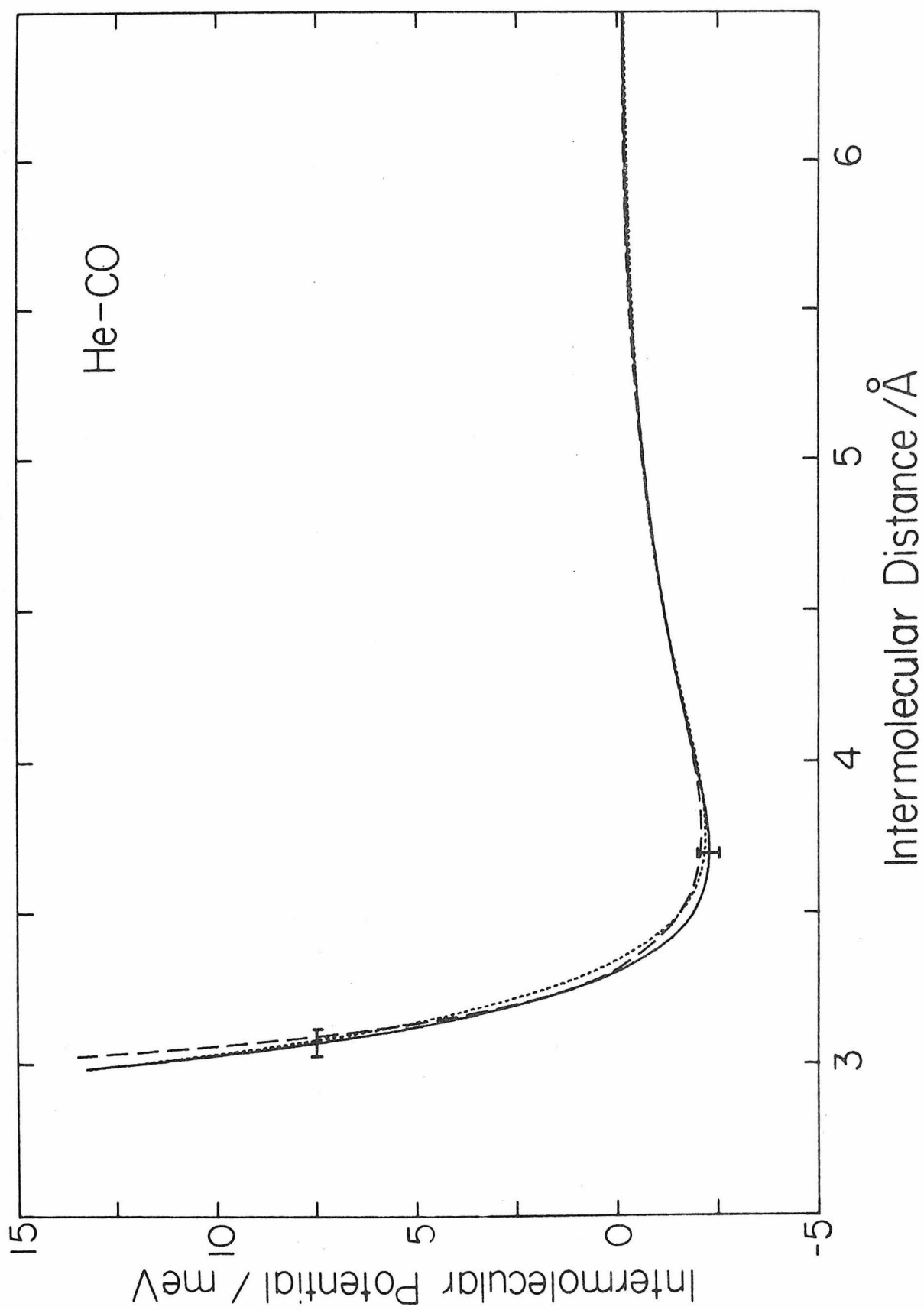


Figure 4

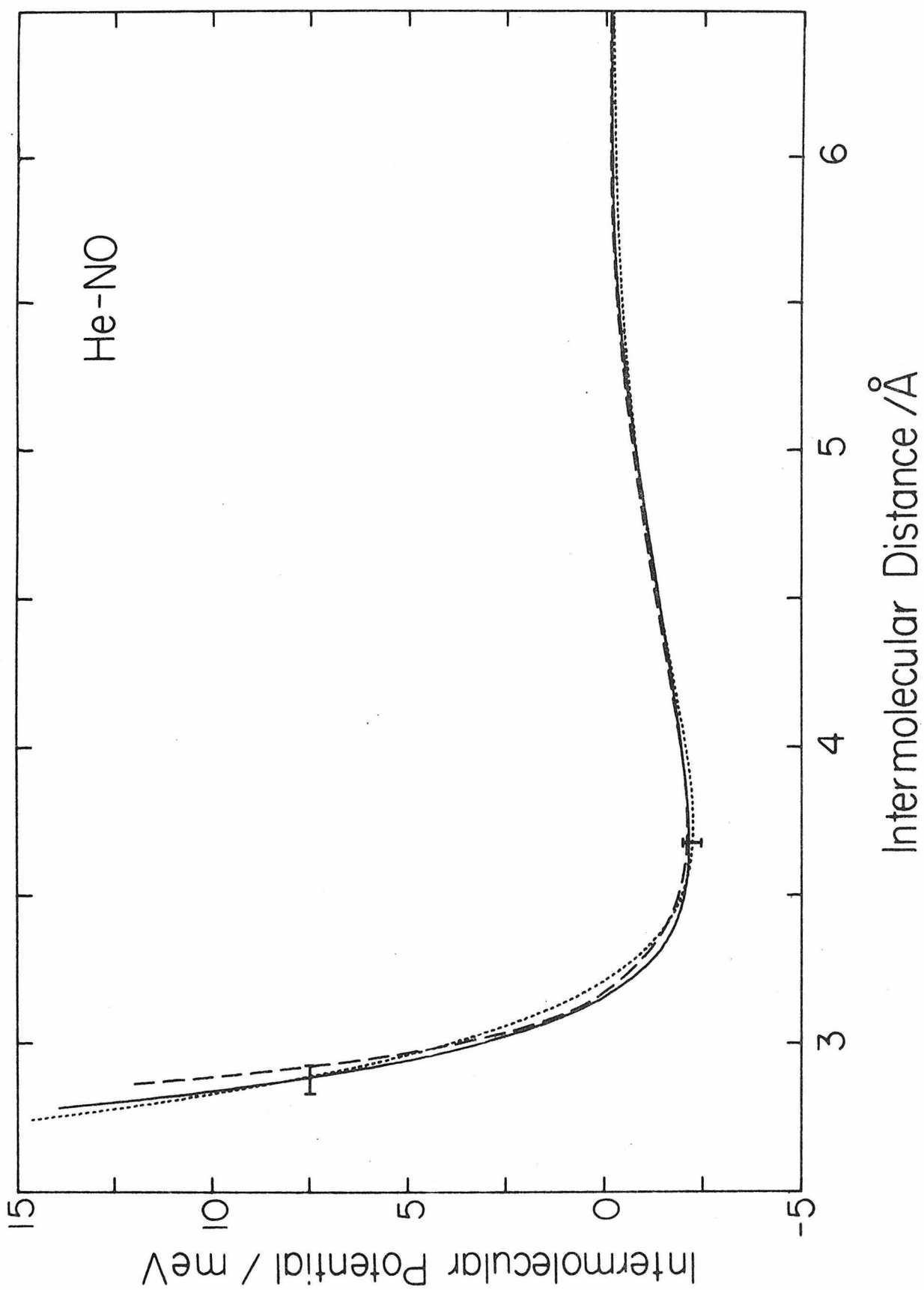


Figure 5

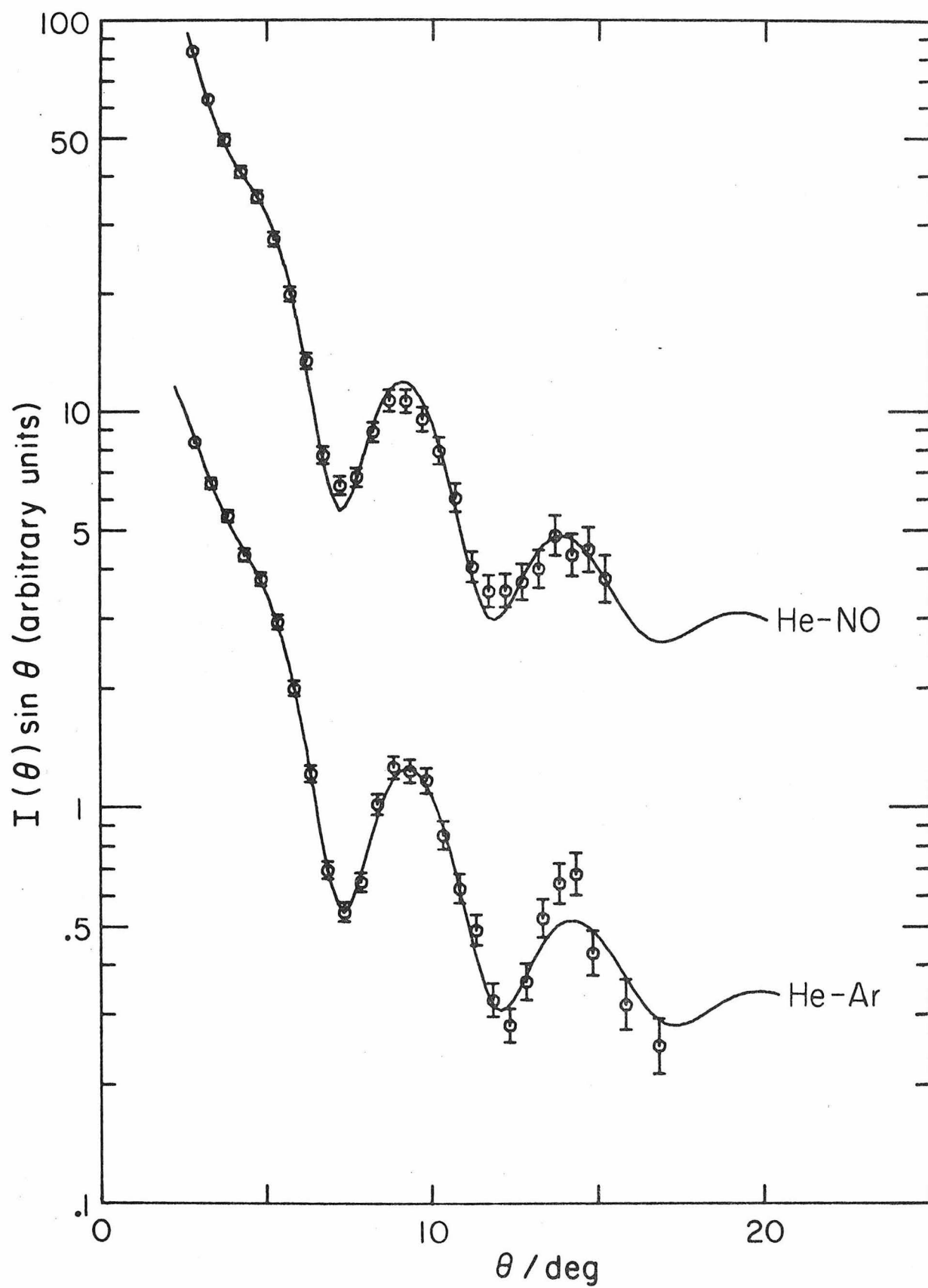


Figure 6

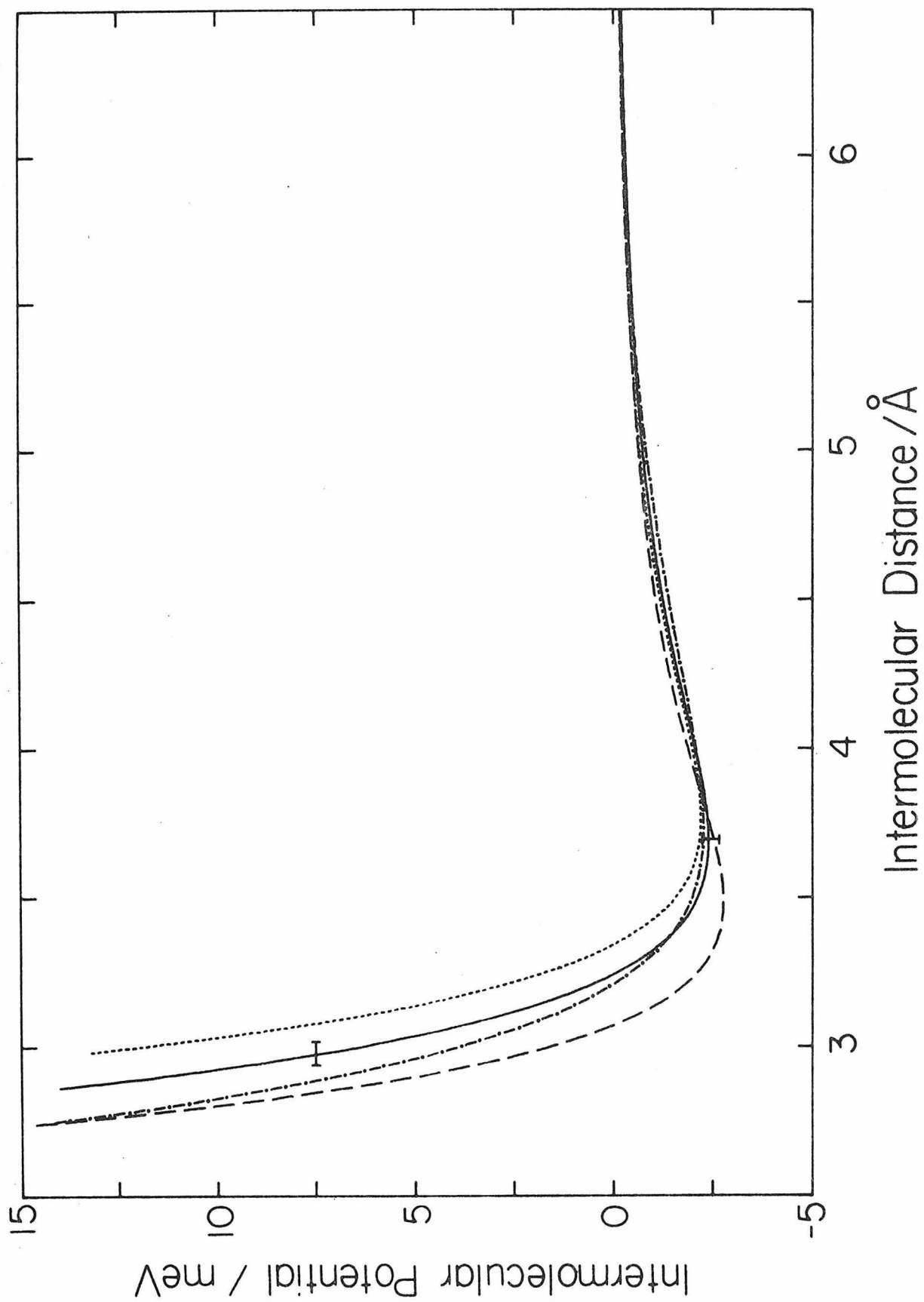


Figure 7

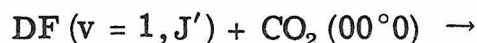
PROPOSITIONS

PROPOSITION I

Abstract: It is proposed that the DF ($v = 0, 1$) + $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ systems be studied in a crossed molecular beam. The purpose of this experiment would be the investigation of the mechanism of $v-v$ resonant vibrational energy transfer as a function of the energy defect between vibrational energy levels and as a function of the relative translational energy.

The development of continuous-wave (cw) lasers whose operation is based on transitions between vibration levels of excited molecules has led to extensive interest in the process of vibrational energy exchange. These exchange mechanisms govern the efficiency of such lasers. Of particular interest has been the DF- CO_2 transfer chemical laser¹ which has a high operating efficiency.² Furthermore, this laser represents a prototype for systems in which the molecule involved in the lasing action may be totally independent of the chemical reaction. Such systems offer the promise of efficient lasing on transitions of species which might not be readily produced through purely chemical means.

