

INTERACTION POTENTIALS OF HELIUM
WITH ATOMS AND MOLECULES FROM
CROSSED BEAM EXPERIMENTS

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To my brother

Leon

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ABSTRACT

This thesis is concerned with the study of van der Waals interactions between He atoms and various atomic and molecular partners. These studies involve measuring differential cross sections (DCS) for scattering of thermal-energy crossed atomic and molecular beams. Although this crossed-beams technique has been used extensively in the past ten or so years, the accuracy with which it may be used to obtain van der Waals potentials for highly quantum systems heretofore has not been examined quantitatively. Under typical experimental conditions, we show in Chapter 1 that the attractive minimum region of the potential is determined to within about $\pm 10\%$. However, this accuracy is attained only when appropriately flexible interatomic potentials are used in the iterative inversion procedures needed to obtain these potentials from the DCS scattering measurements. Suitable parametric representations for the potential are those capable of effectively decoupling the attractive minimum region from the adjacent regions of the potential. This is particularly important for highly quantum systems having shallow attractive minima, since this is the region most sensitively probed by the elastic DCS. The related difficulty of non-uniqueness for iteratively derived potential energy curves is circumvented by introducing these flexible parametric representations. The range of interatomic distances actually sampled in the experiment is found to be significantly wider than would be expected classically.

In Chapter 2, the above results find practical application in the analysis of our measurements for He-Ar scattering. Using two very different mathematical parameterizations having the appropriate

flexibility to represent the He-Ar interaction, an accurate and substantially model-independent potential is determined. This potential is significantly more accurate than previously proposed ones. By further using measurements of properties which are sensitive primarily to repulsive interactions of He-Ar, its potential may now be considered as well known for interatomic separations $\gtrsim 2.4\text{\AA}$ (potential energies $\gtrsim 0.15\text{ eV}$). This potential provides an accurate description of all available gas-phase data for the He-Ar system. The techniques used to obtain it can easily be extended to the other He-rare gas pair potentials.

Later chapters in this thesis emphasize the van der Waals interactions of He atoms with molecular partners, whose intermolecular potentials are anisotropic. To be accurately represented, they should therefore be parameterized in a dimensionality higher than one. The importance of additional degrees of freedom is demonstrated to be slight for small diatomic partners (N_2 , O_2 , CO and NO), for hydrides (CH_4 , NH_3 , H_2O), and even for large but highly symmetric molecules (SF_6). In Chapter 3, the small anisotropic contributions to the He-diatomic intermolecular potentials are determined, using a model in which the locus of the attractive minimum position is represented by an ellipse. In Chapter 4, anisotropies in the He-hydrides and He- SF_6 potentials are ignored, maintaining nonetheless a good description of the DCS's for these scattering partners.

Chapter 5 presents a brief study of the He- CO_2 van der Waals potential, which is sufficiently anisotropic to result in a scattering pattern which cannot be fit with central-field models, even very flexible ones. The anisotropic potential extracted from the experiment may be

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used to predict rotationally inelastic DCS's for thermal-energy
He-CO₂ collisions.

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INTRODUCTION

Studies in the dynamics of atomic and molecular interactions form a significant part of the current interest and research effort in chemistry. The emphasis in many of these researches is on the behavior of "complicated" systems, in order to establish an understanding of chemical processes at a macroscopic level. The complexity of these systems, that makes them so interesting in the first place, often increases the difficulty of extracting information at the microscopic (i.e., molecular) level of detail. Conversely, the desire to extract such detailed information can frequently impose the restriction that the systems be "simple" enough to allow clear identification of its different aspects. These latter studies are pursued in the hope of establishing a repertoire of detailed information and physical insight which may then be suitably applied towards an understanding of more complicated systems. In this way, our knowledge of complicated chemical processes is increased through studies of simpler systems at the microscopic level.

The microscopic properties examined in this thesis are the van der Waals forces for atom-atom and atom-molecule interactions. For uncharged systems composed of atoms and atomic (or molecular) partners, these van der Waals forces are weakly attractive for large interatomic (or intermolecular) separations, eventually becoming repulsive for sufficiently small separations. The long-range potential energy arises from induced dipole-induced dipole dispersion interactions; molecules with permanent (as opposed to induced) dipoles also interact by induction forces with the atomic partner. These forces are well understood from perturbation theory. The short-range repulsive

forces resulting from electronic cloud overlap are as yet poorly understood, however. Competition between the attractive and repulsive forces gives rise to minima in the van der Waals potential energy curves. Such minima are typically two or three orders of magnitude smaller than chemical binding energies, and so do not give rise to stable compounds at room temperature. Nevertheless, these weak forces play a very important role in the understanding of physical and chemical interactions. Van der Waals forces are responsible for the critical phenomena of covalently-bonded compounds, and govern the order or disorder of the condensed phases. Gas imperfection and transport properties are also caused by the interactions between the constituent gas particles. All these properties are macroscopic phenomena, and are related to interatomic and intermolecular potential energies (which are of course, properties of the system at a molecular level), by statistical mechanics. This relationship has been employed extensively in studies of interaction potentials by measurements of what we will call "bulk properties". The detail with which the van der Waals potentials may be characterized is inherently restricted in such measurements by their statistical dependence on molecular-level dynamics. Techniques to examine these properties more directly have only recently become available.

In this thesis, van der Waals potentials are studied by scattering in "crossed molecular beams". Using them, atoms or molecules are prepared, at least in the ideal case, with a specific set of properties (rather than with a statistical distribution), and the results of individual interactions are measured. The beams of atoms or molecules are

allowed to intersect under conditions whereby the scattering of the constituent atomic or molecular particles involve only single collisions between them. The experiment consists of measuring, in a particular angular direction, the number of particles scattered out of one of the beams by the other beam. The resulting scattered intensity vs. scattering angle curve, termed a "differential cross section" (DCS), owes its shape to the interaction potential between the collision partners, and the conditions of the collision. At the thermal energies we use, only elastic scattering is possible for atom-atom systems; rotationally inelasticities may also occur in atom-molecule or molecule-molecule systems. The detailed specification of the collision, as provided by the crossed beams technique, allows us to peer behind the statistical mechanical relationship between bulk properties and interatomic and intermolecular potentials. Unfortunately however, the connection between these potentials, and the quantities measured in crossed beams experiments, remains very complicated. This is especially true of the systems considered here, whose highly quantum mechanical nature complicate physically intuitive insights.

Such physical insights provide a necessary ingredient in understanding the results of the scattering experiments. Chapter 1 is useful in developing these insights, analyzing the correlation between different features of the DCS and regions of the potential energy function. We also address the problem of presently being unable to obtain the interaction potential directly from DCS measurements, having instead to model it. Such models are usually parameterized on the basis of physically significant expectations for the model, and are then

adjusted until the resulting potential provides a satisfactory description of the experimentally measured DCS. Disagreements between the model predictions and the measurements would then directly refute the adequacy of the assumed model. However, the converse is not true: agreement between the experimental DCS and that calculated from the model potential does not necessarily justify the assumed model. Only a detailed understanding of the basis of interatomic and intermolecular forces would allow them to be correctly modeled. Such detailed knowledge is, however, lacking for the region of the potential where the balance between attractive and repulsive forces gives rise to van der Waals attractive wells. Since the DCS experiments described in this thesis are sensitive primarily to precisely this region of the potential, the model used for it must be flexible enough to allow a description of the actual interaction, even without knowing its specific form. Chapter 1 analyzes the flexibility of many of the models used to represent the radial dependence of interatomic potentials. The results are used to choose suitable mathematical parameterizations for our subsequent analyses of DCS scattering data.

In Chapter 2 we present an experimental study of the He-Ar interatomic potential. The He atom's low polarizability causes the attractive well to be very shallow, even on the scale of van der Waals forces. Consequently, the use of bulk property measurements are limited primarily to characterizations of strongly repulsive interactions. Conversely, the highly quantum nature of the system inherently limits the amount of spectroscopic information to be gained in studying the He-Ar van der Waals "molecule". Thus, He-Ar provides

an example of systems for which very detailed information about the van der Waals attractive minimum may be obtained only by thermal scattering experiments. Of course, other sources of information complement the DCS measurements; in particular, bulk properties allow the potential's extension for interatomic distances to which the DCS's are insensitive.

Up to this point, we have considered interactions modeled by potentials which depend only on the distance between the interacting particles. This "central field" assumption is quite valid for the He-Ar atom-atom system, but the degree of its validity for atom-molecule or molecule-molecule systems is not immediately apparent. In order to test the validity of the central-field assumption, Chapters 3 and 4 are concerned with the analysis of He scattered by molecular partners. These partners fall into two series: the diatomics N_2 , O_2 , CO and NO; and the non-linear polyatomics CH_4 , NH_3 , H_2O and SF_6 . As mentioned earlier in this introduction, a necessary, but not necessarily sufficient, condition for the validity of the central-field assumption is that it must provide a good description of the measured DCS's. A more direct test is provided by realistically introducing anisotropic interactions into the intermolecular potential model. Improvements in the description of the data may then be attributed to formerly neglecting interactions which could not be described by the central-field assumption. One particularly important aspect of any such improvement is that rotational excitation or de-excitation of the molecular partner can occur only if the interaction potential is anisotropic within the range of intermolecular distances sampled in the experiment. The extent of

any such anisotropic contributions to the interaction potential are expected to become larger as the asphericity of the molecular partner increases. Chapter 5, involving He-CO₂ scattering, is a brief study concerned with preliminary findings of particular interest in this regard. Because of the DCS's sensitivity to the rather large asphericity of the He-CO₂ interaction potential, both its spherically symmetric and anisotropic components may be extracted from the experiment. The anisotropic potential thus obtained should allow the rotationally inelastic DCS to be calculated, even though it is not experimentally resolved from the elastic DCS (the scattered beams were not velocity-analyzed). Thus, a study of the extent of anisotropic contributions to the van der Waals interaction potential provides detailed, though somewhat indirect, information regarding the microscopic exchange of translational and rotational energy.

The appendices include two additional papers, supplementing the five which comprise the main body of the thesis. Appendix A is a brief amalgamation of the He-Ar results from Chapters 1 and 2, and is presented as a convenient summary of these results. Appendix B concerns the study of a third series of molecules scattered from He atoms: the linear polyatomics CO₂, N₂O and C₂N₂. These were studied as an expansion on the preliminary results of Chapter 5, and as an extension of the diatomics series of Chapter 3, providing more examples of highly anisotropic systems. This study is also a prelude to future work on rotationally inelastic atom-molecule collisions. The last two appendices detail technical aspects of the studies presented in this thesis. Experimental characteristics (and quirks) are discussed

briefly in Appendix C, where we also outline some plans for new work in the immediate future of the crossed-beams project. In Appendix D, we give a brief presentation of elastic scattering theory, and outline its use in the experimental data analysis.

CHAPTER 1

Sensitivity of the elastic differential
cross section to the interatomic potential

Scattering of thermal He beams by crossed atomic and molecular beams.

I. Sensitivity of the elastic differential cross section to the interatomic potential^{a)}

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ABSTRACT

The ability of diffraction oscillations in atomic beam scattering experiments to uniquely determine interatomic potentials for highly quantum systems is examined. Assumed but realistic potentials are used to generate, by scattering calculations and incorporation of random errors, differential cross sections which are then treated as if they were "experimental" data. From these, attempts are made to recover the initial potential by varying the parameters of assumed mathematical forms different from the original one, until a best fit to the "experimental" results is obtained. It is found that the region of the interaction potential around the van der Waals minimum is accurately determined by the "measured" differential cross sections over a range of

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interatomic separations significantly wider than would be expected classically. It is also found, for collision energies at which the weakly repulsive wall is appreciably sampled, that the SPF-Dunham and double Morse-van der Waals types of potentials lead to accurate determinations of the interatomic potential, whereas many other mathematical forms do not. Analytical parameterizations most appropriate for obtaining accurate interatomic potentials from thermal DCS experiments, for a given highly quantum system, may depend on the collision energy used.

I. INTRODUCTION

In recent years, interatomic potentials between closed-shell species have become better determined.¹⁻³ However, the important region of the van der Waals attractive minimum results from the balance between the competing short- and long-range forces, making its theoretical characterization more difficult than that of the adjacent regions.⁴ Various experimental techniques have also been used to obtain potentials with increased reliability over specific ranges of interatomic separations. Recently, a more unified approach has been adopted in the use of various types of experimental data to determine a potential curve describing the interaction over a wide range of separations.⁵ The suitability of virial^{6,7} and transport coefficient^{5b,7,8} data and of integral cross sections^{7b,9} for the determination of the potential has been examined elsewhere.^{2c,10} In this paper we extend this examination to differential cross section (DCS) scattering data--exhibiting rapid quantum oscillations and sometimes also a vestige of the classical rainbow--which are widely regarded as a means of probing the attractive well and low-energy repulsive regions.^{2d,11} The sensitivity of such DCS data to the interatomic potentials for highly quantum systems may be significantly different from that indicated by classical or semiclassical considerations,^{3f} and heretofore has not been examined in detail. In a subsequent paper¹² (hereafter referred to as Paper II of this series), we will analyze the results of our own recent measurements of the He-Ar DCS, in light of the present discussion.

Although the He-Ar system has been studied previously by differential scattering,^{13,14} as well as by a wide variety of other techniques,¹³

considerable differences remain in the resulting potentials. In Sec. II we discuss the limitations that many of these techniques have in determining interatomic potentials for light systems. We also describe several parameterized potentials most commonly used for fitting experimental results which are sensitive to van der Waals interactions. In Sec. III, we use realistic interaction potentials (corresponding closely to, e.g., the He-Ar system) to calculate simulated "experimental" DCS's, to which the model potentials of Sec. II are fit. We then compare the "known" potentials with the fitted ones and discuss the results in terms of these various potential forms' flexibility in fitting the DCS data, as well as the accuracy with which each of these forms reproduce the "correct" potentials. By additionally simulating "experimental data scatter" in the DCS's, we also determine the accuracy with which each of the various stylized potentials may be obtained. We concur with Bickes and Bernstein¹⁵ that the SPF-Dunham (SPFD) potential¹⁶⁻¹⁹ is a simple analytical representation that can be used to reproduce the potential and can easily be used for the analysis of various kinds of experimental data.¹⁵ In Sec. IV we extend (for light systems) their examination of the SPFD potential form, demonstrating the uniqueness of the potential as obtained by an improved regression procedure. We similarly analyze the suitability of a new double Morse-van der Waals (M^2SV) type of mathematical parameterization, which has a flexibility comparable to that of the SPFD potential form. We further determine the range of interatomic separations to which the DCS data are sensitive. This range should also be applicable to He-molecule systems, and useful in the interpretation of H_2 (D_2)-molecule

data.²⁰ In addition, we analyze the degree to which a given region of the potential may be varied independently of the remaining regions by appropriate changes in the SPFD parameters. We use these results to correlate features of the DCS with particular regions of the potential, and to place "confidence levels" on potentials determined by regression techniques from DCS experiments. Finally, we summarize our major conclusions in Sec. V.

II. INTERATOMIC POTENTIALS

With a few notable exceptions,^{3b, 21, 22} experimental attempts to determine the weakly attractive van der Waals region of interatomic potentials suffer from a number of difficulties. Foremost among these is the fact that the dependence of measurable properties on the potential is through an integral relation. We first discuss these exceptions.

Direct inversion of molecular beam scattering data has been used in different ways²¹ to obtain potentials for the highly repulsive short-range ("classical") interactions, and in the attractive well region for systems of a "semi-classical" nature. However, because of the large quantum effects for thermal He scattering due to a low B parameter,²³ these analysis techniques are inappropriate. Quantum mechanical inversion procedures^{2a, b} are only now beginning to be applied to experimental scattering data.^{24, 25}

Spectroscopic studies using the RKR method have enabled accurate information to be obtained about the shape of the potential well of rare gas van der Waals molecules supporting significant numbers of bound vibrational states.²² Unfortunately the potential energies at which the well width may be evaluated are restricted to the positions of these states.²⁶ It is thus possible to obtain only a small amount of information about the potential of most He-containing pairs by this procedure.²⁷

Besides these experimental techniques, semi-empirical theoretical methods have been used to calculate reliable interatomic potentials for some systems. Most early studies were restricted to short-^{3a} or long-range²⁸ interactions, but detailed results for the intermediate range including the potential minimum are currently available.²⁹⁻³¹

Although successfully applied to heavy rare-gas pairs, He- (and to a lesser extent Ne-) containing systems have often been regarded as "anomalous" from the point of view of electron gas theories.²⁹ Accurate ab initio results have been obtained for He₂,³² but such calculations for asymmetric He pairs are still too difficult.