When the DF- CO_2 laser was first developed, the mechanism of vibrational energy transfer from vibrationally excited DF to the first asymmetric stretching mode of CO_2 , i. e., CO_2 (001) was undefined. Because of the large vibrational energy defect, there was a reluctance to attribute the energy transfer to a direct coupling, i. e.,

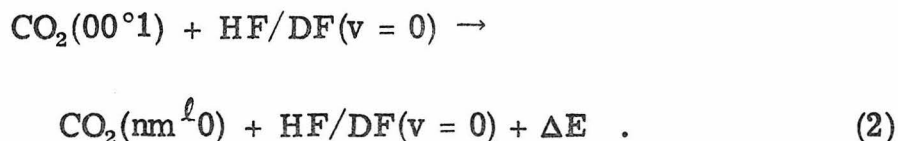


$$\text{DF} (v = 0, J) + \text{CO}_2 (00^\circ 1) + \Delta E = 558 \text{ cm}^{-1} . \quad (1)$$

In fact, for the HF-CO₂ transfer chemical laser in which ΔE in eq. (1) equals 1609 cm^{-1} , the initial investigators proposed that intermediate CO₂ vibrational states were involved in the energy transfer mechanism.³ However, more detailed investigations of both the DF-CO₂ and HF+CO₂ transfer chemical lasers demonstrated that the v-v energy transfer mechanism described by eq. (1) was indeed responsible for all significant energy transfer from vibrationally excited DF to CO₂ (00°0).⁴ Specifically, fluorescence from HF and DF ($v = 1 \rightarrow 0$) and fluorescence from CO₂[(00°1) $\rightarrow$ (000)] were simultaneously monitored and were found to have linear variation. Also, in a private communication,⁴ Hancock and Green were reported to have employed a filter cell for upper vibrational bands of DF to show that contributions from such levels were negligible to the population (fluorescence) of CO₂ (00°1).

In further studies,^{5,6} the rates of vibrational energy transfer from HF($v = 1$) and DF($v = 1$) to CO₂(000) were measured and were found to be much higher than expected. These results were consistent with studies⁷ on the V-V energy transfer between CO₂(001) and HX (X = Cl, Br, I) in which interaction of attractive forces and significant transfer of energy to the rotational mode were offered as an explanation for the unexpectedly large rates for interaction with the hydrogen halides. This explanation was further supported by the facts that deactivation rates with rare gases and N₂ were much slower.⁸

The hypothesis of enhanced attraction and rotational interaction has also been pursued theoretically. Shin⁹ has concluded that the hydrogen bond interaction can explain the behavior of experimentally observed V-R, T transfer rates over the range of temperature from 295 to 670°K.



Dillon and Stephenson¹⁰ have developed a model for the v-v transfer of energy from DF($v = 1$) to CO₂(000) in which the interaction of the two species is taken as a combination of V-V and R-R transfer effects with the intermolecular potential being a Lennard-Jones 12, 6 with parameters estimated from the literature. Agreement with experimental results is good, considering the spread of values. Integral V-V cross sections are approximately 1.0 Å² at 300.K and are found to decrease with increasing temperature. Interestingly the calculations indicate that almost half of the total V-V cross section can be attributed to collisions in which at least one complete revolution of the collision complex occurred. Lucht and Cool^{5a} have concluded in their experimental studies that the V-V transfer described by eq. (1) entirely dominates the V-R, T transfer described by eq. (2). They further propose that short-range anisotropy introduced in the intermolecular potential by hydrogen-bonding might play a significant role in the interaction of DF($v = 1$) with CO₂(000).

The behavior of the $\text{DF}(v = 1) + \text{CO}_2$ system presents intriguing questions, not only because of its application to lasers but also more because of the information which can be obtained on the basic mechanic of energy transfer. Currently exact calculations of the probabilities of energy transfer are too complicated, but approximate approaches are viable.¹¹ Such approximations fall into two categories: (1) simple models which preserve the physical situation and which may be accurately solved and (2) simplifications of the rigorous, formal problem. Since the first category allows greater physical insight, experiments which probe the mechanisms involved in collisions and in the transfer of energy provide necessary information to not only baseline such models but also to allow more developed.

Investigation of the $\text{DF}(v = 0, 1) + \text{CO}_2(000)$ interaction can be made using the molecular beam technique. Angular distributions of velocity-analyzed scattered beams can be made; both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ can be used to study the impact of changing the energy defect in the V-V transfer process; and specific rotational states of $\text{DF}(v = 1)$ can be selected. Additionally the strong possibility exists that laser induced fluorescence could be applied to (1) determine the relative attenuation of the $\text{DF}(v = 1)$ beam and (2) determine the relative angular distribution of $\text{DF}(v = 1)$ scattering.

As mentioned previously, the integral V-V cross section for $\text{DF}(v = 1) + \text{CO}_2(000)$ is approximately $1.0 \text{ \AA}^2$ at 300°K . Farrar et al.¹² have investigated the rotation cross sections of CO_2 and N_2O in

collisions with Ar and Kr at thermal conditions. Time-of-flight data for Kr + CO₂ was taken out to 70° in the laboratory frame which corresponds to an angle greater than 150° in the center-of-mass frame. Their contour map of the center-of-mass flux shows that the inelastic scattering is forward peaked, i.e., indicating that long-range forces represent the primary interaction. Beck and Förster¹³ studied rotational excitation of the K + CO₂ system and found the integral inelastic cross section to be less than 2 Å². K + CO₂ is expected to have as large, if not larger, an integral inelastic cross section as Ar, Kr + CO₂. Although Beck and Förster postulate the formation of a scattering complex, their data is only taken to 30° in the center-of-mass frame which really does not allow discrimination of mechanisms. (In fact, forward scattering could be argued from their data.) Finally, Stephenson et al.¹⁴ give a V-V integral cross section of ~ 8.3 Å² for ¹²CO₂-¹³CO₂ (ΔE = 66 cm⁻¹) at 300°K and a cross section of 0.6 Å² for ¹²CO₂-N₂O (ΔE = 125 cm⁻¹) at 125 cm⁻¹. Consequently, velocity-analyzed angular distributions of scattered DF, which has a low background signal, appear feasible and and reasonable.

Excitation of DF to the v = 1 state has been done by a large number of investigators;¹⁵ excitation of HCl¹⁶ and of N₂O¹⁷ has been done in molecular beam experiments; and laser-induced fluorescence of excited BaO¹⁸ in molecular beam experiments has also been demonstrated. Operation of line-selected DF lasers¹⁹ has been demonstrated on P₁(5)-P₁(13) transitions. Consequently, the ability

to excite DF in a molecular beam experiment. Relative translational energy may also be varied by either increasing the temperature in the feed plenums of the molecular beam or alternatively by seeding the primary beam with DF using He as the carrier gas.²⁰

As stated above, laser-induced fluorescence has been demonstrated in a molecular beam; but this has been for electronically excited molecules whose transition was in the ultraviolet. For DF($v = 1$), fluorescence must be induced to the ground vibrational state, an infrared transition whose detection is very noisy unless cooled to low temperatures. This technique has been used to monitor the deactivation of DF($v = 1$) by a variety of molecules and atoms.²¹ Gas densities are very similar to the conditions of a molecular beam (~ 0.05 torr). Consequently the laser-induced fluorescence technique appears feasible but difficult.

Therefore, our proposed investigation of energy transfer mechanisms for DF($v = 1, J$) + CO₂(000) will be a series of experiments. In the first experiment, angular distributions of the velocity-analyzed scattered DF will be made for ground state DF in the primary beam. The primary purpose of these measurements will be the determination of whether the rotational inelastic differential cross section (rotational spacings for CO₂ are much smaller than the relative-collision translational energy allowing R-R, R-T, and R-V interactions by the CO₂ much more readily) is forward-peaked in agreement with Farrar et al.²⁰ (a direct collision) or is peaked at some intermediate center-of-mass angle as predicted by Beck and Förster²¹ (a complex collision).

Our study will next address the effects of vibrationally exciting the DF($v = 0$) primary beam with a DF laser (no line selection). Initially the DF laser beam will be chopped and the scattered signal will be measured to determine the effect of excitation; then, angular distributions of the velocity-analyzed scattered DF will be made. Because efficient vibrational energy transfer collisions are expected to be nearly collinear (from classical models),⁸ the V-V inelastic differential cross section is expected to be backward-peaked. Furthermore, since the integral V-V resonant cross section is of the same magnitude as the integral rotational cross section, comparison with the DF($v = 0$) contour map should provide insight into whether the mechanism is direct with backward scattering or whether as Dillon and Stephenson have postulated⁷ a collision complex is formed which exists for longer than one revolution. The translational energies of the two beams would also be varied to investigate the effect of changing the collisional (relative translational) energy.

The final experiment to be done is the replacement of $^{12}\text{CO}_2$ by $^{13}\text{CO}_2$ in the secondary beam which increases the energy defect between vibrationally excited DF($v = 1$) and ground state $\text{CO}_2(000)$ by 66 cm^{-1} . Since the intermolecular potential remains the same, this addresses only the effect of changing the energy defect, i. e., whether the relative cross section will decrease as the energy defect increases.

If the above series of experiments were successful, a number of other effects could be investigated. Laser-induced fluorescence could be applied to monitor the relative attenuation of DF($v = 1$) by the

secondary beam. This would permit evaluation of the effect of rotation in the excited DF, since line-selected operation of the DF laser would permit excitation to only one $v = 1$, J state. Additionally, relative collision translational energies could be varied as could the distribution of rotational states in the CO₂ beam. With refinement the role of rotation in the "resonant" V-V interaction could be investigated, a definition which would provide great physical insight and the basis for more realistic interaction models.

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PROPOSITION II

Abstract: It is proposed to examine the effect of vibrational excitation on the reaction



This reaction is substantially endothermic, over 15 kcal/mole, and thus requires addition of significant energy for the reaction. In a molecular beam apparatus, the effects of vibrationally exciting HCl to the first, second, and third levels and the effects of changing the relative collision velocity (energy) would be studied.

Considerable interest exists for the role which reagent energy plays in reaction probability and in reaction dynamics. Despite this interest, the number of such investigations utilizing crossed molecular beams with neutral species is small. Most reactions studied in molecular beams have been chosen for their reasonably large cross sections at modest energies, i.e., experimentally observable systems which are relatively easy to investigate. Since such systems have small or negligible activation energies and are often highly exoergic, possible variations in the reagent energies through heating or cooling the beams can usually be considered negligible in comparison to the system exoergicity.

The few molecular beam investigations which have been made on the effect of reagent energy on reaction dynamics have, however, had interesting results. Jaffe and Anderson² accelerated a beam of HI to

laboratory energies of 40-215 kcal/mole by seeding the HI in a helium carrier beam. They observed no reaction, despite the fact that the activation energy is well defined to be 44 kcal/mole. Since the upper limit of the possible reactive cross section could not account for the observed kinetic rate, they postulated that vibrational enhancement of the reactants was necessary. They cited as further evidence results obtained on four atom-exchange reactions by Bauer and coworkers and by Lifshitz and coworkers. Single pulse shock-tube techniques were used to rapidly heat mixtures of $H_2 + D_2$, $^3_{15+15}N_2 + ^{14+14}N_2$,⁴ and $HD + HD$.⁵ In all cases, the observed rates could only be interpreted if a mechanism was assumed that required population of a critical vibrational level, i.e., no exchange occurred until the level was achieved and the rate was dominated by the population in that level or higher levels.

Valentini et al.⁶ have studied the endoergic bimolecular reactions of F_2 with I_2 , ICl , and HI in a crossed molecular beam. They have varied the collision energy by using either He or Ne as a carrier gas for molecular fluorine and by heating the gas mixture over a range of 300 to 900°K. They have found that the threshold energies of reaction were 4, 6, and 11 kcal/mole, respectively, for collisions between F_2 and XI ($X = I, Cl, H$) to produce XIF and F ; and, furthermore, they have found that as the collision energy is increased the formation of XF becomes important for first $F_2 + I_2$, then later for $F_2 + ICl$, but not for $F_2 + HI$ (maximum collision energy used was 30 kcal/mole). Previously, Dixon et al.⁷ had shown that no $BrCl$ product was detected

in a crossed beam study of $\text{Cl}_2 + \text{Br}_2$ at collision energies up to 30 kcal/mole. Farrar and Lee,⁸ however, had observed the stable formation of CH_3IF in the crossed beam study of $\text{F}_2 + \text{CH}_3\text{I}$ at collision energies greater than 10 kcal/mole. Angular distribution measurements of reactive scattering of halogen atoms Cl and Br by the halogen molecules Br_2 , I_2 , IBr , and ICl were the first non-metal reactions studied in a molecular beam;⁹ these studies were augmented by velocity analysis measurements.¹⁰ These measurements indicated that the cross sections were forward peaked, although total cross sections were estimated to be only 1.0 to $10.0 \text{ \AA}^2$. For the reaction $\text{Br} + \text{CHl}$ when chlorine is the central atom in the trihalogen complex, the cross section is lowered by a factor of 5 and an activation energy of 5 kcal/mole is observed.^{9c} Thus reactive scattering measurements (including velocity analysis) for interhalogen reactions having an activation energy of ~ 5 kcal/mole and a total cross section of $\lesssim 1.0 \text{ \AA}^2$ are feasible.

Sloane et al.¹¹ have investigated the $\text{K} + \text{SF}_6$, CCl_4 , and SnCl_4 systems, varying the temperature of the polyatomics over a range of 300 to 580°K and velocity selecting the K beam. They have found an essentially constant increase in total reactive cross section, comparing systems at 580° and 300°K SF_6 temperature while varying the relative kinetic energy from 2 to 5 kcal/mole. They attribute the increase in cross section to vibrational enhancement of the reaction.

Ordiorne et al.¹² have made an elegant, direct study of the role of vibrational excitation. An HCl chemical laser was employed to

vibrationally excite to the $v = 1$ state a beam of HCl which was crossed with a beam of K. By pulsing the laser and suitably gating their detector with the laser pulses, the investigators were able to discriminate reactively scattered KCl due to HCl ($v = 1$) from that due to HCl ($v = 0$), i.e., they could differentiate between the following two processes:



Analysis of the data led to the estimate that the cross section for reaction in eq. (3) was approximately 100 times the cross section for reaction in eq. (2). Estimation was necessary because the investigators found that only part of the HCl beam could be excited because the rotational distribution in the beam was much lower than found in the laser. (This is caused by the rapid rotational relaxation in the HCl beam as cooling occurs with expansion of the gas through the nozzle.) However, they did find for the matching rotational levels that the HCl beam was near saturation--twenty-five percent of the HCl beam was estimated to be excited. As a check, the laser was detuned to run only on the $2 \rightarrow 1$ vibrational transition. No enhancement in the reaction cross section was observed. In a later study in the same laboratory,¹³ the effects of translational (collisional) excitation were studied on the K + HCl reaction. Translational energy was seen to have a relatively weak effect on the reactive cross section.

Polanyi and coworkers¹⁴⁻¹⁹ have used data from chemiluminescence flow experiments to study the effects of reagent energy upon

reaction. In their studies of endothermic reactions, significant increase in the rate constant was found as the vibrational energy in the reactant molecule increased. Vibrational energy was found to be much more effective than translational energy in endothermic reactions. This observation supports conclusions²⁰ made that for substantially endothermic reactions the barrier to reaction is in the exit valley of the potential energy surface. Furthermore, for both exothermic and endothermic families of reactions in which a qualitative correlation of reaction energy (exothermicity or endothermicity) exists with barrier height, the barrier moves successfully to later positions along the reaction coordinate with increasing barrier height.

Among the endothermic reactions studied by Polanyi et al. has been the system $\text{Br} + \text{HCl}$ ($v = 1, 4$).^{15, 19} This is a substantially endothermic reaction whose endothermicity is 15.5 kcal/mole and whose total reaction barrier is ~ 16.5 kcal/mole. This reaction represents the mass combination light-heavy (LH) + heavy (H) which has been shown to have a larger cross section and stronger response to vibrational excitation than other mass combinations (although the barrier appears not to shift as strongly into the exit channel).¹⁸ In this system, the $v = 2$ vibrational level of HCl is above the reaction barrier and the $v = 4$ vibrational level is approximately double the barrier. In this system the reaction for $v = 1$ was not observed; the relative reaction rate for $v = 2$ was ~ 0.1 ; the relative reaction rate for $v = 3$ was ~ 0.7 ; and for $v = 4$ was 1.0. The total cross section for $v = 4$ was estimated between 1.0 and $10.0 \text{ \AA}^2$.¹⁹

The reaction of vibrationally excited HCl with Br has also been studied by Leone et al.²¹ and Arnoldi et al.²² Leone et al. studied the reaction of HCl ($v = 2$) + Br in a low-pressure flow system using the laser-induced fluorescence method to monitor the total deactivation rate of HCl ($v = 2$) and estimating the role of collisional deactivation. Br atoms are produced by passing Br₂ through a microwave discharge; excitation of HCl to $v = 2$ was done using a tunable optical parametric oscillator (OPO) - efficiency of the OPO on HCl (0-2) transition allowed the investigators to use HCl pressure to as low as 0.04 torr. The average thermal cross section for HCl ($v = 2$) + Br reaction was given as $0.39 \text{ \AA}^2$. Arnoldi et al.²² have investigated the HCl ($v = 2$) + Br reaction using an HCl pulsed chemical laser to sequentially excite from $v = 0$ to $v = 1$ to $v = 2$. Their reaction rate constant was given as $K = (8.8 \pm 3.1) \times 10^{11} \text{ cm}^3/\text{mole sec}$, corresponding to a thermal average cross section of $0.31 \text{ \AA}^2$. Excitation to $v = 1$, not to $v = 2$, was found to be process-limiting.