Thus, the above techniques have been exploited profitably, but are still inappropriate for the He-Ar system, herein used as an example for similar systems. Other means must therefore be used to deduce these potentials. A common procedure, which is used to analyze transport and virial coefficient data or low-energy DCS data, is to assume a functional form for the interaction potential and then optimize its parameters to fit the experimental results. Among the possible disadvantages of this method are the lack of uniqueness of the resulting potential,³³ and the restriction of the potential obtained from the experiment to the assumed form. Furthermore, there is no point-to-point correspondence between the derived potential and the measurements (i.e., they are related by integral expressions), making it difficult to determine the sensitivity of the potential to the data. To some extent all these difficulties may be addressed by the use of different functional forms for different regions of the potential, which are joined smoothly. This procedure has already been used extensively for rare-gas atom-atom scattering data.^{2a, 34} Another approach is to use a multiparameter functional form with sufficient flexibility to enable the potential to be changed in only one region at a time.^{2a}

Of course, the flexibility that justifiably may be used is limited by the variety and accuracy of the available data, and by its sensitivity

to the potential. With the extensive compilations of data that are available for Ar_2 , it is possible to construct a numerical potential by a multivariate technique.^{7a} Because such an abundance of data is not available for most systems, our goal, for the analysis of low-energy DCS data, is to examine the suitability of some of the more common functional forms,³⁵ each with only a few adjustable parameters. We also compare³⁶ these potentials with some of the less flexible but more traditional ones.¹ All of these are of the "corresponding-states" form,^{3h} with

$$V(r) = \epsilon \cdot f(\rho), \quad \rho = r/r_m,$$

where r_m and ϵ are the potential minimum position and depth, respectively; the position of the zero of the potential σ may be related to r_m and the potential shape $f(\rho)$.

The potential shapes we consider are:

$$\text{a) Kihara, }^{1, 3d, g} \quad f(\rho) = \frac{6}{n-6} \left[\left(\frac{1-\gamma}{\rho-\gamma} \right)^n - \frac{n}{6} \left(\frac{1-\gamma}{\rho-\gamma} \right)^6 \right], \quad (1)$$

where γ is the hard-core radius parameter and n is the repulsive term exponent. The Lennard-Jones (LJ) $n-6$ potential may be recovered by setting $\gamma = 0$. Note that for $\gamma \neq 0$ the asymptotic behavior includes ρ^{-7} and higher-order terms.

$$\text{b) Buckingham (exp-6), }^{1, 3d, g} \quad f(\rho) = \frac{1}{\alpha-6} \left[6e^{\alpha(1-\rho)} - \alpha\rho^{-6} \right]. \quad (2)$$

The only shape parameter available is α , governing the behavior of the exponential repulsion term.

c) Klein-Hanley,³⁷

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

Shape parameters designed to primarily govern the short- and long-range regions are n and c_6 ,³⁸ respectively. The second dispersion term in ρ^{-8} is included, but its coefficient is fixed by the other parameters.

d) Buckingham-Corner (BC),¹

$$f(\rho) = \frac{e^{b(1-\rho)}}{b-8} (8 - 2c_6) - \left[c_6 \rho^{-6} + \frac{\rho^{-8}}{n-8} (6c_6 + b - bc_6) \right] g(\rho), \quad (4)$$

where

$$g(\rho) = e^{-[4(\frac{1}{\rho} - 1)^3]} \quad \text{for } \rho < 1 \quad \text{and} \quad g(\rho) = 1 \quad \text{for } \rho \geq 1.$$

As for the Klein-Hanley potential, the shape parameters b and c_6 are designed to govern the short- and long-range regions, respectively. Similarly, the second dispersion term in ρ^{-8} is included, but its coefficient is fixed by the other parameters. The Tang-Toennies semi-theoretical^{31a} and Hartree-Fock dispersion^{31b} models are variants of the BC potential.

e) Barker-Bogetic-Pompe (BBP),^{5e, 39}

$$f(\rho) = e^{\alpha(1-\rho)} \left[A_0 + \sum_{i=1}^N A_i (\rho - 1)^i \right] - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad (5)$$

with

$$A_0 = \sum_{i=1}^3 c_{2i+4} - 1$$

and

$$A_1 = \alpha A_0 - \sum_{i=1}^3 (2i+4) c_{2i+4}.$$

Available parameters are α [bearing some resemblance to the $\exp^{-6}$ α of Eq. (2)], the A_i coefficients ($i = 2, \dots, N$), and the dispersion constants (c_6, c_8, c_{10}). The expansion order N is usually no larger than 5. This N^{th} -order BBP potential is highly flexible and is appealing theoretically, with the dispersion series being added to the exponentially repulsive term.

Although some of the potential energy functions above are rather flexible, they all suffer from the drawback that the long- and short-range behaviors are interdependent. To ameliorate this problem, we also investigated several piecewise analytical potentials with smooth joining conditions.

f) Double Lennard-Jones,⁴⁰

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

Use of the LJ form [Eq. (1) with $\gamma = 0$] for each branch assures smoothness at $\rho = 1$. Available shape parameters are n_1 , m , and n_2 ; the last may be used to determine the leading dispersion term independently of the repulsive region.

g) Morse-Spline-van der Waals (MSV)⁴¹ and M^2SV ,

$$\begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] \quad \text{for } \rho \leq \rho_1 \\ f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho_1 < \rho < \rho_2 \\ &\quad \text{for } \rho \geq \rho_2. \end{aligned} \quad (7)$$

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 is usually held fixed at 1.6.^{29a} 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 by using a second Morse function for $r < \sigma$, joined smoothly to the first at $r = \sigma$. This M^2SV potential then has the additional parameter β' .

h) SPF-Dunham (SPFD),¹⁸

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

Smoothness conditions at $\rho = \rho_f$ are used to fix the highest-order coefficients b_N and b_{N-1} . The joining point ρ_f is treated in the same fashion as the second spline point of the MSV form and is normally larger than 1; similarly, the b_i ($i=1, \dots, N-2$) SPFD coefficients determine the shape of the repulsive and well regions while the dispersion series constants are also independent parameters.

For reduced distances below $\rho = 0.65$, the exp-6, BBP, and SPFD potentials often show spurious maxima or oscillations. These are removed by using an exponentially repulsive piece, i.e., $f(\rho) = A e^{-b\rho}$, from some joining value 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 use $\rho_i = 0.70$.

All these potentials are used for the scattering calculations presented here and some of them are used for the experimental data reduction procedures that are described in detail in Paper II. Care has been taken to perform these calculations with a high degree of accuracy and consistency in order to be able to make distinctions between various closely related interatomic pair potentials. The procedure consists of the standard partial wave summation (using exact quantum or Rosen-Yennie^{3c, 42} phase shifts for $\ell \gtrsim 50$, after which JWKB phase shifts are adequate), followed by kinematic transformations to the laboratory frame (using room-temperature hypersonic beams and out-of-plane detection of He atoms). The calculations include extensive velocity and angular averagings. The calculational parameters used are chosen to simulate the experimental conditions of Paper II, which are typical for DCS measurements for highly quantum systems, and are described in detail in that paper. Experimental conditions assumed for this study are a relative collision energy of 64 meV, with a corresponding relative velocity resolution of $\sim 11\%$, and an overall angular resolution of $\sim 2^\circ$. The range of scattering angles considered is from 1.5° to 20° , with intensity measurement errors of $\sim 2.5\%$ to $\sim 20\%$, respectively.¹² The simulation described here enables us to gain detailed insight as to the amount of information that may be extracted from the actual experiments. It further suggests criteria helpful in choosing mathematical parameterizations (in addition to those specifically included in this study) suitable for iteratively determining the van der Waals attractive regions of highly quantum systems.

III. POTENTIAL FORM SUITABILITY

The suitability of a particular functional form chosen to represent the potential must be judged by several criteria. Obviously, it must reproduce experimental data which are sensitive to it. This form should also have sufficient flexibility to approximate closely the true potential, whose mathematical form is usually unknown. Finally, the potential obtained must be unique over the range of interatomic distances for which the data are sensitive. The correspondence to the real interaction of any stylized potential derived from experimental measurements depends directly on the extent to which the experiment and the potential meet the above criteria. Our method of determining this correspondence is to use the potentials of the previous section to fit the scattering results corresponding to an assumed interaction.

As noted in the Introduction, He-Ar is an example of a system whose interatomic potential is still the subject of considerable controversy. Because our purpose here is merely to discuss the suitability of the iterative procedures used to determine potentials from scattering experiments, we arbitrarily use as the known potential one which very closely resembles a recently published potential for He-Ar¹³ as the "known" interaction. We use it to calculate DCS's and then add appropriate data scatter. Treating these as simulated experimental results, we can then obtain fitted potentials iteratively. The analytical forms used in this procedure are different from those used to represent the "correct" potential, just as in the actual data reduction procedure. This somewhat circular route enables us to determine the suitability of a given functional form according to the first two criteria outlined above.

Compliance with the third criterion is later gauged for the particularly successful SPFD functional form [Eq. (8)]. Because the potential governing the interaction is "known", the circular approach is more pertinent to the present discussion than would be comparisons of experimentally determined potentials with one another or with theoretical ones, where none of the potentials are known to be "correct".

We choose two different "known" potentials for the present simulation studies. One is given by the MSV functional form [Eq. (7)], with the following parameters,¹³

$$\begin{aligned} r_m &= 3.540 \text{ \AA} ; & \epsilon &= 2.085 \text{ meV} ; & \beta &= 5.45 ; \\ \rho_2 &= 1.40 ; & c_6 &= 1.434 ; & c_8 &= 0.220 ; & c_{10} &= 0.00. \end{aligned}$$

It must be emphasized that this potential need not actually be "correct" for the discussion presented here to be valid, nor should one construe any particular significance to the choice of the MSV shape. The other "known" potential is given by the Klein-Hanley functional form [Eq. (3)], as discussed in Sec. IV.A. Using the experimental conditions of Paper II, the MSV reference potential was used to calculate a DCS versus scattering angle curve (points exactly on the solid curve of Fig. 1), which then serves as one set of experimental scattering "data". Five more simulated experimental DCS's are shown in Fig. 1. These were generated by the pointwise introduction of random data scatter about the first DCS, using a normal distribution with the error bars of Paper II representing the standard deviation at each scattering angle, as shown in the figure.

Submitting each of these sets of generated DCS's to the data reduction procedures outlined in the previous section yields six different sets of potential parameters for each potential form. The sensitivity of the data to the potential at a given point is reflected by the potential energy spread among the six potentials at that point. Note, however, that this will not apply to potentials with shapes that are too rigid to reproduce the scattering results, because their parameters necessarily reflect only the gross scattering features.

For each functional form used (excluding the MSV and M^2SV forms which are treated independently in Sec. IV.A), each of the DCS curves is fit independently to potentials differing only in the values of their parameters. In Table I we show the corresponding average r_m and ϵ parameters as well as the standard deviations of their means. Because the DCS data are sensitive to the well region, comparing the fitted r_m and ϵ values with those of the original MSV potential is a first indication of the accuracy with which they are obtained. To this extent, their precision for a particular form is then reflected by the standard deviations of Table I. We also show in that table two goodness-of-fit statistical indices. We define the first as

$$\chi^2 = \sum_{i=1}^n g_i (I_i - \alpha \sigma_i)^2 . \quad (9)$$

At each of the n scattering angles, the calculated cross section σ_i must be scaled to the "experimental" DCS I_i by the scaling factor α because only relative intensity measurements are made. The weighting factors (the g_i) are calculated from error bars corresponding to the data.

Because the scaling factor is adjusted to bring the calculated and

experimental DCS into vertical register, we may also calculate a confidence level for it;

$$\Delta\alpha_{0.95} = t_{0.05}(n-k) \left[\frac{\chi^2}{(n-k) \cdot \sum_{i=1}^n g_i \sigma_i^2} \right]^{\frac{1}{2}}. \quad (10)$$

Here $t_{0.05}(n-k)$ is Student's t-distribution statistic for a confidence level of 0.95 with n data points and k parameters.⁴³ The goodness-of-fit statistic, $\Delta\alpha_{0.95}/\alpha$, is then independent of the arbitrary units chosen for the data, whereas χ^2 is not. The former also takes into account that a fit with a greater number of parameters must have a lower χ^2 in order to be of the same quality because $t_{0.05}(n-k)$ increases with k for a given n ; the $\Delta\alpha_{0.95}/\alpha$ statistic therefore provides a more appropriate measure of the goodness-of-fit. The five DCS's with data scatter as shown in Fig. 1 have an average $\Delta\alpha_{0.95}/\alpha$ value of 1.8%. We find that fits having $\Delta\alpha_{0.95}/\alpha$ values considerably higher than this (say, 2.2% or greater) are not satisfactory.

Referring to Table I, we see that the simple two- and three-parameter potentials are generally too inflexible to reproduce the scattering results (i.e., they result in high values of $\Delta\alpha_{0.95}/\alpha$), even for the DCS with no data scatter. Comparison of plots of the derived LJ 12-6 potentials with that of the "known" MSV one show that the former have repulsive walls which are too "hard" (a generally observed deficiency^{2c, 13, 32}) and values of r_m which are consistently too small. By using LJ n-6 fits, the repulsive wall is made more flexible and allows a better determination of this region, but the values of r_m and ϵ obtained are still systematically low. The exp-6 shape is better able to

reproduce the scattering results and the repulsive wall of the potential, but the resulting values of r_m and ϵ are only marginally improved. The LJ n-6 and exp-6 potential forms of Eqs. (1) and (2), respectively, are examples of three-parameter models using a single analytical parameterization. Another example of such a parameterization, also based on an inverse-power dependence of the radial distance, is the " $n(\rho)$ -6" potential of Maitland and Smith.^{35a} It utilizes a repulsive term exponent n which is a function of the radial distance [see Eq.(1) with $\gamma = 0$], and has been of some use in fitting gas phase bulk properties.^{14a, 35a} As noted by Maitland and Smith, however, it cannot reproduce the multipole expansion appropriate for long-range interactions, nor can the shape parameter controlling the radial dependence of n be related easily to physically meaningful features of the potential.^{35a} As with the other potentials considered explicitly above, a more serious objection to the $n(\rho)$ -6 parameterization is that it necessarily couples the long-range attractive region to the short-range repulsive region.

Only the well depth parameter is improved by the Kihara modification of the LJ n-6 form. The DCS fits are marginally improved, but the repulsive region remains unrealistically "hard". Moreover, a very high statistical correlation⁴³ exists between the repulsive parameters γ and n , indicating that only one of them is truly independent. Consequently, using a Kihara-modified LJ 12-6 potential [i.e., fixing $n = 12$ but fitting γ of Eq.(1)] results in no substantial change from the analytically simpler and asymptotically more appropriate LJ n-6 model. On the other hand, the Klein-Hanley modification [Eq.(3)] of the LJ model yields better fits to the DCS data, and r_m and ϵ values systematically

low by only 1% (Table I). Although the attractive well is thus accurately reproduced, the short-range region is still too repulsive and the region beyond the minimum is insufficiently attractive. There is again a very high parameter correlation, in this case between the repulsive exponent n and the reduced dispersion coefficient c_6 , indicating that the short- and long-range regions are not independent within the framework of this model. This correlation precludes any meaningful values from being obtained for the dispersion coefficients. The BC parameterization [Eq. (4)] also yields good fits to the DCS data, and potentials whose r_m parameter values are in good agreement with that of the MSV reference potential. However, the ϵ values are systematically low by $\sim 5\%$. In addition, the region beyond the minimum is insufficiently attractive, as reflected by fitted values of the C_6 dispersion constant that are systematically too low by a factor of three. Fixing the long-range part of the BC potential for systems for which the dispersion coefficients are known would be inappropriate, since this would also fix the shapes of the short-range repulsive and attractive minimum regions of the potential. We see that the BC parameterization does not allow the long- and short-range regions of the potential to be independent of each other, precluding meaningful potentials from being obtained for them.

The highly flexible BBP potential [Eq. (5)] is the most successful of the forms with a single analytical expression. The second-order parameterization with only the first term of the dispersion series included (the three adjustable shape parameters are c_6 , α , and A_2) yields good fits to the DCS. The potential obtained and the fitted r_m and ϵ parameters also agree very well with those of the original MSV

potential, as seen in Table I. The attractive region immediately beyond the potential well is slightly too weak, a defect that can be cured by the addition of a second dispersion term, which further improves the DCS fitting.

In spite of the above advantages of the BBP parameterization, there are several difficulties which curtail its usefulness. By directly fitting the BBP form to other reduced potential functions, without the intermediate DCS calculations, we find that it is unable to reproduce the repulsive wall unless the expansion is carried out to fourth order [$N = 4$ in Eq.(5): the fitted shape parameters are c_6 , c_8 , α , A_2 , A_3 , and A_4]. As an example, we show in Fig. 2 the original MSV potential, and deviations from it for $N = 2$ and $N = 4$ BBP fits. It is apparent that although the fit is good in the attractive region, an excessive number of parameters is required to gain sufficient flexibility for the repulsive region. Because the non-reduced BBP potentials which are fit to the DCS's reproduce well the "correct" potential, as noted earlier, it is seen that the additional r_m and ϵ parameters must be used to compensate for the reduced potential form's apparent lack of flexibility (at least for a reasonably low expansion order N); these potential well parameters thus cannot be determined independently of the potential shape, within the framework of the BBP model. A further objection to the BBP parameterization may be anticipated on theoretical grounds. The attempt made merely to "add on" the dispersion series to a suitable short-range potential is inappropriate at intermediate and short-range interatomic separations^{2c, 29a, 45} because the perturbation method used in the dispersion series formulation fails there. The fitted dispersion constants, as obtained from this model, cannot there-

fore be regarded as physically meaningful; this is reflected in the very high parameter correlations observed between any of the shape parameters of the second-order ($N = 2$) DCS fitting, even if c_8 is held fixed.