The large observed change in cross section for reaction when HCl is in the $v = 2$ vibrational level and when HCl is in the $v = 3$ vibrational level (a factor of 7 increase) coupled with the ability to make large collisional energy changes in a molecular makes the molecular beam investigation of the HCl + Br reaction system appealing. Although as previously mentioned, Ordiorne et al.¹² have seen a large effect on the cross section of the K + HCl system when HCl was vibrationally excited, this system is marginally endothermic, $\sim 1.5 \text{ kcal/mole}$,¹³ and does not address strongly the issue of the

reaction barrier existing relatively far in the exit channel. Whether translational (collisional) energy can efficiently be utilized after the reaction has achieved sufficient vibrational energy to overcome the barrier is of great interest, especially in isotope separations with multi-photon excitations. Of as great an interest is the question whether a combination of vibrational-translational energy to overcome the barrier can be efficiently utilized.

The first investigation made would be the reactions of $\text{Br} + \text{HCl}$ ($v = 2, 3$) at one collisional energy. The excitation of the HCl would be done in a sequential manner as described by Arnoldi et al.²² Since this sequential excitation has also been used by several workers²³ to achieve excitation of HF in the $v = 2, 3$ states in studies of excited state deactivation, excitations to the $v = 2, 3$ levels should be feasible. A greater problem is matching the rotational states of the HCl beam with those of the HCl laser. Use of a graphite oven to heat DCl over 1700° has been demonstrated by Polanyi et al.²⁴ Use of such an oven would permit raising the temperature of the beam a factor of 5, large enough to permit matching of the rotational levels. This would also improve the kinematics, important if HBr is formed primarily in a backward scattering mechanism (as defined by the Br beam). Laser-induced fluorescence would be the most direct means to monitor the efficiency of excitation as fluorescence signals could be monitored as a function of laser intensity. Such techniques have been already successfully applied by Zare and coworkers²⁵ in molecular beam experiments; furthermore, Kinsey²⁶ has proposed such a technique

for obtaining velocity-angle distributions as superior from signal-noise considerations when the species studied have suitable spectroscopic transitions.

The other series of investigations would be to vary the collisional energy over a range of approximately 30 kcal/mole by varying the beam temperatures and the amounts/proportions of He/Ne carrier gas in the beams.²⁷ This would be done for the cases of HCl excited to $v = 1, 2$, and 3 and would permit evaluation of the role of translational energy in the reactions. Velocity-analyzed angular distributions would be taken, although it is highly questionable whether any reaction would be observed for the $v = 1$ case; for the $v = 3$ case, an integral reactive cross section of $\lesssim 2 \text{ \AA}^2$ should be observed.

In summary, the roles of reagent energy would be examined for a substantially endothermic reaction. Efficiencies of both vibrational and translational excitations of the reagents would be examined, especially in the energy regime near the reaction barrier.

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range of available collisional energies when 'heavy' gases are the reactants.

PROPOSITION III

Abstract: It is proposed that the reactions of selected trialkylboranes with 2-methyl-2-nitrosopropane be investigated. The reaction with the tri-*s*-alkylboranes formed by reaction with cis- and trans-3-methylpent-2-ene, respectively, has been found to involve stereospecific cis-elimination with different yields. Steric effects would be investigated, and primary isotope effects also would be investigated by using deuterium-labelled trialkylboranes.

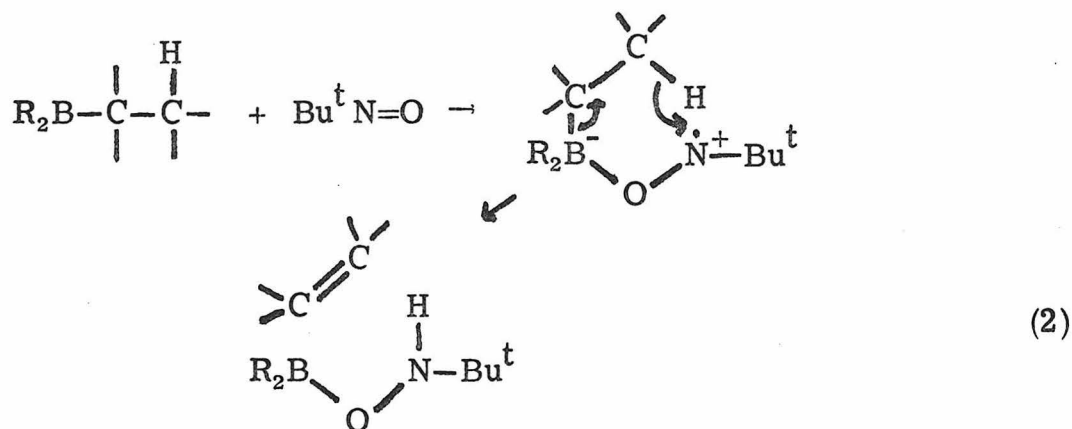
The thermal reactions of alkynes,¹ of olefins,² of aldehydes,³ of azo-compounds,⁴ and of 2-methyl-2-nitrosopropane⁵ with trialkylboranes have been reported. In all cases the reaction is described by the equation



where $X=Y$ may be $\text{RC}\equiv\text{CR}$, $\text{R}_2\text{C}=\text{CR}_2$, $\text{RHC}=\text{O}$, cis $\text{PhN}=\text{NPh}$ or $\text{Bu}^+\text{N}=\text{O}$, respectively. In each case, reaction with the trialkylborane is found to give the corresponding olefin. In their experiments with cis-azobenzene reacting with erythro- and threo-tris-(1,2-dimethylbutyl)-borane (obtained from hydroboration of the cis- and trans-3-methylpent-2-ene, respectively), Davies et al.⁴ found that the dehydroboration was stereospecifically cis. Similar behavior was observed for the displacement reactions with olefins² and aldehydes³ as well as for 2-methyl-2-nitrosopropane. Furthermore, in their study of the 2-methyl-2-nitrosopropane reactions with trialkylboranes, Foot and Roberts^{5b} observed that (1) trineopentylborane, which has no

β C-H bonds in the B-alkyl groups, did not react with the nitrosoalkane and (2) triphenylborane also did not react. Later studies on the reaction of azobenzene with trialkylboranes was also stereospecifically cis while trans-azobenzene did not react.

These observations (coupled with the earlier proposal of a cyclic six-membered transition state for the olefin displacement reactions^{3e, 3h}) strongly support the postulate of a cyclic six-center mechanism for the displacement reactions of trialkylboranes.



Breaking the β -CH bond in the trialkylborane represents a key factor in forming the proposed transition state. Understanding of the role which the bond breaking plays could be obtained by replacing the hydrogen with its deuterium isotope. If breaking of the bond is strongly developed during the transition state, the reaction rate would be slowed significantly (up to a factor of ~ 6). If, however, the bond does not break until late in the reaction (after the transition state) or breaks early in the reaction (before the transition state), the effect would be much less.⁶

2-Methyl-2-nitrosopropane can readily be obtained. Both Forrester⁷ and Foot and Roberts^{5b} describe the synthetic procedure.

Trialkylboranes can be formed by two methods. In the first, the selected olefin is reacted with diborane to form directly the trialkyl borane. This method is excellent for unhindered olefins;⁸ all three available H-B bonds are utilized. It is almost a trivial matter to use B_2D_6 instead of B_2H_6 . This may be obtained by the dropwise addition of a solution of $LiAlD_4$ (lithium aluminum deuteride) in diglyme (diethyleneglycol dimethyl ether) to a stirred mixture of boron trifluoride etherate and diglyme. The generated gas is swept by a slow stream of nitrogen into a reaction flask containing THF (tetrahydrofuran) as the solvent.⁹ In the cases of hindered olefins, the reaction will not go to R_3B but rather only one or two of the three available H-B bonds will be utilized, i.e., BRH_2 or BR_2H . In these cases, the trialkylboranes can often be formed through reaction with the appropriate Grignard reagent.¹⁰

The reaction of 2-methyl-2-nitrosopropane appears to have the promise of synthetic utility because of its stereospecific cis-elimination.^{5b} Reaction with erythro-tris-(1,2-dimethylbutyl)-borane with 2-methyl-2-nitrosopropane and with cis-azobenzene give 33% and 70% yields respectively for the original cis-olefin with the remainder appearing as terminal olefin; for the reaction with the threo-trialkylborane respective yields are 37% and 86% for the original trans-olefin. Thus it is seen that yields are different for the two olefin. Thus it is seen that yields are different for the two olefin stereoisomers; and, furthermore, it appears from the azobenzene results that steric requirements in the transition state may play a major role in determining product yields.

These observations suggest that reactions with trialkylboranes formed from olefins which have greater steric hindrance than the 3-methylpent-2-ene may have attractive yields of the cis and/or trans stereoisomers and may represent a means of enriching mixtures of stereoisomers. Deuterium-labelling may also enhance the process if the ratio of median olefin to terminal olefin rates increases, i.e., if the transition states are favorably affected. Of further interest could be the investigation of nonsymmetrical deuterium-labelled trialkyl boranes.

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PROPOSITION IV

Abstract: It is proposed that the thermal decomposition of nitrogen trifluoride be studied over the range of temperatures 1150 to 2100°K. Study would include the dissociation of NF_3 to $\text{NF}_2 + \text{F}$ and the dissociation of NF_2 . Intermediate concentration of NF_2 as a function of temperature in the decomposition of NF_3 would be measured.

The thermal decomposition of nitrogen trifluoride (NF_3) has been reported in several investigations¹⁻⁴ as has the thermal decomposition of nitrogen difluoride (NF_2).^{5,6} Both of these systems have been studied using shock tubes to produce a very rapid ($\leq 1 \mu\text{sec}$) essentially homogeneous increase in the temperature of the gas.⁷ Nitrogen trifluoride (NF_3) is a stable gas with a dissociation energy (for the first bond) between 55 and 60 kcal/mole; nitrogen difluoride (NF_2), while quite stable, can only be obtained from the dissociation of NF_3 or of tetrafluorohydrazine (N_2F_4).⁸ Studies on both NF_3 decomposition and NF_2 decomposition have resulted in controversy, especially for the NF_3 results.⁹ Both of the involved laboratories agree that the mechanism of the shock-induced decomposition of NF_3 highly diluted in argon is unimolecular, but severe disagreement exists concerning the Arrhenius rate parameters.

The thermal decomposition of NF_3 at temperatures in the 1150 to 2100°K is expected to give varying mixtures of NF_2 , F , and N_2 .¹⁰ The first NF bond in NF_2 is stronger than the first NF bond in NF_3 ; $\sim 75 \text{ kcal/mole}$ vs. $\sim 57 \text{ kcal/mole}$ is the energy required to break the

bond.^{8b, 8d} Consequently the reaction path $\text{NF}_3 \rightarrow \text{NF}_2$ is expected to strongly dominate the reaction; and NF_2 is expected to be a significant intermediate, although as the temperature approaches 2100°K little NF_2 is expected.¹¹ NF is highly reactive and is not expected to be present in any significant quantity.^{5a}

Besides being a small molecule with a relatively stable intermediate and consequently an interesting molecule to study, NF_3 plays a major role in a number of laser systems. Laser emission of excited DF and HF molecules has been investigated wherein the $\text{DF}(\text{HF})$ was produced by the chemical reaction of $\text{D}_2(\text{H}_2)$ with NF_3 .¹² The time-dependent intensities of the different lasing lines observed reflect the necessity of understanding the dissociation/reaction mechanisms of NF_3 . Schott *et al.*¹³ have studied the $\text{NF}_3\text{-H}_2$ reaction in a shock tube and have found that above 1500°K no NF_2 was detectable and yield of HF was complete with significant chemiluminescence of $2.7\ \mu$ radiation. (Detailed studies were not performed on the $\text{NF}_3\text{-Ar}$ system, but decomposition of NF_3 at 1400°K was found to be unimolecular accountable by the reaction,



followed by slower, irreversible NF_2 removal via formation of products, N_2 and F atom.) Laser studies have also been made on mixtures of He/Kr/NF_3 ¹⁴ and He/Xe/NF_3 .¹⁵ Intense laser emission was observed from the KrF and XeF molecules formed, respectively, by chemical reaction initiated by a pulsed electric discharge. Laser

studies have also been made on the chemically-pumped electronic transition NF laser system. H or D atom reacts with NF_2 to form NF in the $a^1\Delta$ state and excited HF(DF) which can pump the $a^1\Delta$ state up to the $b^1\Sigma^+$ state which has a 0.529μ observed transition.¹⁶ Finally, NF_3 is used as a fluorine atom source for combustion driven chemical lasers.¹⁷ In these systems NF_3 , considerably in excess of stoichiometric ratio, is reacted with a fuel such as H_2 , D_2 , or C_2H_4 in a combustion flow chamber diluted with He. The reacted mixture (now containing the reaction products and the decomposition products of NF_3 , i.e., NF_2 , N_2 , and F) is then admitted through expansion nozzles into a second chamber. In this chamber (laser cavity), the free fluorine is mixed with $\text{D}_2(\text{H}_2)$ to produce excited DF(HF) which can have significant laser emission. Because of the material survivability requirements in the combustion chamber and because of the need to trade off kinetic effects of production vs. deactivation, control of the combustor temperature with maximum dissociation to fluorine atom is necessary. To do this, the thermal dissociation of NF_3 and its intermediary NF_2 in the range of 1150° to 2100°K must be well defined.¹⁸

The major problem in observing the rates of decomposition is that the absorption spectra the far infrared region and with the exception of the 905 cm^{-1} band for NF_3 is weak. For NF_3 the fundamental band assignments lie between 400 and 1025 cm^{-1} for $\nu_1 - \nu_4$;¹⁹ for NF_2 , the fundamental absorption bands are 931 and 1070 cm^{-1} ; and for NF, the fundamental band is 1115 cm^{-1} .²⁰ Absorption studies in the ultraviolet region of the spectra have been made by La Paglia and Duncan who report no significant absorption bands from $960\text{ \AA}$ (close to the

lowest ionization potential) to $1800 \text{ \AA}$ where they report the absorption coefficients to be effectively zero.²¹ Makeev et al.²² report absorption spectra in the region $2100\text{--}2400 \text{ \AA}$ to be extremely weak and further state that NF_3 is transparent in the region $2600\text{--}25000 \text{ \AA}$ (all measurements were taken at 22.5°C). NF_2 has been shown to have a strong absorption band in the near uv at $2600 \text{ \AA}$ ^{8a} but some controversy exists whether interference by other emitting species occurs at the elevated temperatures necessary for dissociation.^{9a, 9b} Controversy further exists whether i.r. emission observed at 5.18μ is due to NF_3 .^{9a, 9b}

Consequently, considerable question exists concerning the "real rate" constants. Over the past few years, fluorine-atom probe techniques have been investigated for use in HF and DF chemical lasers, Schlossberg²³ has shown that coherent anti-Stokes Raman scattering (CARS) should permit determination of F-atom concentrations of less than $10^{15}/\text{cm}^3$, i.e., ~ 0.1 torr. Since this concentration is substantially smaller than is expected in our experiment, the CARS technique does represent a viable measurement of F-atom concentration. The F-atom concentration increase could be monitored against the NF_3 and NF_2 depletion. A more direct and probably simpler approach would be to seed the NF_3 with a small amount of D_2 or H_2 . The D(H) atom produced by the reaction $\text{F} + \text{D}_2(\text{H}_2) \rightarrow \text{DF}(\text{HF}) + \text{D}(\text{H})$ would react with NF_2 . The 0.529μ transition of the excited NF and overtone emissions of the DF(HF) could be used to track the NF_2 concentration and determine the validity of using the $2600 \text{ \AA}$ absorption band as a concentration

diagnostic for NF_2 . In conclusion, the concentration of the intermediate NF_2 as a function of temperature in the dissociation of NF_3 could be determined; and seeding with D_2 or H_2 could provide the means to determine the rate of dissociation of the intermediate NF_2 .

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PROPOSITION V

Abstract: It is proposed that the gain and the relative change in the frequency-dependent component of the refractive index (anomalous dispersion) be simultaneously measured in a combustion-driven HF chemical laser. Measurements would be made with (a) no lasing, (b) single axial mode lasing with varying intra-cavity lasing fluxes, and (c) multi-mode lasing. Collision (homogeneously)-broadened linewidths within the doppler profile would be determined; and determination of the change in anomalous dispersion would be made.