The piecewise analytical potentials may be expected to reduce the problem of correlations between the long- and short-range components of the potential. For example, use of the double-LJ model [Eq.(6)] enables good fits to be obtained, with the long-range potential being recovered very well. The short-range repulsion is slightly too steep, but a more serious deficiency is in the well region and is apparent from Table I. Fitted r_m and ϵ values are systematically too large, by about 2% and 10%, respectively. Thus it appears that the repulsive region parameters (n_1 and m) are only weakly statistically correlated with the attractive region parameter (n_2). The motivation for using the double-LJ parameterization is to decouple these two regions of the potential. However, n_1 and m are still highly correlated with the well region parameters r_m and ϵ . Moreover, there exists a high parameter correlation among n_1 and m , leaving only one of them available to determine independently the shape of the repulsive wall. Indeed, fixing $m = 6$ and fitting to the DCS with the remaining four parameters results in little change of either the DCS or of the derived potentials (Table I).

The MSV form [Eq.(7)] could not be tested in the usual manner because of its use as the starting potential. This form was, as a result, tested independently against a Klein-Hanley reference potential, as discussed in Sec.IV.A. However, it is already clear that the MSV form also suffers from a parameterization that forces correlation between the repulsive region and the attractive well, since both regions are

essentially determined by, and are very sensitive to, the Morse β parameter. In order to avoid this restriction, an exponential repulsion may be splined onto the MSV curve in the short-range region, giving the ESMSV form.^{34c} This modification has been used in a number of studies to obtain potentials simultaneously describing dilute gas transport and equation-of-state properties (which are primarily sensitive to the repulsive interactions), and thermal energy scattering results.^{11, 13} This approach, however, still leaves a substantial portion of the low-energy repulsive wall parametrically coupled to the attractive well. In order to avoid this coupling, we may use the M^2SV potential with a different Morse parameter β' for interatomic separations $r < \sigma$. For either the MSV or M^2SV potentials, however, changes in the long-range region are not restricted to values of ρ beyond ρ_2 because of the effect of such changes on the splined portion between ρ_1 and ρ_2 .^{14a}

A similar problem could also be expected to plague the SPFD potentials [Eq. (8)]. In this case, changes in the long-range region also affect the potential for all $\rho \leq \rho_f$ because of the smoothness conditions imposed upon the two highest-order coefficients. Fortunately, as we show in Sec. IV, the fitted SPFD potentials (with only the c_6 term beyond $\rho_f = 1.6$ and $N = 2, 3$, or 4) can have their long-range regions modified with no substantial effect on the potential for $\rho \gtrsim 1.3$. Consequently, these forms should allow good recovery of the potential in the long-range region. Furthermore, they all show sufficient flexibility to fit the scattering data just as well as the original MSV potential does. This is

reflected in the good agreement between the original and fitted potentials throughout the well (Table I) and adjacent regions, although the repulsive region seems to be slightly too steep, as seen in Fig. 3. Values of r_m and ϵ are recovered to within 0.5% and 5%, respectively. Most of the discrepancy in ϵ is due to the second-order SPFD fits [$N = 2$ in Eq.(8)], which have systematically deeper wells than those of higher order; third- and fourth-order fits each reproduce ϵ to within 1%. These results substantiate previous claims that the SPFD potential form is eminently suitable for use in analyzing thermal scattering results.^{15, 18, 33b} It should be emphasized that the second-order potentials are obtained with only two of the available shape parameters [c_6 and b_0 of Eq.(8)]. The third-order potentials show additional flexibility and result in better fits to the DCS, but those of fourth-order show no further improvement.

IV. UNIQUENESS, FLEXIBILITY, AND SENSITIVITY

Because of the ability of the SPFD potential to adequately reproduce the scattering results and to recover the original MSV potential, we have investigated it further. We pay particular attention in this section to its uniqueness, flexibility, and sensitivity.

A. Uniqueness

Previous users of this potential cautioned that there may exist multiple local minima on the least-squares hypersurface; that is, the fitted potential may depend on the first-guess parameters of the iterative fitting scheme.¹⁵ We address this problem by arbitrarily beginning second-order SPFD fits with parameters corresponding to the LJ 12-6 shape; $b_0 = 36.0$ from the curvature at the bottom of the well, and $c_6 = 2.0$ from the long-range behavior. Starting values of r_m and ϵ were up to 10% and 30% different from their "correct" values, respectively. Fitting to one of the DCS with data scatter gives the same parameter values, within four to six iterations, as those obtained with first-guess parameters corresponding to the original MSV potential.⁴⁶

Initial values of r_m and ϵ cannot be too different from the "correct" ones, however. A difference of 20% and 50%, respectively, in these parameters is sufficient to cause the iterative scheme to converge to a grossly incorrect potential. In this case, the difficulty is indicated by the very poor fit and contorted potential obtained and may easily be avoided a priori. For example, initial fitting with any one of the simpler functional forms may be used to obtain values of r_m and ϵ

within the (apparent) convergence radius of the second-order SPFD potential. Indeed, the range of values obtained for the r_m and ϵ parameters from all the fits to each of the DCS with data scatter are within 3% and 15% of their "correct" values, respectively.

Using the smoothness conditions, the second-order fit provides a reliable value for the b_1 parameter which can be used as a starting point for the third-order fit. This in turn provides a good guess for the b_2 parameter; SPFD potentials with unique parameter values can thus be obtained for fits up to at least fourth-order.

A possible bias in our analysis is that the SPFD potential might be adaptable only to the MSV shape, in part because of their similar piecewise long-range behaviors and smoothness conditions. To test this possible bias, we calculated a new input "experimental" DCS from an assumed potential of the Klein-Hanley form [Eq.(3)], rather than of the MSV shape. The former is represented by a single analytical function bearing no mathematical relation to any but the LJ family of potentials [Eqs. (1) and (6)], and includes a second dispersion term in ρ^{-8} . We then fit this DCS, including "data scatter", to the third-order SPFD form (fitting the r_m , ϵ , c_6 , b_0 , and b_1 parameters, but setting $c_8 = 0$). To allow a more rigorous evaluation of the MSV and M^2 SV forms than that outlined towards the end of the previous section, we also submit the "experimental" DCS's to fits with these potentials (also without terms in ρ^{-8}). The results are displayed in Table II and Fig. 4.

From Table II, it is seen that the "correct" range parameter r_m is recovered quite well by all three potentials (error < 1%). The third-order SPFD potential is able to reproduce the "experimental" DCS's

calculated from the Klein-Hanley assumed potential just as well as those calculated from the MSV assumed potential (Table I); although the average well depth parameter value ϵ is too large by about 4%, this is within the estimated error limit of 10% for the attractive well region of the potential (see the end of this section and Table IV). For the MSV potential, the average parameter values and quality-of-fit statistical indices are less favorable than for the third-order SPFD potential; its ϵ value is about 11% too large and the fitting quality is not quite as good. Use of the M^2SV potential, which has a second Morse function to describe repulsive interactions independently of the attractive well, results in potentials which have very good average parameter values (r_m and ϵ values in error by $< 1\%$). The fits are of the same quality as those of the third-order SPFD potentials, although the short-range repulsive behavior of the M^2SV potential is too "hard" (by $> 40\%$ at $r = 2.9 \text{ \AA}$ compared with $< 15\%$ for the SPFD and MSV potentials; also see Table IV).

The second series of simulation results, using a Klein-Hanley "reference" potential, thus clearly shows that the SPFD potential is sufficiently flexible [with $N \geq 3$ in Eq. (8)] to recover two realistic potentials of very distinct mathematical forms, both of which are quite different from the SPFD form. This second simulation study complements the first, which in using an MSV "reference" potential, showed that of all the mathematical forms analyzed [Eqs. (1) through (8), except for (7)], only the SPFD one was adequate to reproduce the simulated DCS's and to recover the original potential. Our analysis of the MSV and M^2SV potentials [Eq. (7)] in the second simulation study clearly indicates that the M^2SV potential may be preferred over the

MSV potential, and perhaps even over the SPFD potential in the attractive well region. It is important to note that the third-order SPFD and the M^2SV potentials, both of which have five adjustable parameters, are indistinguishable from each other and from the Klein-Hanley reference potential (see Fig. 4) within the estimated uncertainty of the derived potential energy curves (see the end of this section and Table IV). The MSV potential, having only four parameters, is distinguishable from the reference potential (Fig. 4), indicating that it provides a representation for the potential which, in view of the improvements to be gained by using the five-parameter models, is not quite as adequate. Although the M^2SV potential appears to be slightly superior to the third-order SPFD potential, we feel that the latter provides a more unified representation,^{15,18} as well as having a sounder basis in theory;¹⁷ we also recall that the M^2SV potential is too "hard" in the short-range region ($r < 2.9 \text{ \AA}$), despite the sensitivity of the DCS to the potential there as shown later in this section.

We also assess the degree to which independent scattering experiments may complementarily be used to determine the interaction potential. Using the five sets of third-order SPFD parameters obtained by fitting the individual DCS's with "experimental data scatter", we calculate the corresponding five potentials and display the arithmetic average of these at each interatomic separation in Fig. 5. It can be seen that the data obtained from the five "independent experiments" are indeed complementary; the averaged potential is significantly closer to the original MSV potential than are any of the third-order SPFD fits to the DCS (compare with Fig. 3), with the only significant discrepancy occurring in the repulsive wall region.

B. Flexibility and Sensitivity

Besides fitting the SPFD potential to the "experimental" DCS's, we may also fit its reduced form to other reduced potential functions, without the intermediate DCS calculations, as was done with the BBP potential in Sec. III. The reduced potentials of Eqs. (1) through (7) with "reasonable" shape parameter values are reproduced almost identically by the numerically fitted SPFD shapes (third-order or higher), demonstrating the latter's ability to fit interaction potentials of any reasonable form in the region beyond about $\rho = 0.65$ ($\lambda = -0.5$). Thus, when fitting to the DCS's, the two reduction parameters r_m and ϵ have a large degree of independence from the shape parameters (in contrast, for example, to the BBP potential, see Sec. III); the resulting potential energy function in general, and the well depth and position in particular, are parameterization-independent.

With the flexibility attained by the SPFD potentials, we now embark on an investigation of the possibility of analytically varying only a selected region of the potential. This would enable a determination to be made of the sensitivity with which each region is probed by the thermal scattering results.

Classically, of course, this could be determined simply by reference to the deflection function,^{3f, 48} which would also serve to locate the limits of the interatomic distance range sampled by the experiment (hereafter called the range of sensitivity). Such arguments have been used in some instances to provide an indication of the correspondence between specific regions of the potential and the scattering results. On this classical basis, it has been claimed that these

experiments are insensitive to the long-range region,^{14, 49} or even that they are sensitive only to the low-energy repulsive wall of the potential.^{2c, 15, 50} The further implication is that the attractive well and long-range behavior are probed only by very low scattering angles, since the classical rainbow occurs at a laboratory angle of 3.7° for this system. However, the quantum mechanical results discussed below indicate a greater range of sensitivity.

The SPFD potential form is suitable for a determination of the upper limit of the range of sensitivity because of the availability of the ρ_f parameter. Thus, C_6 coefficients³⁸ obtained by fitting the various DCS having data scatter may show large deviations from the "correct" value and from each other, only for cases in which ρ_f lies beyond the range of sensitivity of the potential to the scattering results. For third-order fits, the average of the C_6 values obtained (see Table III) agree well with the C_6 coefficient of the original MSV potential for all the ρ_f 's tested ($\rho_f = 1.4, 1.6, 1.8, 2.0, \text{ and } 2.2$). However, standard deviations of those C_6 values for each ρ_f are below 10% only for the lower values of ρ_f ($\rho_f = 1.4, 1.6, \text{ and } 1.8$). The much less consistent C_6 values for $\rho_f = 2.0$ and 2.2 indicate that the data are not sensitive to the potential beyond about $\rho = 1.8$. To assess the extent to which the scattering results are sensitive to the long-range region, we may also fit the c_8 parameter of the SPFD potential, for $\rho_f = 1.6$. Third-order fits to the DCS with data scatter yield widely varying values of C_8 . Furthermore, through statistical correlations with the c_8 parameter, even the fitted values of C_6 deteriorate markedly.

Thus the C_6 coefficient obtained from the third-order SPFD fits should be reliable to within 15%, insofar as the contribution from higher-order dispersion terms is small (for the original MSV potential, $c_8\rho^{-8}/c_6\rho^{-6} = 6\%$ at $\rho_f = 1.6^{13}$); however, these higher-order terms may not be determined reliably^{45,51} from experiments at present. It is seen that the upper limit of the range of sensitivity of about 6.5 Å ($\rho = 1.8$) extends well beyond the 4.8 Å value imposed by classical considerations.

The approach we use to determine the lower limit of sensitivity is to modify exponentially the third-order fitted SPFD potential at chosen values of ρ_i , as discussed in Sec. II. The DCS's calculated with these potentials begin to show manifestations of the modification (which "hardens" the repulsive wall) for values of ρ_i greater than about 0.82. It is interesting to note that the first effect of increasing ρ_i is to decrease the DCS at angles beyond the first minimum (10° in the lab frame). Values of ρ_i nearer the zero of the potential (at $\rho = 0.873$) cause radical changes throughout the angular range of the calculated DCS. In particular, the low-angle shoulder near the classical rainbow becomes smoother. The ρ_i obtained from this analysis corresponds to significant differences between the exponentially modified and original SPFD potentials for values of ρ below about 0.81. Thus the lower limit of sensitivity to the potential is about 2.8 Å, very close to the 2.9 Å value determined from a classical analysis. Because of the highly repulsive wall encountered in short-range interactions, it is not surprising that the lower limit of sensitivity would be estimated more reliably by classical arguments than the long-range interactions.

Having thus determined an approximate range of the potential sampled by thermal DCS scattering results for this system, we now address the question of the accuracy with which the potential is determined. The original MSV potential is numerically modified within each of a few chosen regions having the somewhat arbitrary limits imposed in Table IV. The SPFD shape obtained by direct fitting to the new reduced potential may then be analyzed for its ability to adjust to these discrete changes.

With four available shape parameters (b_0 , b_1 , b_2 , and c_6) of the fourth-order SPFD potential, an initial attempt to specify a like number of regions was made. As indicated toward the end of Sec. III, the long-range region of the potential is largely independent of the others; the short-range region apparently also shows such independence. However, within the SPFD parameterization, this initial attempt indicates that the intermediate range should be treated as one, rather than as two independent regions. Subsequent fitting to the MSV potential with numerical modifications in three regions instead of four show a moderate degree of success in decoupling the long- and short-range behaviors from the intermediate region, as well as from each other. It may also be seen from Fig. 6 that the ability of the fourth-order SPFD model to fit the modified MSV potential is largely independent of the magnitude of the changes made.

It is also apparent that because the reduced SPFD potential can adjust to changes in just three regions, there are only three uncorrelated shape parameters within the range of interatomic separations to which the DCS data are sensitive. This conclusion is further supported by the

earlier observation that improvements in the DCS fits are noted for SPFD potentials up to third-order, but not for higher orders. In addition, since the r_m and ϵ parameters independently determine the scale of the potential, we conclude that up to five independent parameters may justifiably be used for fitting DCS data of the type being considered, with SPFD potentials.

The effects on the calculated DCS due to these parametric modifications of the potential may most easily be seen by neglecting the loss of angular resolution caused by experimental averagings (see Fig. 7). Alterations in the intermediate range produce the largest effects, especially in the rainbow region around 3.7° where an increased attraction produces a more pronounced shoulder. Similar changes in the long-range attraction are reflected primarily in an increased cross section in the low-angle portion of the DCS. The entire low-angle region (below 10°) is largely unaffected even by the more drastic short-range modifications made. The effects of the latter appear mostly in the wider-angle oscillatory pattern of the DCS (beyond 15°).

By repeating the type of calculations displayed in Fig. 7 at some energy different from 64 meV (see end of Sec. II), the sensitivity of the DCS to different regions of the potential may crudely be gauged as a function of the collision energy. Such calculations are necessitated by the non-monotonic relation between the collision energy and the sensitivity with which the potential may be determined, in a given range, from arbitrarily normalized DCS experiments. For example, at very high collision energy, attractive interactions are insignificant compared with repulsive ones, while at very low collision energy, the DCS

becomes isotropic, and information can be extracted only if absolute measurements are made.⁵³ Figure 8 shows the effect on the DCS of making the parametric modifications to the MSV reference potential shown on the right-hand panels of Fig. 6, but at a collision energy of 19 meV.⁵⁴ Thus Fig. 8 is analogous to Fig. 7, but at only 30% of the collision energy. We see again that large changes in the repulsive wall region of the potential affect the DCS only for wide scattering angles (beyond $\sim 30^\circ$), but that these effects are less pronounced than at the higher energy. The low-energy DCS is thus less sensitive to the weakly repulsive wall than is the high-energy one. Comparisons between Figs. 7 and 8 regarding the effects of potential modifications in the attractive well and attractive tail regions show that the long-range potential is more sensitively probed by the low-energy DCS, but that the attractive well region is not (cf. the first three oscillations). The overall effect of lowering the collision energy from ~ 64 meV to ~ 19 meV is evidently to shift the range of interatomic separations probed most sensitively by the DCS experiments, from the attractive minimum region outward to the attractive tail region. That is, the DCS becomes dominated by the long-range attractive potential. Consequently, parametric forms most suitable for the analysis of low-energy DCS data should have more flexibility in the attractive tail region than those used for extracting the potential from higher-energy DCS curves. This may easily be accomplished by introducing a second adjustable dispersion term into the MSV, M^2SV or SPFD potentials [Eqs.(7) and (8)]. Flexibility of the repulsive wall independent of the attractive well is probably no longer needed at the lower energy; the MSV or second-order SPFD potential forms are probably sufficient.