In 1965, Kasper and Pimentel¹ experimentally observed laser emission from a photolytically-induced hydrogen chloride laser. The demonstration of this first chemical laser was followed in 1969 by operation of continuous-wave chemical lasers² which was followed in 1970 by the demonstration of a combustion-driven HF (or DF) chemical laser.³ Since that time many developments and refinements have been made in the understanding and operation of chemical lasers, particularly the HF/DF chemical laser.⁴ The schematic for a typical HF chemical laser is given in Figure 1, where fluorine atom and diluent enter the lasing cavity through a supersonic expansion nozzle and mix there with hydrogen also admitted through a supersonic expansion. The fluorine atom and hydrogen react to form vibrationally excited HF which is observed to have significant laser emission on the $2 \rightarrow 1$ and $1 \rightarrow 0$ vibrational bands. Despite the tremendous volume of research done on the HF/DF chemical laser (and on specific areas

such as kinetic rates), it can be said that only the global phenomena governing the performance of HF and DF chemical lasers are basically identified. Much of the detailed characterization/definition remains in question in such areas as velocity and species profiles at the nozzle exits, mixing/reaction mechanisms, and interaction of the radiation field with the excited HF.

Lasing in the HF chemical laser is observed on a number of vibrational-rotational transitions (between $J = 4$ and $J = 10$ on both the $P_{1 \rightarrow 0}$ and $P_{2 \rightarrow 0}$ bands) which for normal conditions of laser operation (pressure in reaction is maintained at less than 10 torr) are observed to have a doppler-broadened spectral line shape, i.e., the radiation field only interacts with a portion of the excited molecules. Doppler broadening is caused by the random thermal motions of molecules which induce doppler shifts in the frequencies observed. Thus the apparent resonant frequencies are distributed about the transition line center resulting in a broadening of the overall frequency response. The doppler half-width is given as⁵

$$\Delta\nu_D = \left(\frac{2 \times 10^7 N_A k \ln 2}{c^2} \right)^{\frac{1}{2}} \omega(v, J) \left(\frac{T}{M} \right)^{\frac{1}{2}} \quad (1)$$

where N_A is Avogadro's number, k is the Boltzmann constant, c is the speed of light, $\omega(v, J)$ is the frequency of the vibrational-rotational transition (v, J), T is the translational temperature, and M is the molecular weight of the molecule. Homogeneous or collision broadening is much more complicated, usually requiring different treatment for

different gas mixtures, and is still an area of active research.

Emanuel in his chapter on modeling chemical lasers in reference 4 presents a good overview of collisional broadening and basically shows our knowledge is quite limited. Studies that have been made have shown that the variation in line width with rotational level J is often considerable and complex.⁶ Collision-broadened half-widths in the fundamental bands of DF broadened by HF, of DF broadened by DF, and HF broadened by DF are seen to decrease a factor of four with increasing J .⁷ These observations are supported by later studies on rotational nonequilibrium which show that the rotational cross sections for molecules in high J states are significantly lower than for low J states.⁸

The fact that doppler broadening dominates has led to the observation of the "Lamb dip" in HF chemical lasers by a number of investigators.⁹⁻¹¹ Glaze,⁹ who was the first to investigate hole burning (Lamb dip) in an HF laser, found the effect to be small; Boncyk¹⁰ also found the effect to be small but found an explicit dependence on J , i.e., the depth of the observed hole increased with increasing J . A comprehensive theory for inhomogeneous broadening effects in a steady-state oscillator has been developed by Lamb for atomic lasing systems¹² and has been extended by Kan and Wolga for molecular systems where the excited lifetime is long compared to the time between collisions (the collisions cause filling of the hole burned in the doppler profile and hence must be considered).¹² This theory indicates that broadening of the frequency interval (width) of the dip occurs.

In addition to the interaction of the gain profile, interaction also occurs with a frequency-dependent component of the refractive index

near resonance, i.e., the anomalous dispersion. Siegman develops the relationships for gain and index for a model representing a collection of classical oscillators (see Figs. 2 and 3).¹⁵ Yariv, on the other hand, presents derivation for these relationships applying density matrix formalism.¹⁵ From their derivations we may obtain expressions for the laser gain coefficient and the laser phase shift which may be expressed in the simple form for the homogeneously broadened transitions

$$\alpha_m(\nu) = \alpha_{m0} \frac{1}{1 + [2(\nu - \nu_0) / \Delta\nu_a]^2} \quad (2)$$

$$\Delta\beta_m(\nu) = \alpha_{m0} \frac{2(\nu - \nu_0) / \Delta\nu_a}{1 + [2(\nu - \nu_0) / \Delta\nu_a]^2} = \alpha_m(\nu) \frac{2(\nu - \nu_0)}{\Delta\nu_a} \quad (3)$$

where $\alpha_m(\nu)$ is the value for gain, ν_0 is the line center frequency of the transition, ν is the frequency of operation. $\Delta\nu_a$ is the linewidth, and $\Delta\beta_m(\nu)$ is phase shift due to the laser. In eq. 2 we see that the frequency-dependent phase shift (i.e., a nonlinear frequency-dependent change in the index of refraction) is negative if $\nu < \nu_0$ and is positive if $\nu > \nu_0$. This results in a "pulling" of the frequency ν toward ν_0 . This "mode pulling" has been observed by Lynds et al. in a continuous-wave HF chemical laser who observed strong frequency pulling effects between axial (longitudinal) modes located symmetrically about the transition line center. Hinch¹⁷ also observed frequency pulling between axial modes and further related this shift to the gain constant following the procedure developed by Casperson and Yariv¹⁸ for

longitudinal modes in a high gain doppler broadened He-Ne laser.

The value of the gain coefficient α_{m0} obtained in this way was close to the value obtained by independent measurement, 3.3%/cm vs. 3.0%/cm, after the temperature was adjusted. In spite of this apparent success much information is lacking in defining the interaction of radiation with the doppler broadened transition in an HF chemical laser. Questions exist on the width of the collision broadened "hole" in the doppler-broadened transition profile, especially since the system undergoes reaction with large heat release producing the excited HF molecule (which has a fast rate of self-deactivation). Calculations under these conditions are very difficult and require information concerning concentration profiles and mixing mechanisms which are not readily available.

Experimental measurement of the full doppler-broadened transition profile thus can provide significant information about the basic operating mechanisms of low pressure HF chemical lasers which is not currently available. Zero-power (small signal) gain measurements have been made for a large number of vibrational-rotational lines in HF(DF) chemical lasers but always at line center and only as a function of distance along the direction of flow.¹⁹ No measurements of gain as a function of frequency nor of anomalous dispersion as a function of frequency have been made for HF chemical lasers. These measurements would be of special interest near the "holes" burned in the doppler profile. Measurement of gain has been limited to-date by the use of HF probe lasers tuned to line center; HF probe lasers can only be stabilized with one frequency at line center--operation, otherwise, is multi-mode

with both axial and transverse modes. Hence, an HF probe laser is not suitable to scan frequencies. There are alternative tunable laser systems which can scan frequency and which have good resolution (~ 1 MHz);²⁰ such lasers could be employed instead of the probe laser. Measurement of the anomalous dispersion has been made near the doublet of sodium at wavelengths of 0.5890μ and 0.5895μ utilizing an interferometry technique.²¹ Such a technique could be extended to our system using the probe laser as the radiation source. Lynds et al.¹⁶ in their study of mode pulling effects estimated an average value for the component of the index of refraction due to anomalous dispersion as 3.2×10^{-6} in the region ± 80 MHz about line center of the $P_2(5)$ transition.²² Based on their numbers for gain and the estimated values of gain perpendicular to the optical axis, phase changes of 180° or more are expected to be observed due to anomalous dispersion if measurement is made perpendicular to the laser optical axis. Consequently, measurement of the gain and of the phase shift perpendicular to the optical axis of the laser cavity is quite feasible. Simultaneous measurement of the gain and refractive index change, as the reflectivities of the laser cavity are varied (and thus the laser radiation), would provide much information about saturation/broadening effects. In conclusion, measurements of the gain profile and the change in anomalous dispersion would be made with (a) no lasing, (b) single axial mode lasing with varying intracavity lasing fluxes, and (c) multi-mode lasing.

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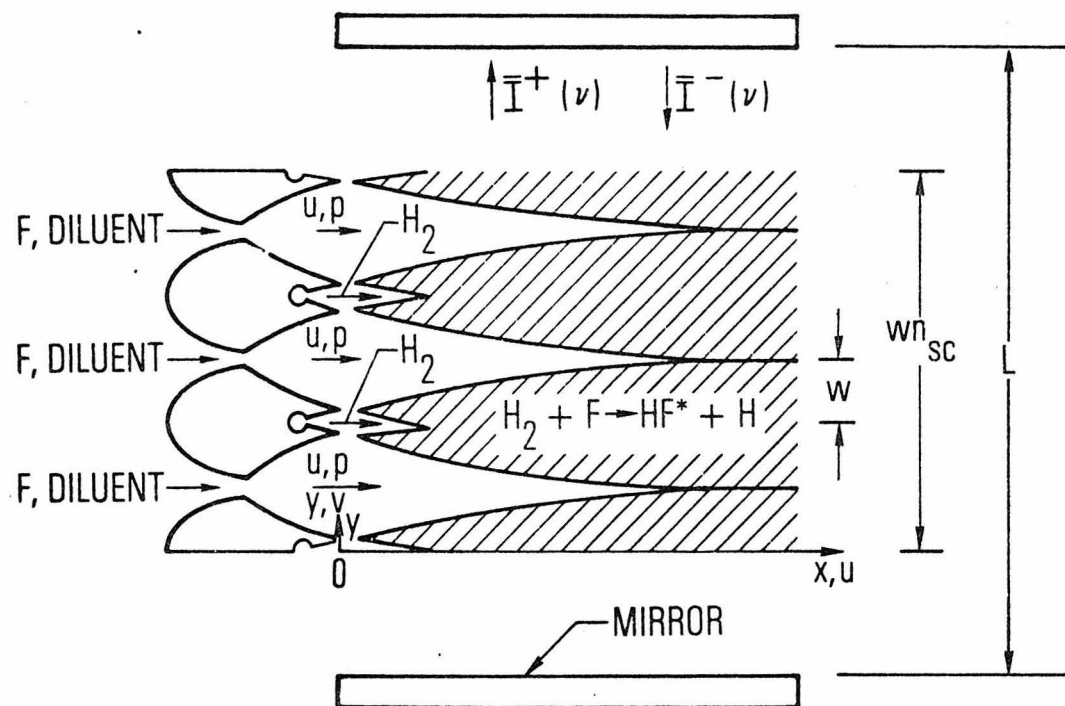
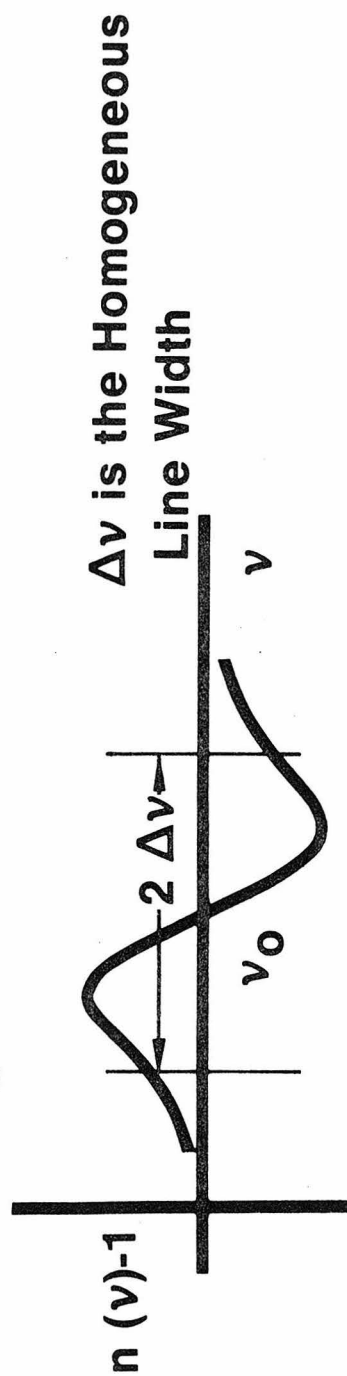


Fig. 1.

RESONANT INDEX FREQUENCY DEPENDENCE

a. Absorbing State



b. Gain State

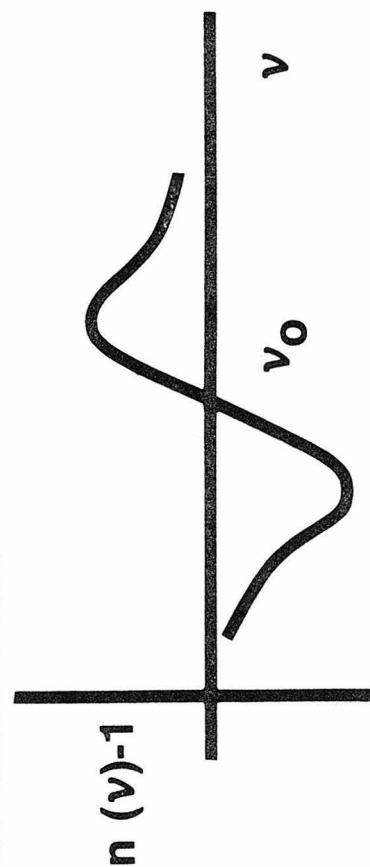


Fig. 2.

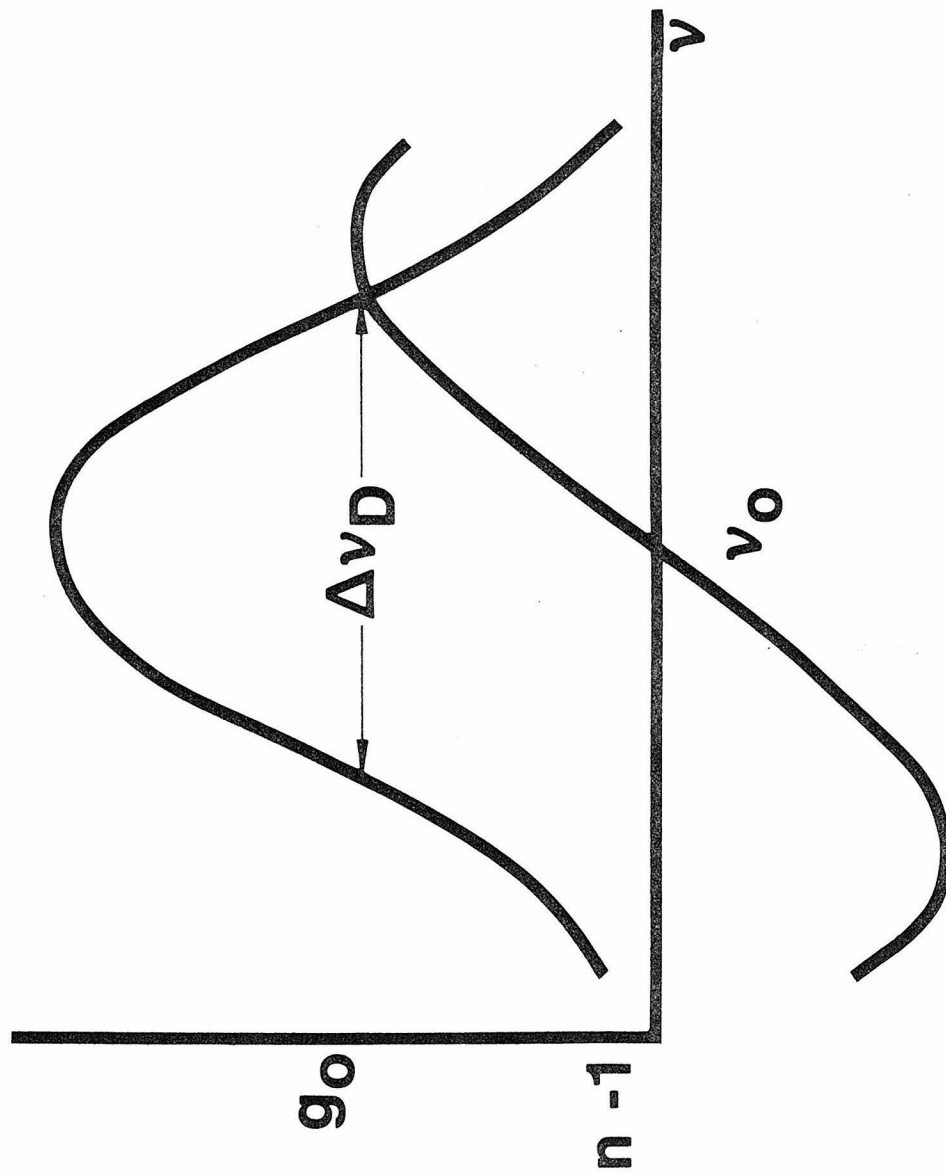


Fig. 3.