Although the above conclusions^{13, 55} appear to be similar to ones based on classical arguments, the differences must be emphasized. Changes in the attractive region of the potential produce significant differences throughout the DCS, whereas such differences classically would be less pronounced at angles beyond the rainbow. Furthermore, these potential changes (at a given energy) affect the amplitudes of the wide-angle oscillations (but not their positions), which are especially intensified by a stronger attractive region. These conclusions are, of course, somewhat predicated upon the experimental conditions, e.g., collision energy, resolution, signal-to-noise ratios, etc.

The above trends are largely preserved upon inclusion of the simulated experimental averaging. The effects are, of course, less visible but are nevertheless statistically appreciable.⁵² Significant deteriorations in the DCS fitting at 64 meV appear to the extent shown in the last column of Table IV, indicating that the accuracy with which the potential can be determined in the repulsive wall, attractive well, and attractive tail regions defined in that table are approximately 30%, 10%, and 20%, respectively. Approximately the same sensitivities are indicated by the range of third-order SPFD potentials fitted to the five DCS's with data scatter (Fig. 3). Referring to the standard deviation columns of Tables I and II, it is apparent that for the realistic experimental conditions assumed in the present simulation (see the end of Sec. II), the DCS's are sensitive, for a particular potential shape, to changes of the r_m and ϵ parameters of about 0.5% and 5%, respectively.¹¹ This reflects the precision with which these parameters are obtained from the fits to any one of the DCS's with data scatter. The accuracy of the

r_m and ϵ parameters approach this level of precision only for those functional forms having sufficient flexibility to parametrically decouple different regions of the potential from each other. This is best accomplished by the M^2SV and third-order SPFD potential forms. Using them, the well depth parameter ϵ is accurate (i.e., agrees with the "known" ϵ as well as being precise) to within $\sim 10\%$, while r_m is similarly accurate to within $\sim 2\%$ (Table II). The distance σ at which the potential changes sign is completely determined by r_m and the other potential parameters, and is accurate to within $\sim 1\%$ (not shown in Table II, but see Fig. 4). Under the conditions considered in this paper, these are the limits to which the interatomic pair potential may be determined by thermal DCS scattering measurements.

V. SUMMARY AND CONCLUSIONS

In this paper we have attempted to extend the usefulness of the techniques prevailing for the determination of interatomic potentials. Our method, as applied to crossed molecular beam experiments for highly quantum systems, is to begin with a "known" spherically symmetric interaction. This serves as the basis for calculating scattering cross sections as the hypothetical "experimental" data, to which data scatter is added. By fitting these cross sections to interatomic potentials, which are functionally different from the original one, we have arrived at the following qualitative conclusions:

1. Different parameterizations for different regions of the potential are generally helpful in avoiding high statistical parameter conditions.
2. The mathematical form assumed to represent the potential energy functions must be chosen with great care if accurate results are to be obtained. This choice may be dependent upon the collision energy.
3. The thermal DCS scattering results are sensitive to the potential significantly beyond the limits imposed by classical mechanics.

These conclusions are substantiated quantitatively for collision energies ~ 30 times the van der Waals attractive well depth as follows:

1. The potential forms most suitable for accurately reproducing both the scattering patterns and the original potential have at least four parameters. Up to five independent potential parameters may justifiably be determined.

2. The SPFD and M^2SV forms are the most successful of the potentials in the above sense, combining a high degree of flexibility with uniqueness. We concur with the conclusion of Bickes and Bernstein¹⁵ that the SPFD form provides a unified and accurate parameterization for the attractive well and adjacent regions of the potential. The M^2SV form, with the same number of parameters as the third-order SPFD form, is an equally successful representation of the potential energy, but it does not provide as systematic or as unified a representation compared with the SPFD form, nor is it quite as adequate in the short-range repulsive region.
3. The sensitivity is greatest in the well region, allowing r_m to be determined with an accuracy of $\pm 2\%$ and the potential to $\pm 10\%$, for realistic experimental conditions. These experiments are also very sensitive to the shape of the well region and, to lesser extents, to those of the long- and short-range regions.
4. Unique potentials may be obtained from suitable analyses (in the sense of the above conclusions) of scattering results of the type considered here, even under realistic experimental conditions. This is indicated by the indistinguishability (within error limits) of the SPFD and M^2SV potentials from the original potential assumed in the simulation, despite the very different parameterizations of all three of these potentials.

Although the above conclusions are based on the poignant example of He-Ar thermal scattering, they can be extended to other highly quantum systems. These include the range of systems for which the dimensionless A and B parameters^{3f} do not differ excessively from

those explicitly considered in this paper ($A \simeq 20$ to 40 and $B \simeq 50$). Within the validity of the central-field assumption for atom-molecule systems, the conclusions enumerated here may be extended, allowing a more systematic approach to the problem of analyzing scattering data for nonspherical systems.²⁰

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TABLE I. Results for the fits to the DCS having "experimental" data scatter, using an assumed MSV potential.^a

Potential Type	$\bar{r}_m^b/\text{\AA}$	$\bar{\epsilon}^b/\text{meV}$	$\sigma(r_m)^c/\text{\AA}$	$\sigma(\epsilon)^c/\text{meV}$	$\bar{\chi}^a$	$\frac{\Delta\alpha_{0.95}^{b,e}}{\alpha} \times 100\%$	$\frac{\Delta\alpha_{0.95}^f}{\alpha} \times 100\%$
original MSV	3.540	2.085	--	--	--	--	--
LJ 12-6	3.441	2.030	0.007	0.044	916. (2)	2.61	2.13
LJ n-6	3.461	1.933	0.011	0.107	886. (3)	2.60	2.03
exp-6	3.502	1.972	0.008	0.078	580. (3)	2.10	1.17
Kihara n-6	3.452	2.043	0.008	0.125	795. (4)	2.50	1.97
Klein-Hanley	3.498	2.068	0.006	0.091	500. (4)	1.97	1.26
BC	3.547	1.982	0.012	0.093	409. (4)	1.76	0.75
BBP, second-order, fit c_6 , fix $c_8 = 0$	3.533	2.133	0.005	0.046	554. (5)	1.90	0.49
BBP, second-order, fit c_6 and c_8	3.528	2.153	0.009	0.095	389. (6)	1.80	0.23
D-LJ, fit m	3.607	2.272	0.012	0.128	433. (5)	1.87	0.40
D-LJ, fix m = 6	3.600	2.249	0.014	0.137	435. (4)	1.84	0.42
SPFD, second-order	3.537	2.189	0.009	0.089	408. (4)	1.79	0.20
SPFD, third-order	3.523	2.084	0.006	0.114	364. (5)	1.71	0.15
SPFD, fourth-order	3.533	2.071	0.023	0.121	358. (6)	1.72	0.14

^a This potential was chosen to correspond closely with one recently proposed for He-Ar.¹³ The MSV shape parameters are: $c_6 = 1.434$; $c_8 = 0.220$; $\rho_f = 1.40$; $\beta = 5.45$ of Eq.(7).

^b Average of the values of the five fits.

^c Standard deviation of the mean for the five fits.

^d Scattering intensity normalized to 500.0 at 5.0° ; the number of parameters varied is given in parentheses.

^e The average χ^2 and $\Delta\alpha_{0.95}/\alpha$ statistical indices for the original MSV potential are 448(0) and 1.77%, respectively.

^f This $\Delta\alpha_{0.95}/\alpha$ statistical index is for fits to the DCS without data scatter.

TABLE II. Results for the fits to the DCS having "experimental" data scatter, using an assumed Klein-Hanley potential.^{a, b}

Potential Type	$\bar{r}_m/\text{\AA}$	$\bar{\epsilon}/\text{meV}$	$\sigma(r_m)/\text{\AA}$	$\sigma(\epsilon)/\text{meV}$	$\bar{\chi}^2$	$\Delta\alpha_{0.95}/\alpha \times 100\%$	$\Delta\alpha_{0.95}/\alpha \times 100\%$
original Klein-Hanley	3.500	2.500	--	--	--	--	--
MSV	3.496	2.783	0.011	0.098	324. (4)	1.93	0.59
M ² SV	3.516	2.481	0.016	0.172	253. (5)	1.74	0.22
SPFD, third-order	3.469	2.603	0.009	0.131	244. (5)	1.70	0.17

^a This potential was chosen to correspond closely with one recently proposed for He-Ar.¹⁴ The Klein-Hanley [Eq. (3)]

shape parameters chosen are: $c_g = 1.80$; $n = 12.0$, and therefore $c_g = 0.30$.

^b Headings have the same meanings as in Table I.

TABLE III. Dependence of the third-order SPFD fitted dispersion coefficients on the joining point ρ_f .

ρ_f	$\bar{C}_6^a / \text{eV} \times \text{\AA}^6$	$\frac{\bar{C}_6 - C_6^b}{C_6} \times 100\%$	$\frac{\sigma(C_6)^c}{C_6} \times 100\%$
1.4	5.84	-0.8	5.8
1.6	5.64	-4.2	4.9
1.8	5.51	-6.5	6.5
2.0	5.74	-2.5	14.8
2.2	6.30	+7.0	26.7

^a $\bar{C}_6$ is the average of the dispersion coefficients obtained from the fits to the five "experimental" DCS's with data scatter.

^b $C_6 = 5.89 \text{ eV} \times \text{\AA}^6$ ^{28a} is the dispersion constant used in the original MSV potential.

^c $\sigma(C_6)$ is the standard deviation of the fitted coefficients.

TABLE IV. Definition of regions for the numerically modified MSV potential.

region	range ^a	sensitivity ^b
1. repulsive wall	$\rho < 0.87$	$\pm 30\%$
2. attractive well	$0.87 < \rho < 1.40$	$\pm 10\%$
3. attractive tail	$\rho > 1.4$	$\pm 20\%$

^a Early attempts to define four regions split region 2 into two parts at $\rho = 1.10$; the attractive tail region was then defined by $\rho > 1.5$.

^b Minimum change in the potential shape needed to produce statistically significant changes in the corresponding DCS.⁵²

FIGURE CAPTIONS

FIG. 1. He + Ar calculated DCS using the MSV potential. $I(\theta)$ is the DCS in arbitrary units at the scattering angle θ , corresponding to out-of-plane detection of He atoms. The data points exactly on the DCS curve have error bars representing the assumed "experimental" noise at each angle. Other data points are chosen at random from a normal distribution using these error bars at each angle as one standard deviation.

FIG. 2. Deviations of various reduced potentials from the original MSV form (broken curves). $(\Delta f/f) \times 100$ is the deviation, at each reduced interatomic separation ρ , of BBP forms obtained by direct fitting to the MSV form. The dashed curve shows the deviation of the second-order BBP form; the dotted line shows the deviation of the fourth-order BBP form. The solid curve, corresponding to the scale on the right, shows the original MSV reduced potential, f , for comparison. The discontinuity near $\rho = 0.87$ is due to the zero of the potential; the absolute deviation, Δf , of the second-order BBP potential is 0.017 there.

FIG. 3. Deviations of various potentials from the original MSV one (broken curves). $(\Delta V/V) \times 100$ is the deviation, at each interatomic separation r , of third-order SPFD potentials obtained by fitting to the "experimental" DCS's. The dashed curve shows the deviation of the SPFD form fit to the DCS having no data scatter; the dotted curves show the deviations for fits to three of the DCS's with data scatter. The solid curve, corresponding to the scale on the right, shows the original MSV potential, V , for comparison. The discontinuities near

$r = \sigma = 3.1 \text{ \AA}$ are due to the zero of the potential; the absolute deviations, ΔV , for the dotted potentials are about $\pm 0.2 \text{ meV}$ there. The arrows at $r = 2.8 \text{ \AA}$ and $r = 6.5 \text{ \AA}$ delineate the range of sensitivity of the "experimental" DCS to the potential (see Sec. IV of the text).

FIG. 4. Potentials obtained from fits to the "experimental" DCS's generated using the Klein-Hanley potential. V is the interatomic potential at each interatomic separation r ; the inset magnifies the vertical scale of the potential energy minimum region by a factor of 2.5. The solid curve is the original Klein-Hanley potential and the broken curves show the average potential V at each r for a particular potential form. Long dashed curve: MSV potential; dotted curve: $M^2\text{SV}$ potential; short dashed curve: third-order SPFD potential. The error bar in the inset indicates the estimated uncertainty of $\pm 10\%$ at the potential minimum; the arrows on the abscissa are placed as in Fig. 3.

FIG. 5. The deviation of a numerically averaged potential from the original MSV one (broken curves). $(\Delta V/V) \times 100$ is the deviation, at each interatomic separation r , of the numerical average of the five third-order SPFD potentials of Fig. 3. The solid curve, corresponding to the scale on the right, shows the original MSV potential, V , for comparison. The discontinuity near $r = 3.1 \text{ \AA}$ is due to the zero of the potential; the absolute deviation, ΔV , of the numerical potential is -0.02 meV there. The arrows on the abscissa are placed as in Fig. 3.

FIG. 6. Deviations of various reduced potentials from the original MSV potential form (broken curves). $(\Delta f/f) \times 100$ is the deviation, at each reduced interatomic separation ρ , of fourth-order SPFD potential forms obtained by direct fitting to numerically modified MSV potentials. Solid lines are the step-function modifications made to the original MSV potential; dashed lines show the response of the SPFD potential forms in fitting them. Graphs in the right column represent changes twice as large as the ones in the left column (note scale change). The upper panels show the response to 15% and 30% changes in the repulsive wall region; the middle panels, to 5% and 10% changes in the attractive well region; and the lower panels, to 10% and 20% changes in the attractive tail region of the potential. The discontinuity near $\rho = 0.87$ is due to the zero of the potential.

FIG. 7. He + Ar calculated DCS's at a collision energy of 64 meV using the fourth-order SPFD potentials fitted to the numerically modified MSV potentials. $I(\theta)$ is the DCS in arbitrary units at the scattering angle θ , corresponding to out-of-plane detection of He atoms. The solid line corresponds to scattering calculated from the original MSV potential, with error bars representing the assumed "experimental" noise at representative angles. The long dashed line corresponds to a potential modification of +30% in the repulsive wall region; the dotted line, to a +10% modification in the attractive well region; and the short dashed line, to a +20% modification in the attractive tail region. Note that the ordinate is very sensitive to the oscillatory structure of the DCS.^{3f}

FIG. 8. He + Ar calculated DCS's at a collision energy of 19 meV, using the fourth-order SPFD potentials fitted to the numerically modified MSV potentials. Symbols are as in Fig. 7; error bars from that figure are transferrable to Fig. 8 provided the signal-to-noise ratio is the same for both energies. Note the difference in the angle scales of these two figures.

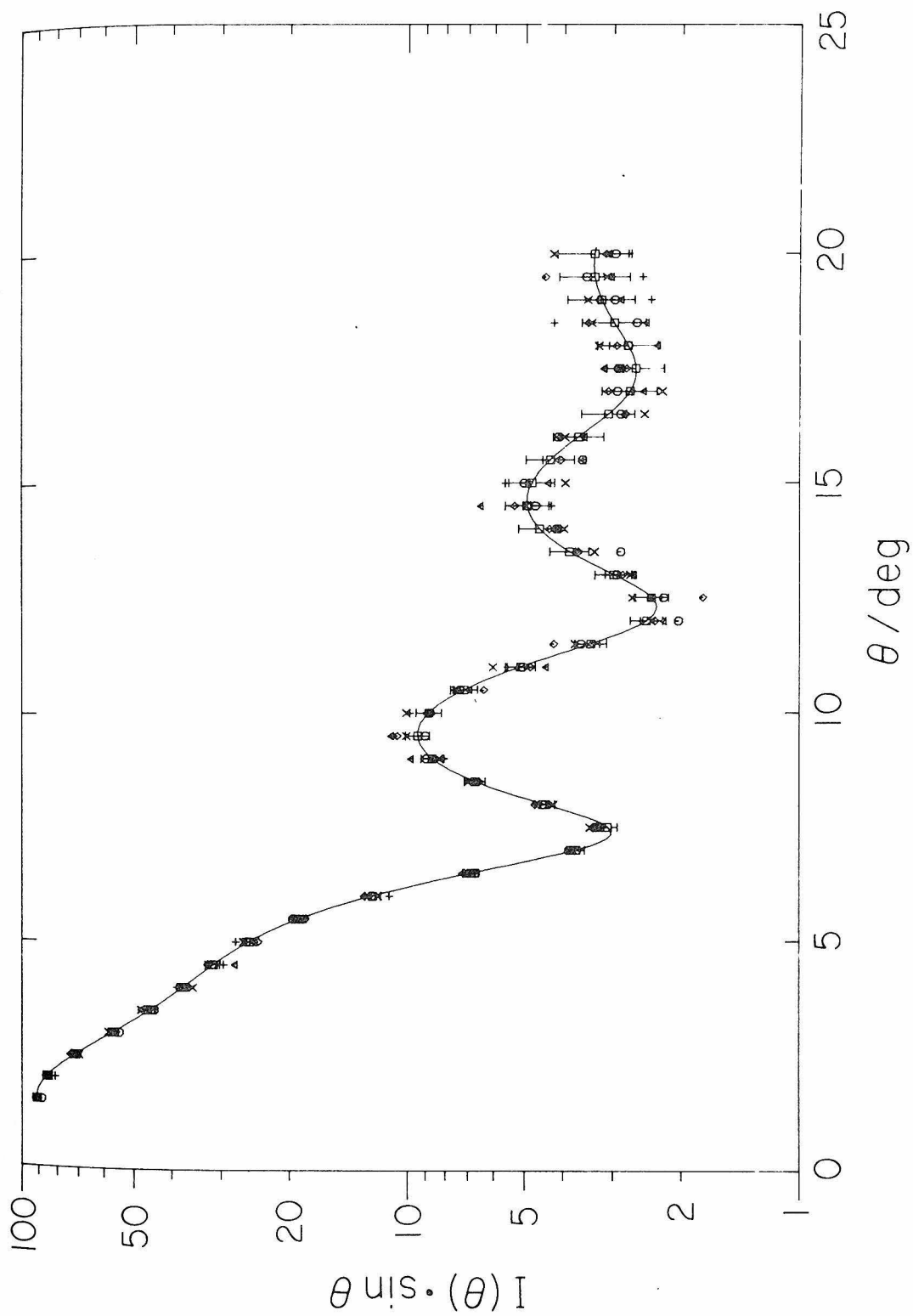


Figure 1

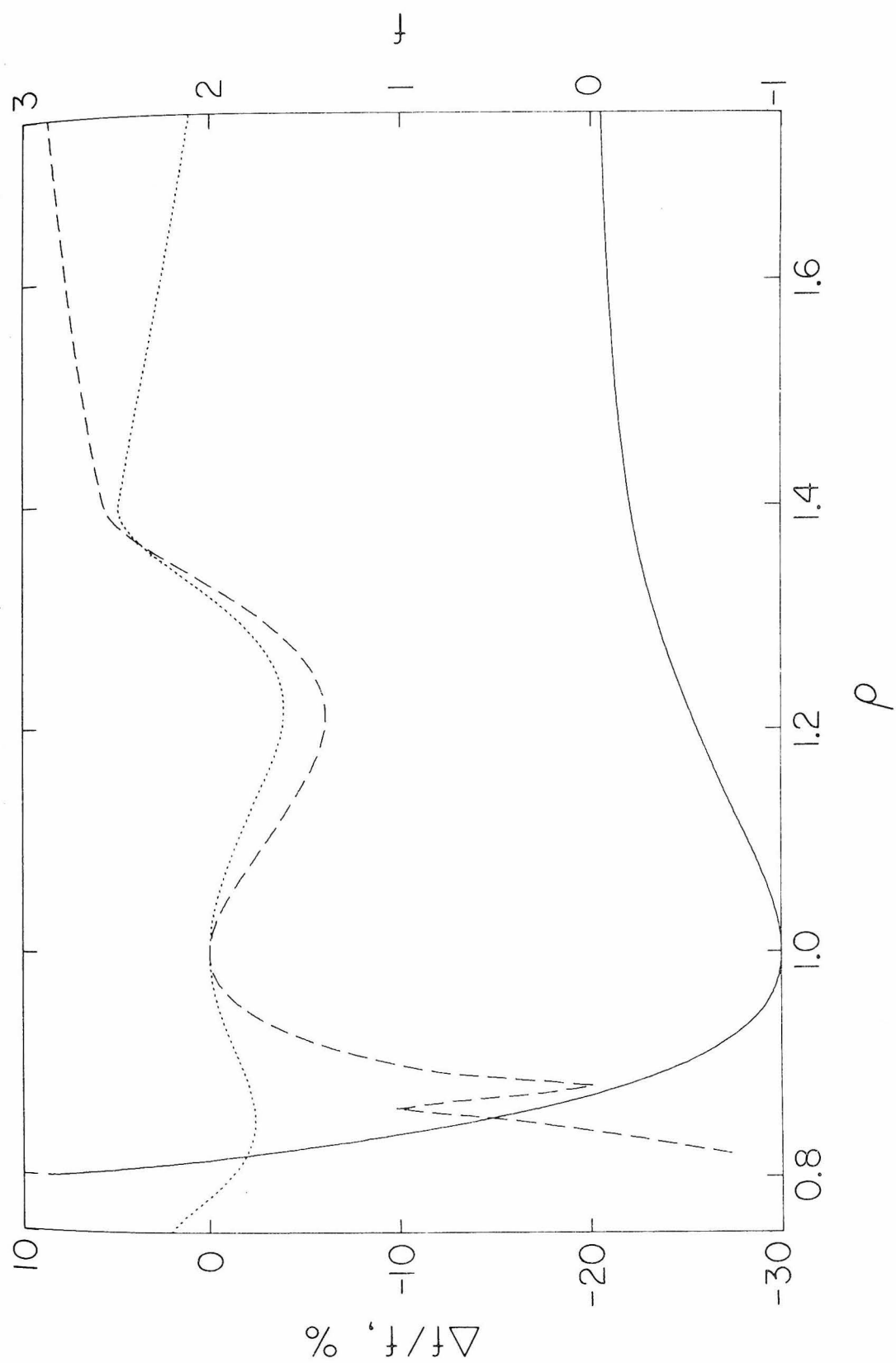


Figure 2

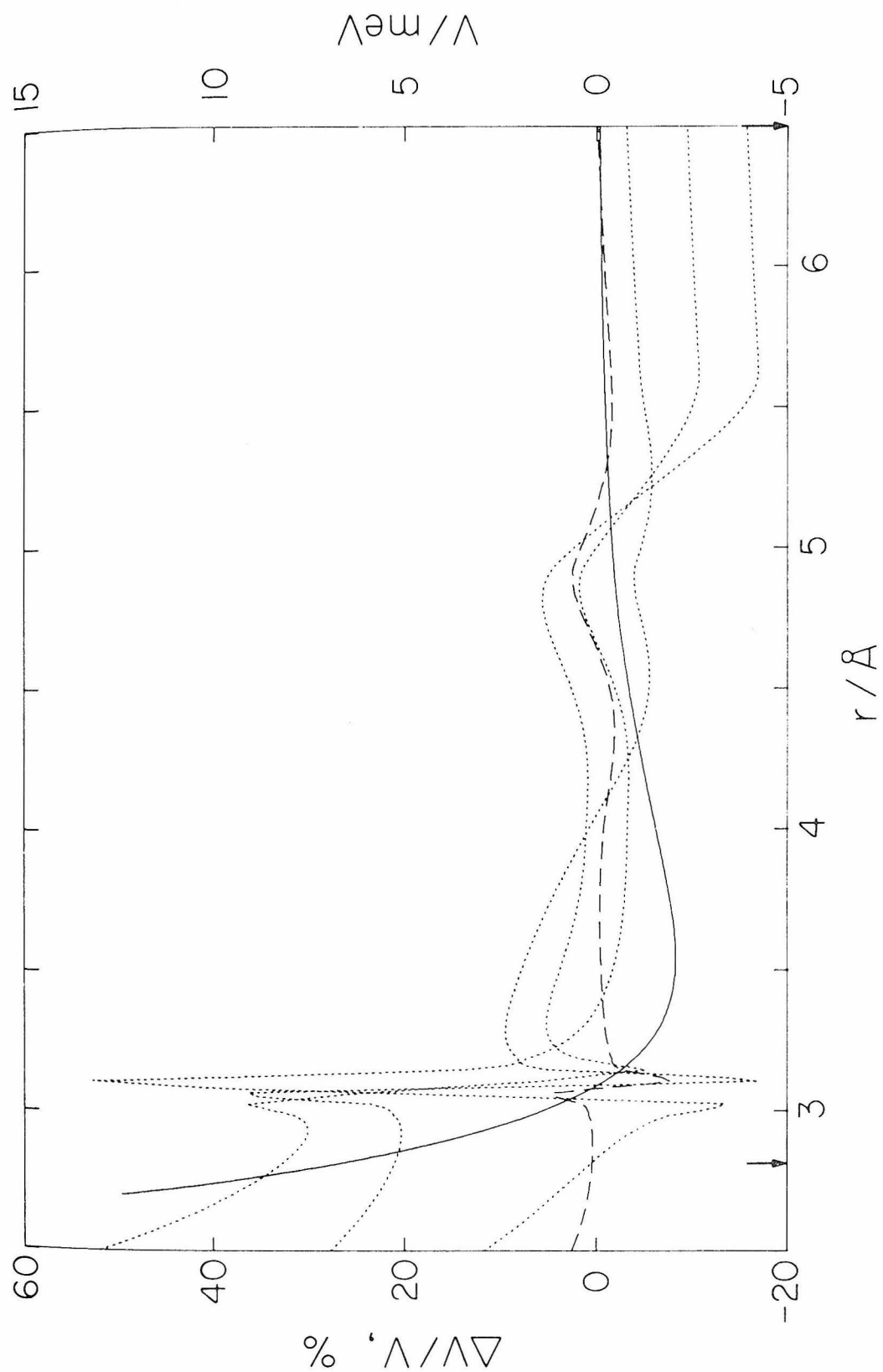


Figure 3

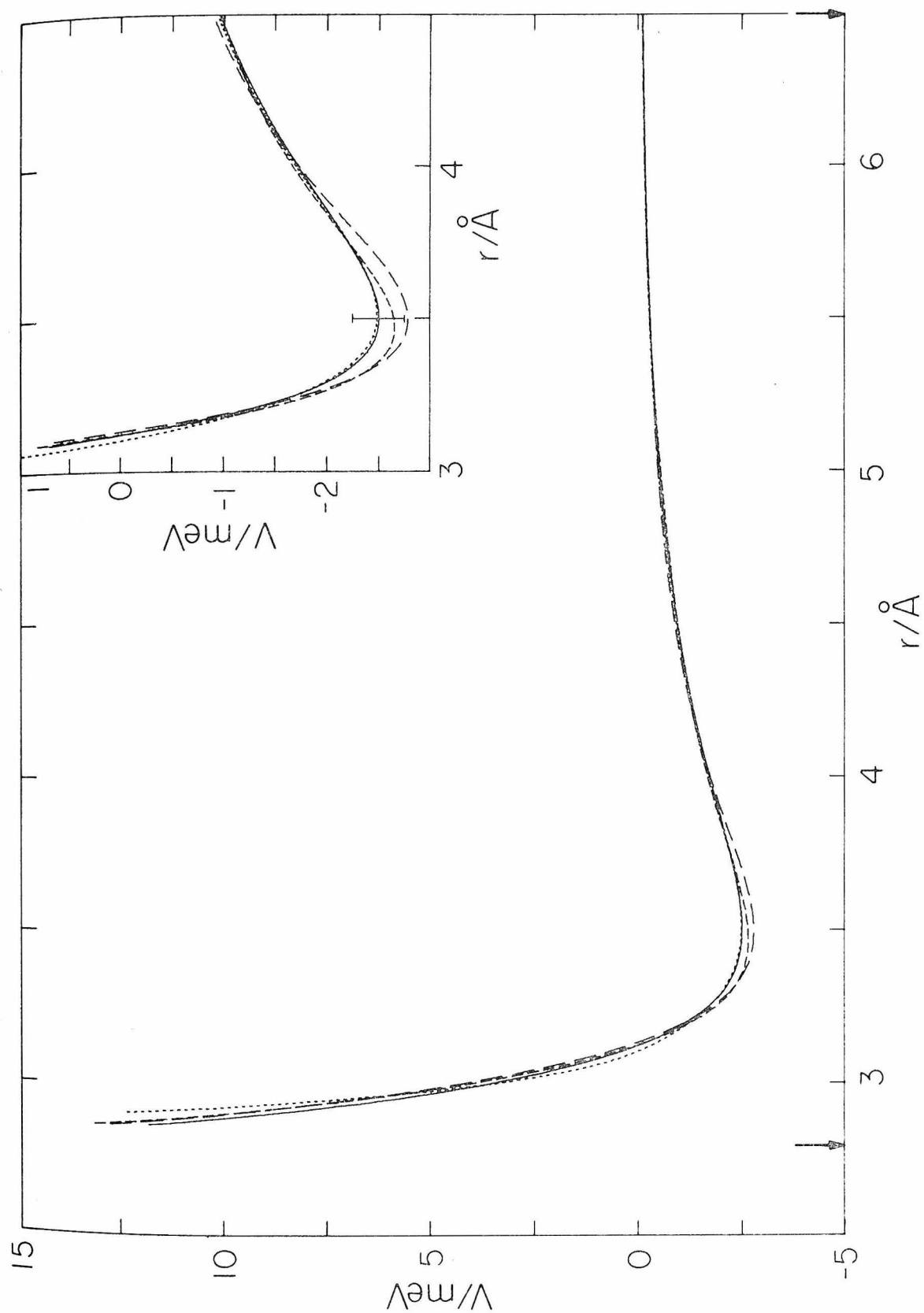


Figure 4

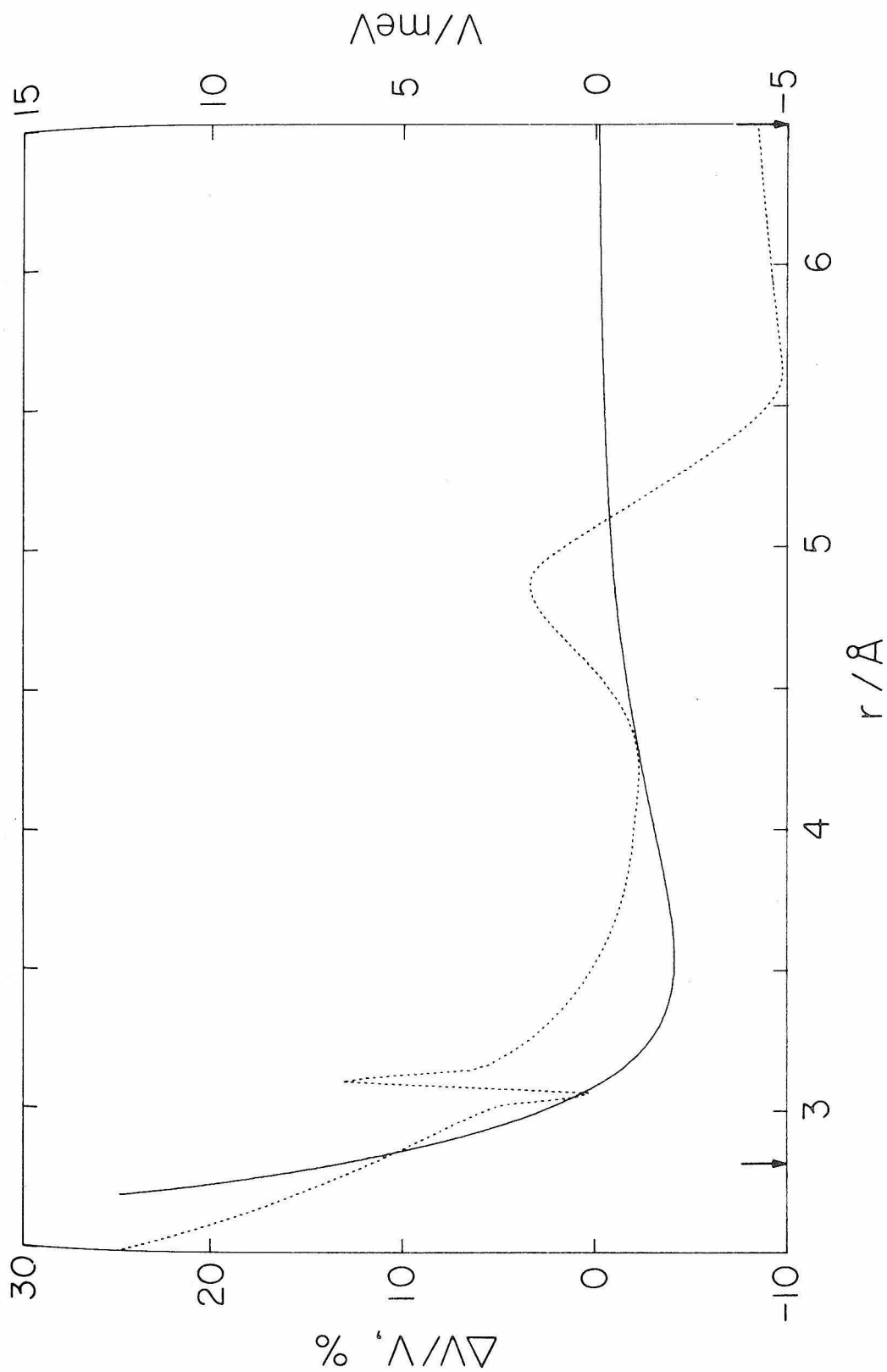


Figure 5

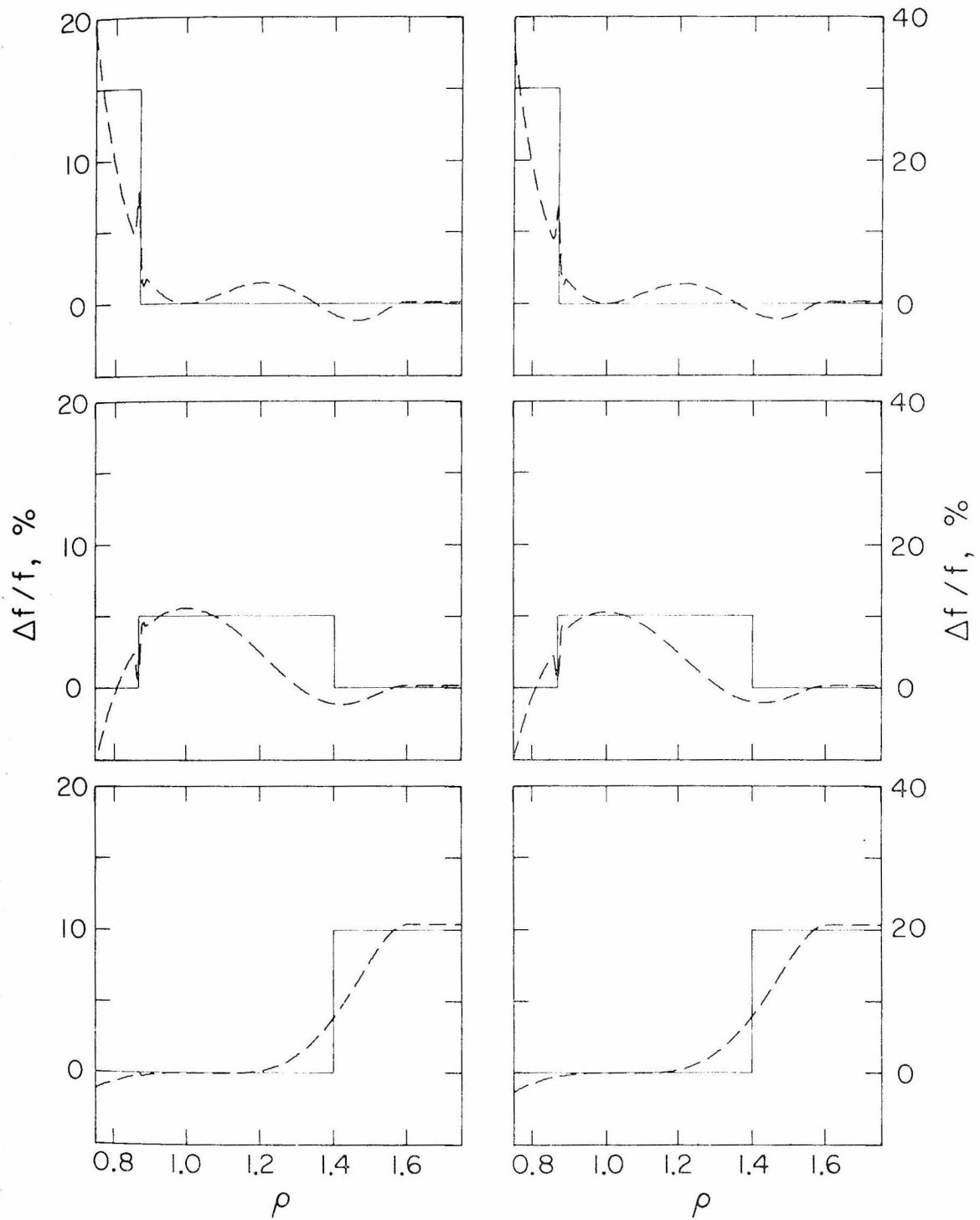


Figure 6

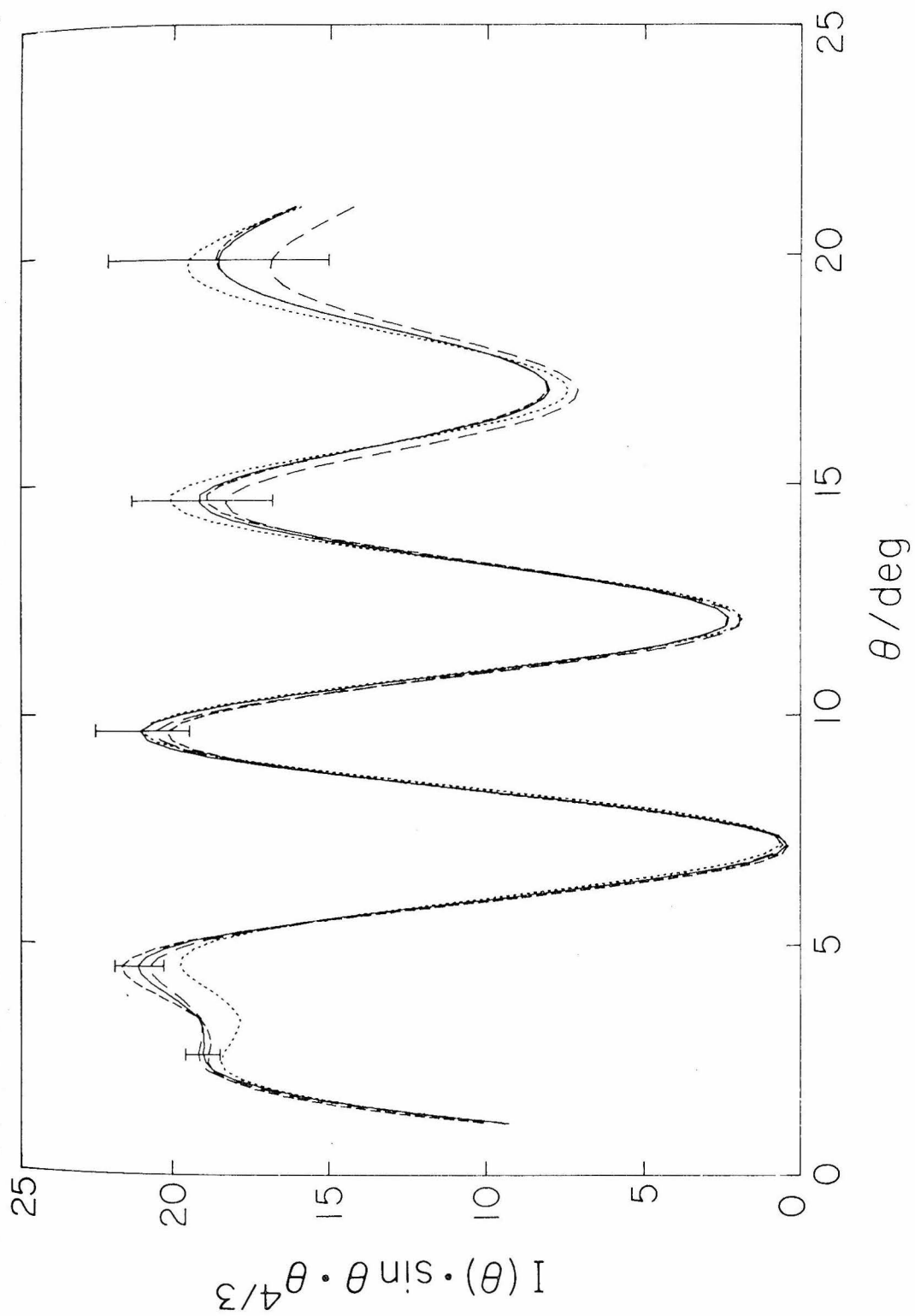


Figure 7

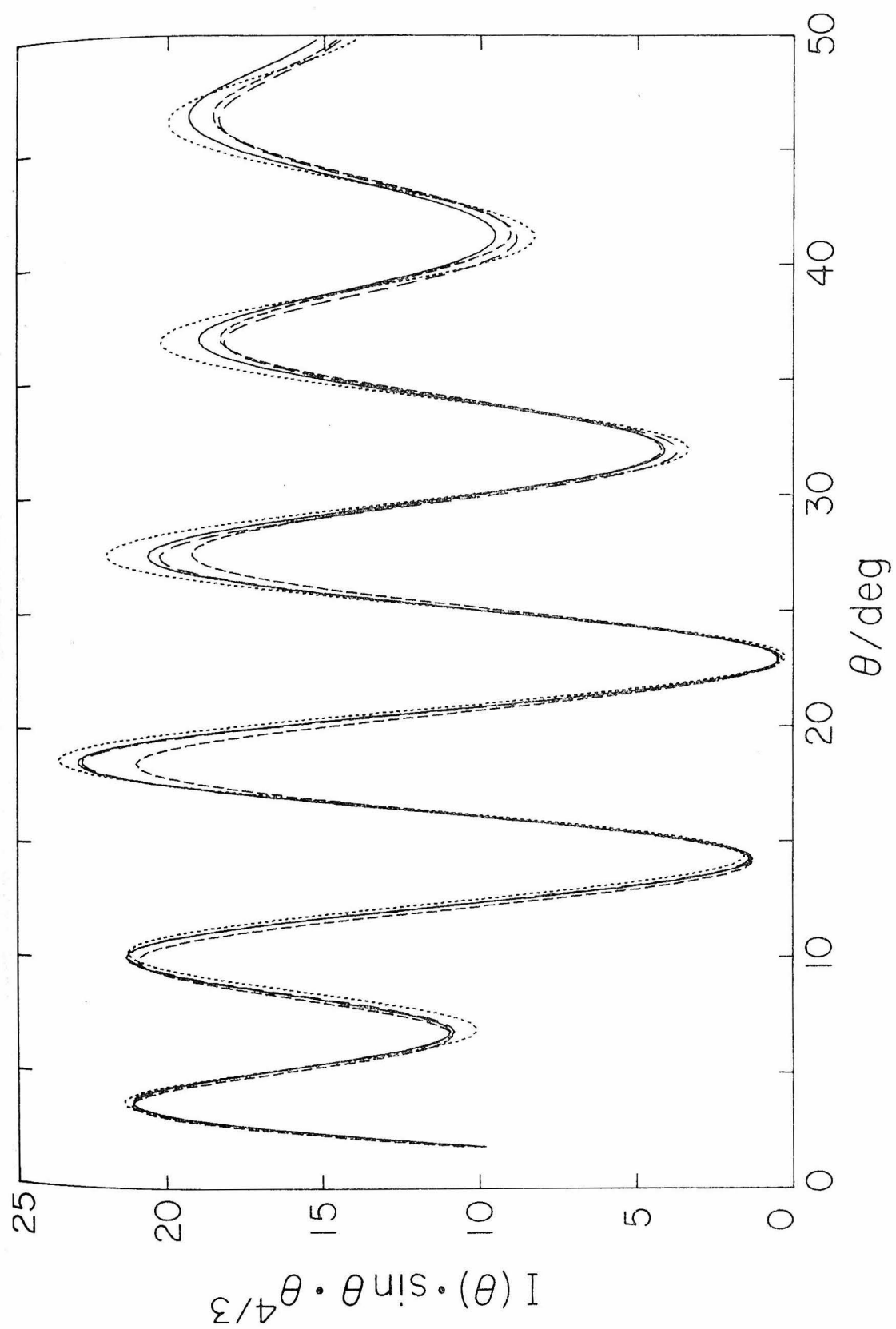


Figure 8

CHAPTER 2

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

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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 to 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 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 ($\gtrsim 10^{-8}$ 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 $\theta_v \lesssim 3.5^\circ$).

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 sources 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 $\simeq 0.2^\circ$. 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 interatomic 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

$$g_i = \frac{n s_i^{-2}}{\sum_{i=1}^n s_i^{-2}}. \quad (2)$$

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, was 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 M²SV 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 $\approx 3.5\%$). 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 exist 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 ($\theta \gtrsim 15^\circ$) 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_6 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

$$V_{\text{BM}}(r) = Ce^{-\alpha r} \quad \text{for} \quad 2.4 < r < 2.7 \text{ Å}, \quad (10)$$

with the nonreduced values of $C = 1.23 \times 10^5$ eV and $\alpha = 5.69 \text{ Å}^{-1}$. 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 $3.659 \text{ \AA}$ or $3.573 \text{ \AA}$ 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,

$$f(\rho) = V(r)/\epsilon ; \quad \rho = r/r_m . \quad (4)$$

The first of these is the modified SPFD,^{21, 22} written as

$$\left. \begin{aligned} f(\rho) &= h(\rho)Ae^{-b\rho} + [1 - h(\rho)] \cdot \left[b_0\lambda^2 \left(1 + \sum_{i=1}^N b_i\lambda^i \right)^{-1} \right] , \\ \text{with } h(\rho) &= \frac{1}{1 + e^{\tau(\rho-\rho_0)}} ; \quad \lambda = 1 - 1/\rho \text{ and } \rho < \rho_f \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho \geq \rho_f . \end{aligned} \right\} (13)$$

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:

$$\left. \begin{aligned}
 f(\rho) &= h(\rho)Ae^{-b\rho} + [1 - h(\rho)] \cdot \frac{e^{(\beta' - \rho\beta\omega)}}{\omega} \left[e^{(\beta' - \rho\beta\omega)} - 2 \right], \\
 \text{where} \quad h(\rho) &= \frac{1}{1 + e^{\tau(\rho - \rho_0)}}; \quad \omega = \frac{\beta' - \ln 2}{\beta - \ln 2} \text{ and } \rho < 1 - \beta^{-1} \ln 2 \\
 f(\rho) &= e^{\beta(1-\rho)} \left[e^{\beta(1-\rho)} - 2 \right] \quad \text{for } 1 - \beta^{-1} \ln 2 \leq \rho \leq \rho_1 \\
 f(\rho) &= (\rho_2 - \rho) [s_1(\rho_2 - \rho)^2 + s_3] + (\rho - \rho_1) [s_2(\rho - \rho_1)^2 + s_4] \\
 &\quad \text{for } \rho_1 < \rho < \rho_2 \\
 f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} \quad \text{for } \rho \geq \rho_2.
 \end{aligned} \right\} (14)$$

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 $r \gtrsim 1.4$ 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.

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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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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.,

$$|\underline{u}| = u = u_1 . \quad (A1)$$

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 $\hat{\tilde{i}}$, $\hat{\tilde{j}}$ and $\hat{\tilde{k}}$. These unit vectors are related by:

$$\left. \begin{aligned} \hat{\tilde{i}} &= \hat{i} \cos \alpha + \hat{k} \sin \alpha & (i) \\ \hat{\tilde{j}} &= \hat{j} & (ii) \\ \hat{\tilde{k}} &= -\hat{i} \sin \alpha + \hat{k} \cos \alpha & (iii) \end{aligned} \right\} , \quad (A2)$$

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

$$\underline{u}_r = \underline{u}_1 - \underline{u}_2 = \underline{v}_1 - \underline{v}_2 . \quad (A3)$$

The scattered velocity vectors $\underline{v}$ and $\underline{u}$ are related by

$$\underline{v} = \underline{v}_\sigma + \underline{u} , \quad (A4)$$

where

$$\underline{v}_g = \frac{1}{M} [\hat{k} (m_1 v_1 + m_2 v_2 \cos \gamma) + \hat{i} m_2 v_2 \sin \gamma] ; \quad (A5)$$

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

$$\begin{aligned} \underline{v} &= v(\hat{i} \sin \theta \cos \phi + \hat{j} \sin \theta \sin \phi + \hat{k} \cos \theta) & (i) \\ \underline{u} &= u(\hat{I} \sin \Theta \cos \Phi + \hat{J} \sin \Theta \sin \Phi + \hat{K} \cos \Theta) & (ii) \end{aligned} \quad (A6)$$

From Eqs. (A2), (A4), (A5), and (A6) we obtain

$$\begin{aligned} Mv \sin \theta \cos \phi &= m_2 [v_2 \sin \gamma + u_r (\sin \Theta \cos \Phi \cos \alpha - \cos \Theta \sin \alpha)] & (i) \\ Mv \sin \theta \sin \phi &= m_2 u_r \sin \Theta \sin \Phi & (ii) \\ Mv \cos \theta &= m_1 v_1 + m_2 [v_2 \cos \gamma + u_r (\sin \Theta \cos \Phi \sin \alpha + \cos \Theta \cos \alpha)] & (iii) \end{aligned} \quad (A7)$$

It is now useful to express θ , Φ and v in terms of Θ , ϕ and u .

Eqs. (A7i) and (A7ii) furnish

$$\begin{aligned} \Phi &= 0 & \text{for } \phi = 0 & (i) \\ \Phi &= \cos^{-1} \left[\frac{r_2 \sin \gamma (\cos \Theta - 1)}{u_r \sin \Theta \cos \alpha} \right] & \text{for } \phi = \frac{\pi}{2} & (ii) \\ \Phi &= \cos^{-1} \left[\frac{C_\phi (B_\phi^2 + C_\phi^2 - A_\phi^2)^{\frac{1}{2}} - A_\phi B_\phi}{B_\phi^2 + C_\phi^2} \right] & \text{for } \phi \neq 0, \neq \frac{\pi}{2} & (iii) \end{aligned} \quad (A8)$$

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

$$\delta = \cos^{-1} \left[\frac{u^2 + v^2 - v_g^2}{2uv} \right] \quad . \quad (\text{A13})$$

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,

$$\sigma_{\text{lab}} = C \cdot \frac{I_{\text{sc}} v}{I_{\text{inc}} v_1} \quad , \quad (\text{A14})$$

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

$$I_{\text{sc}} = \frac{C}{I_{\text{inc}}} \cdot \sigma_{\text{CM}} \cdot \frac{vv_1}{u^2 |\cos \delta|} \quad , \quad (\text{A15})$$

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^2_{SV} ^{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 $C = 1.23 \times 10^5$ 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^2_{SV} 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	$\chi^2_{b,c,d}$	$\Delta\alpha_{0.95}/\alpha$ (%) ^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 M^2SV 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 M^2SV form of Eq. (14), parameter symbols are used there and in Eq. (4). $\sigma = 3.08_4 \text{ \AA}$ 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 $\rho = \rho_1$, ρ_2 , or at σ/r_m .

^c This work.

^d Nonreduced dispersion coefficients are^{53, 54} $C_6 = 5.867 \text{ eV} \cdot \text{\AA}^6$; $C_8 = 25.68 \text{ eV} \cdot \text{\AA}^8$; $C_{10} = 152.1 \text{ eV} \cdot \text{\AA}^{10}$.

^e Reference 54.

^f Nonreduced Born-Mayer parameters are $C = 1.23 \times 10^5 \text{ eV}$; $\alpha = 5.69 \text{ \AA}^{-1}$.

^g References 26 and 27.

^h References 28 and 29.

FIGURE CAPTIONS

Fig. 1. Vertical cross section of the molecular beam apparatus, drawn approximately to scale. FT - copper gasket feedthroughs, DP₁₋₅ - oil diffusion pumps, DP₆ - 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, IP₁ - 5 ℓ /sec ion pump, IP₂ - 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°), C₁ - primary beam collimator, C₂ - secondary beam collimator, C₃ - detector entrance collimator, C₄ - 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.

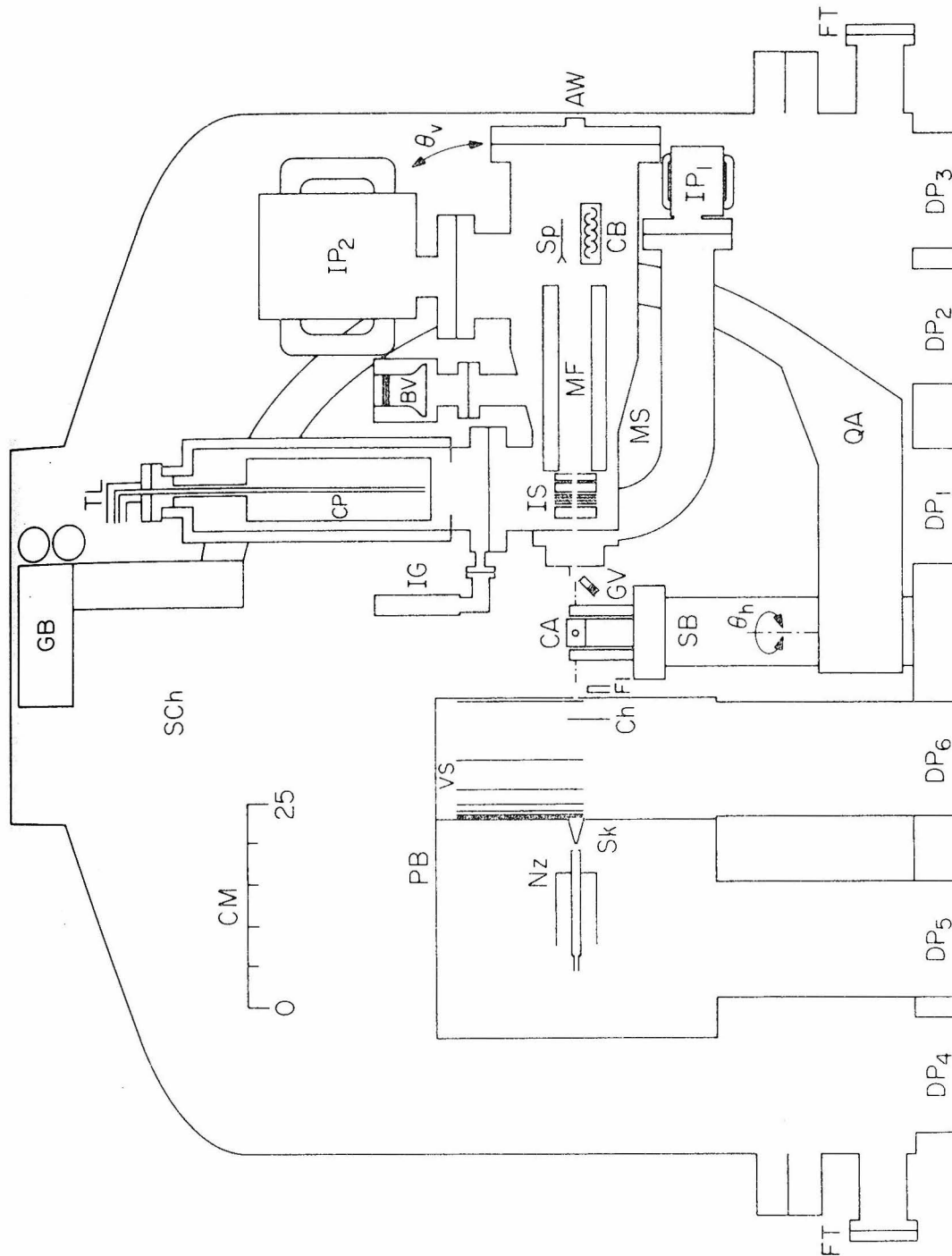


Figure 1

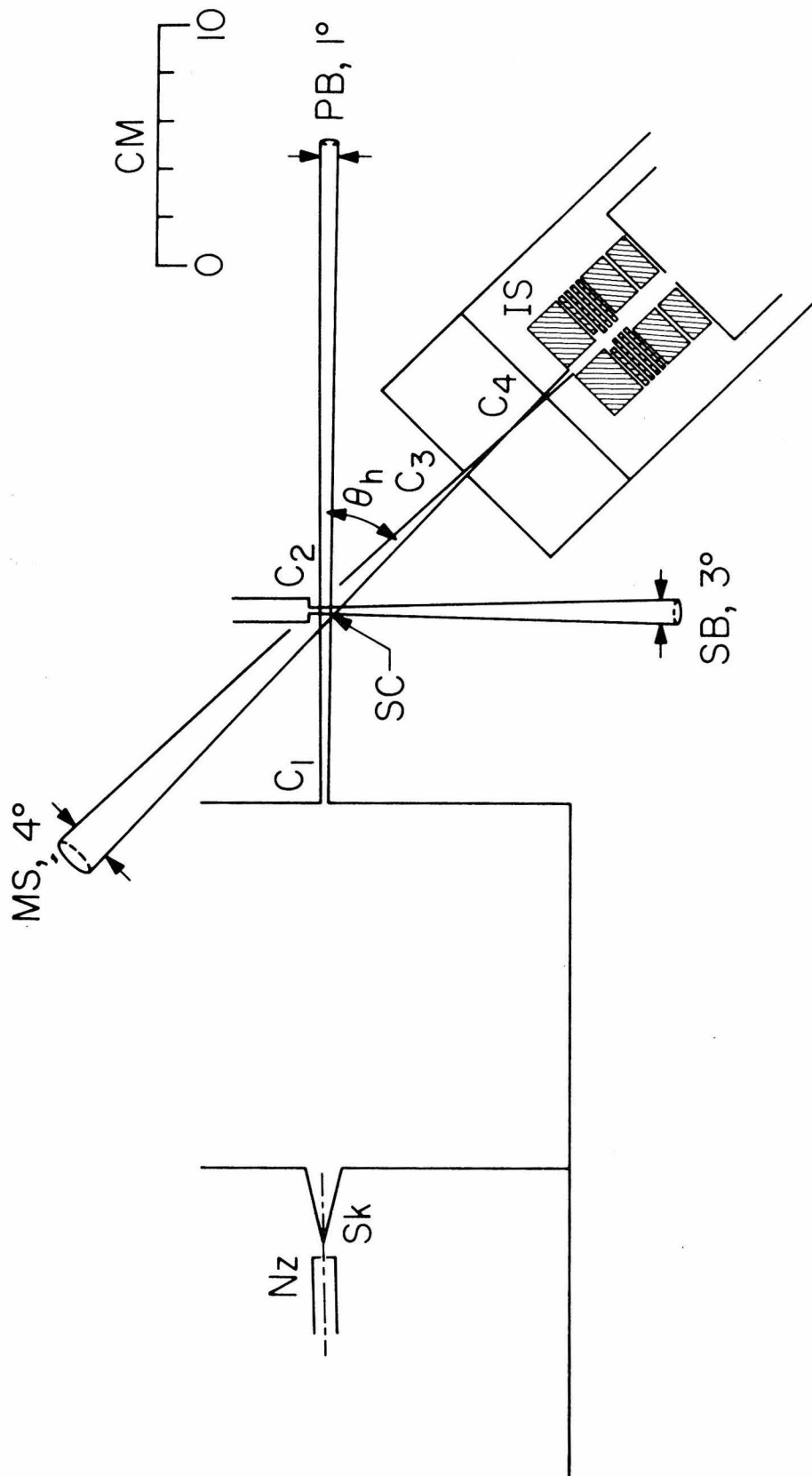


Figure 2

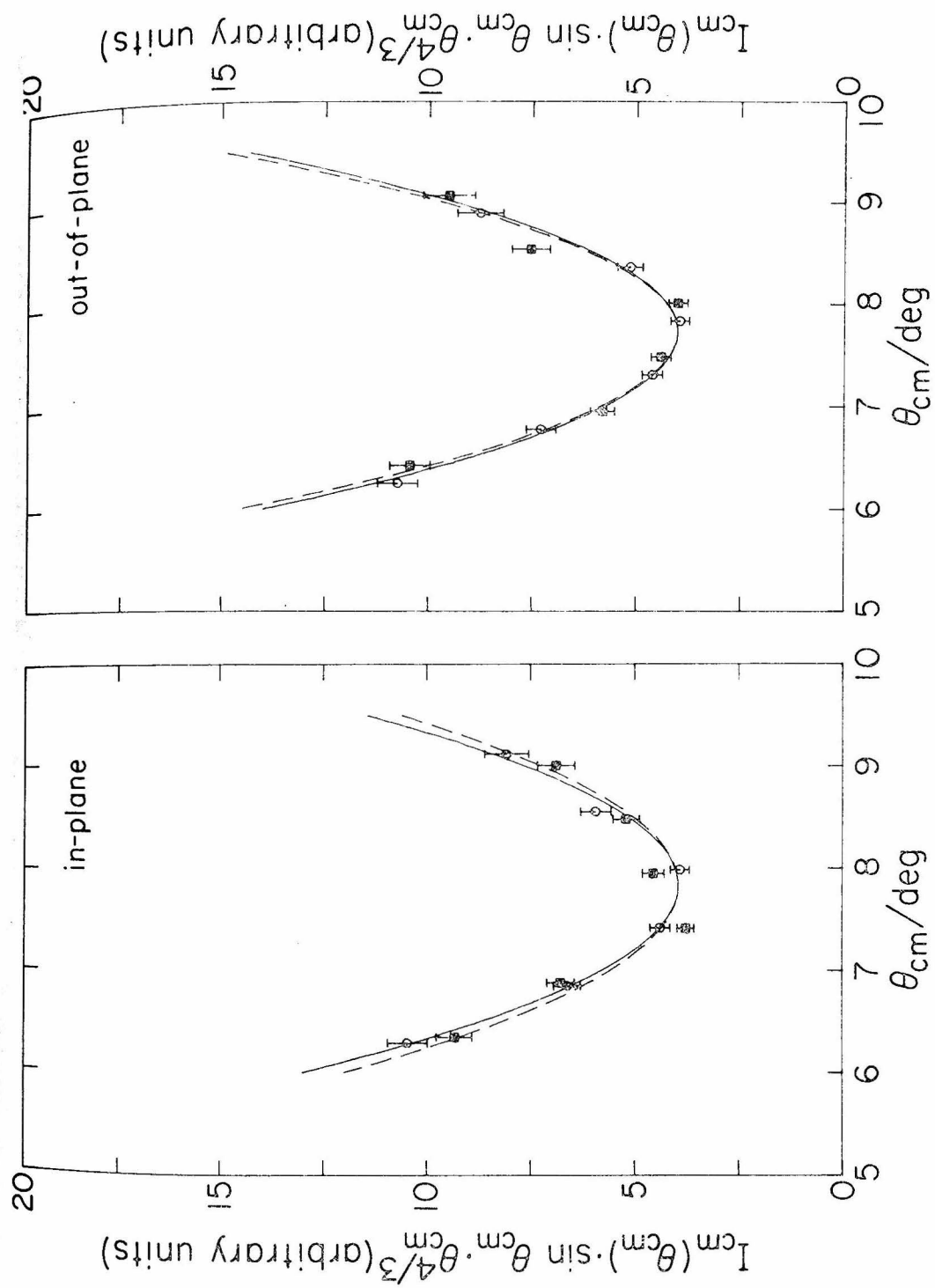


Figure 3

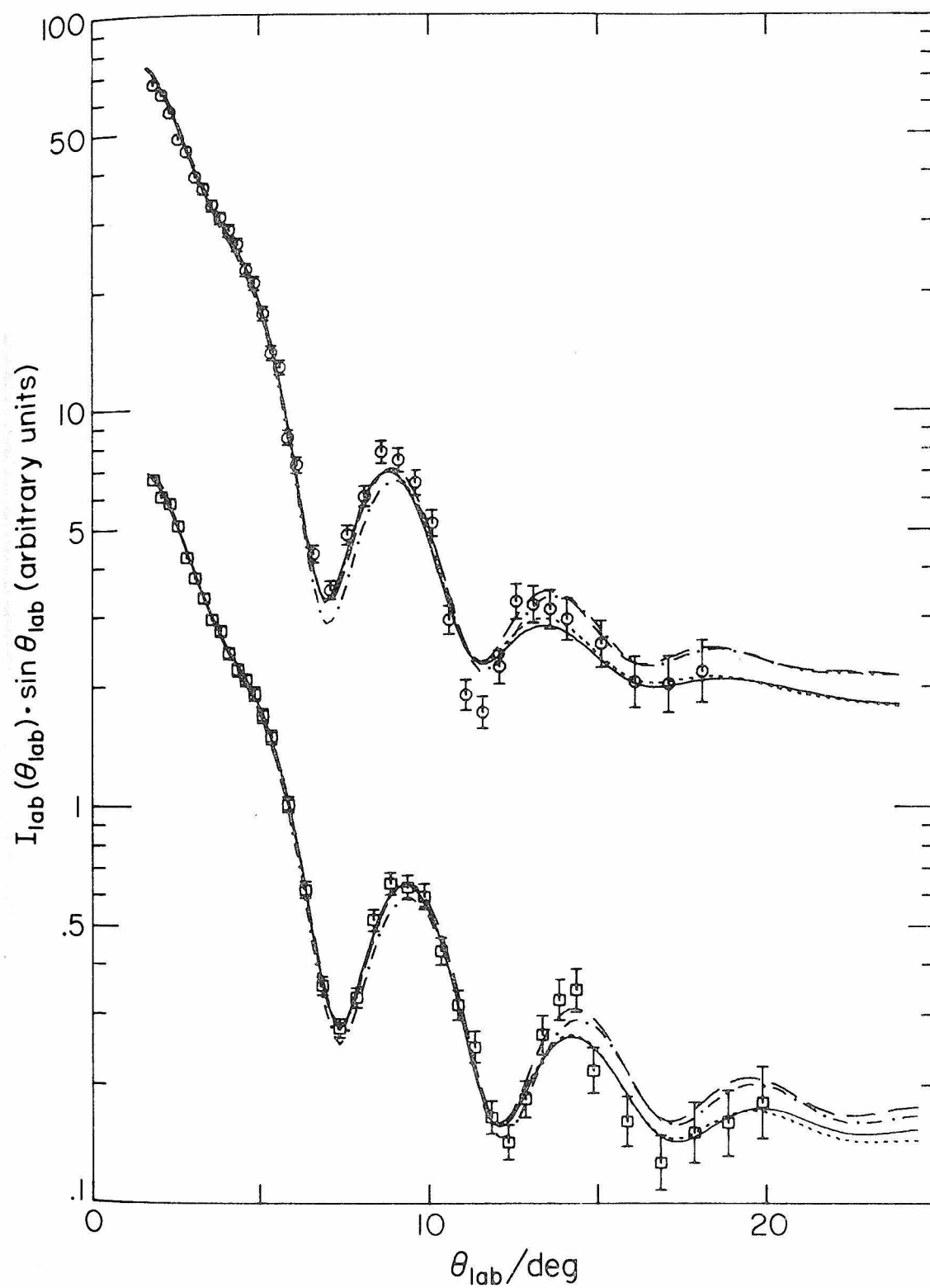


Figure 4

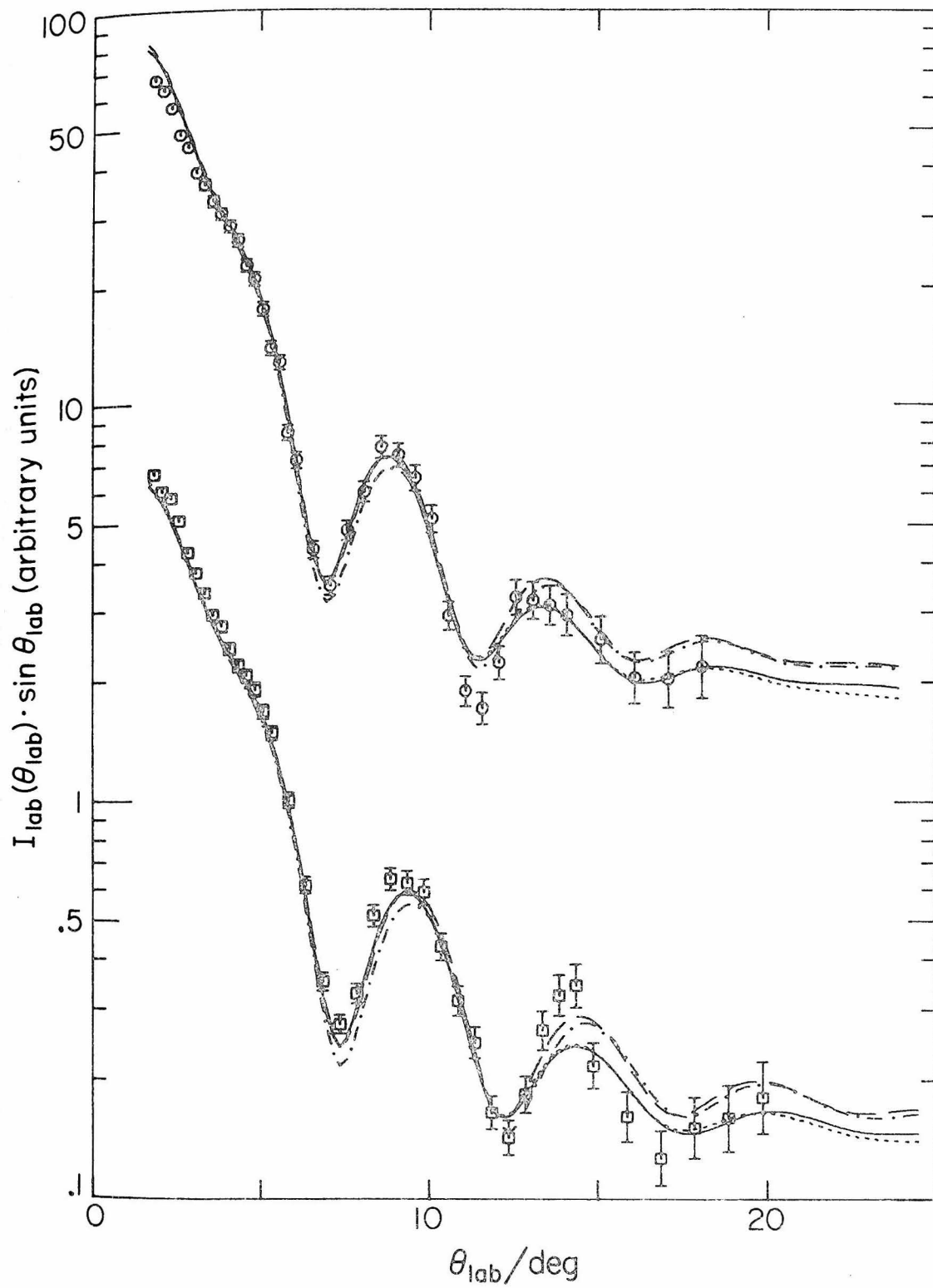


Figure 5

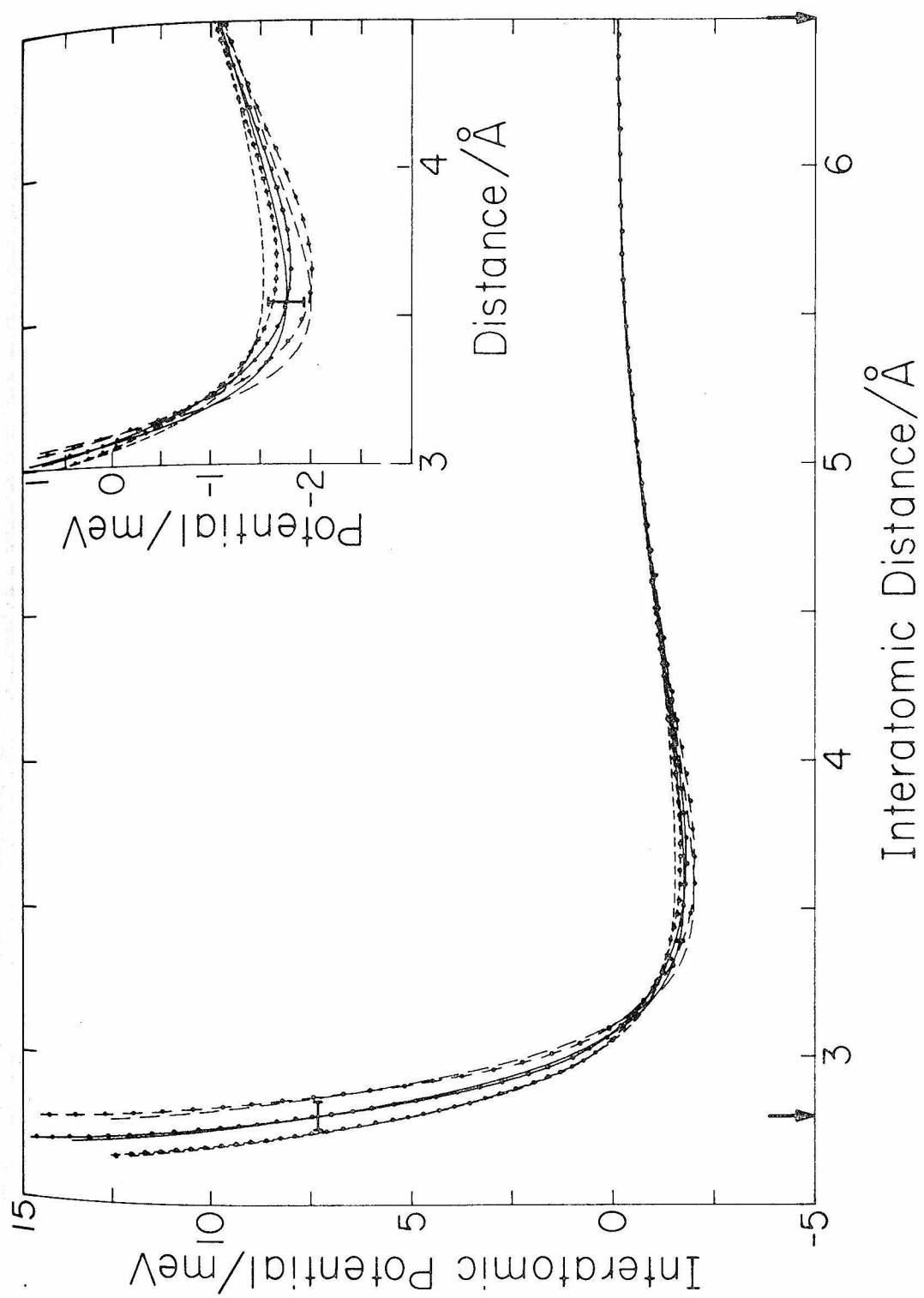


Figure 6

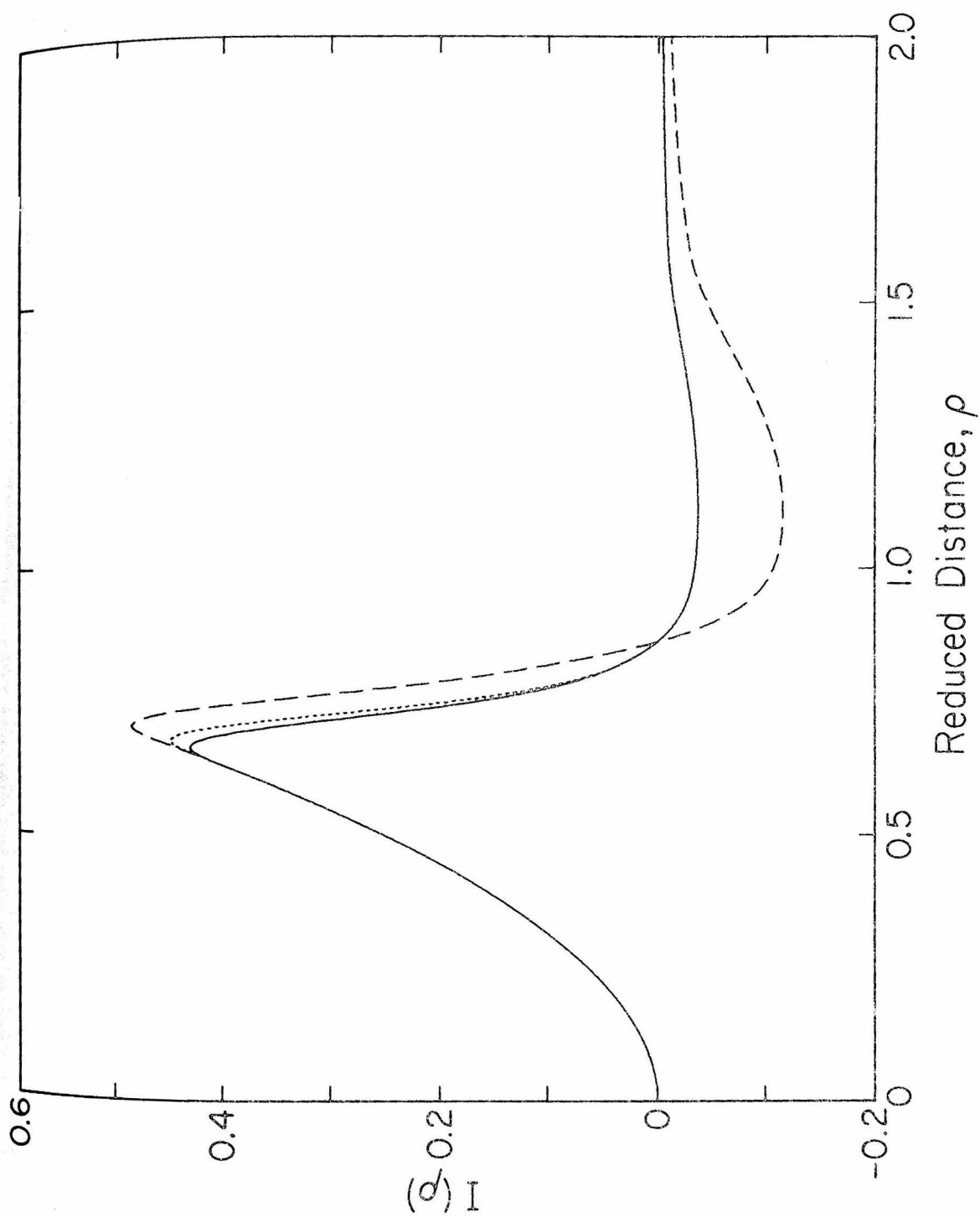


Figure 7

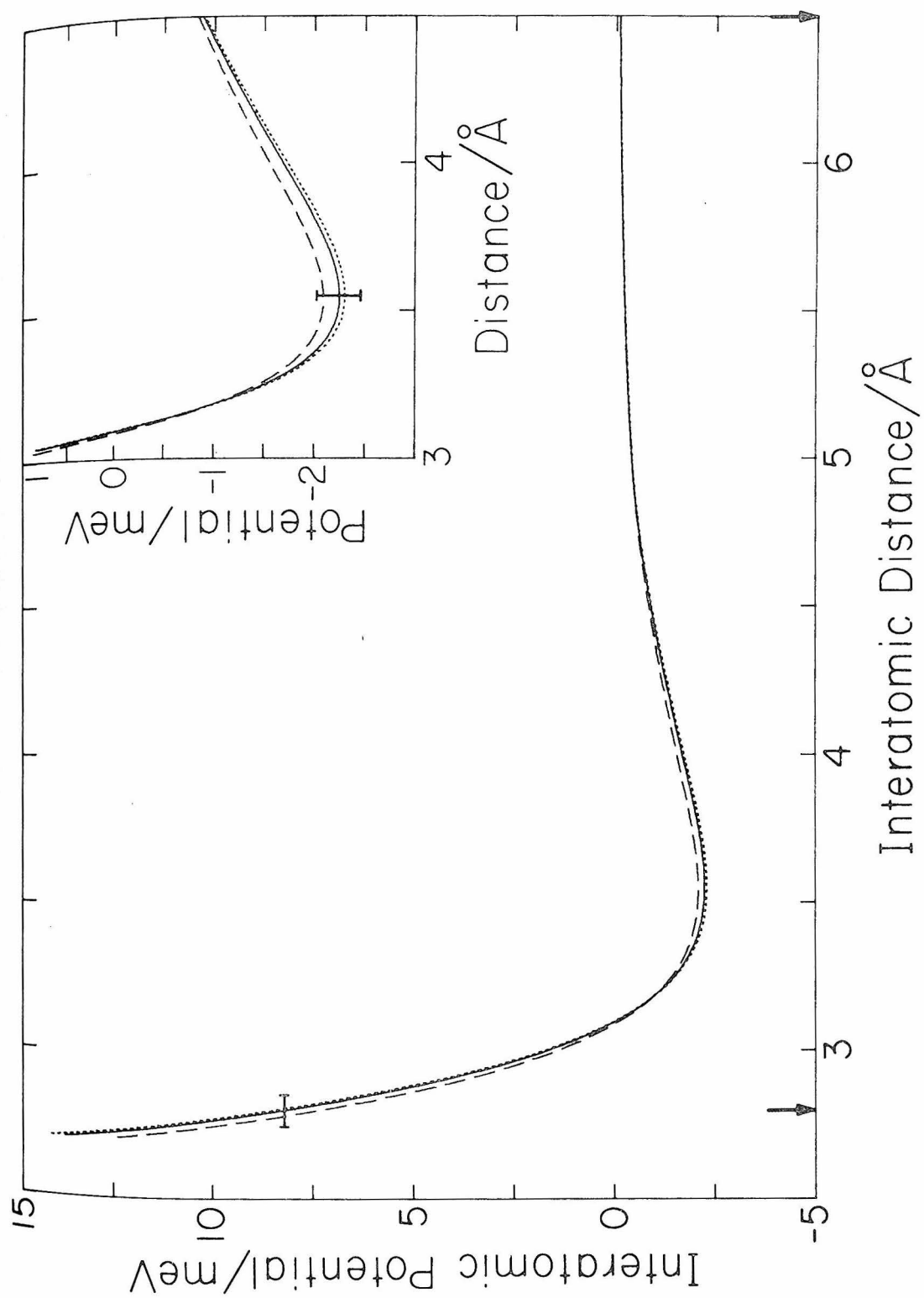


Figure 8

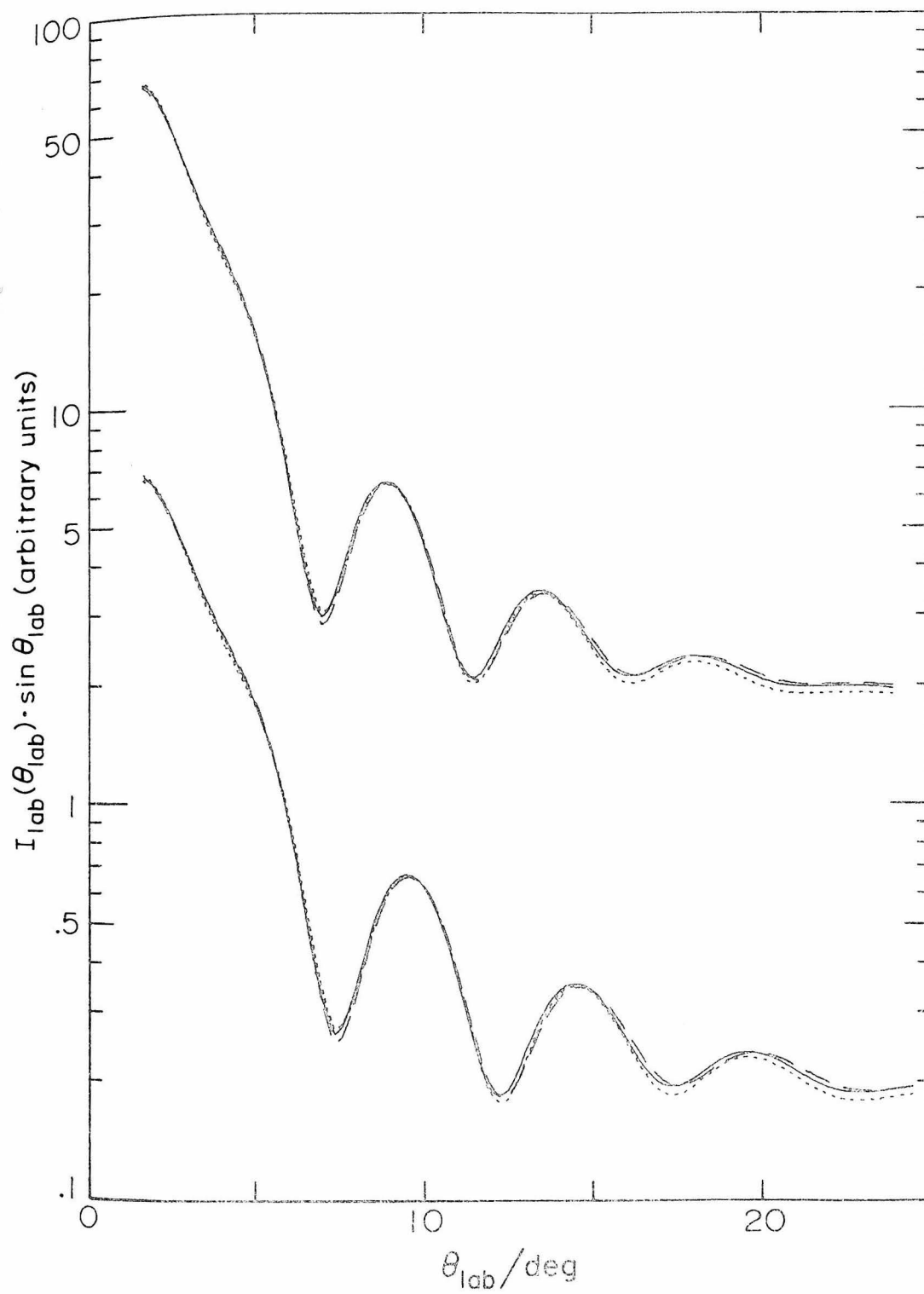


Figure 9

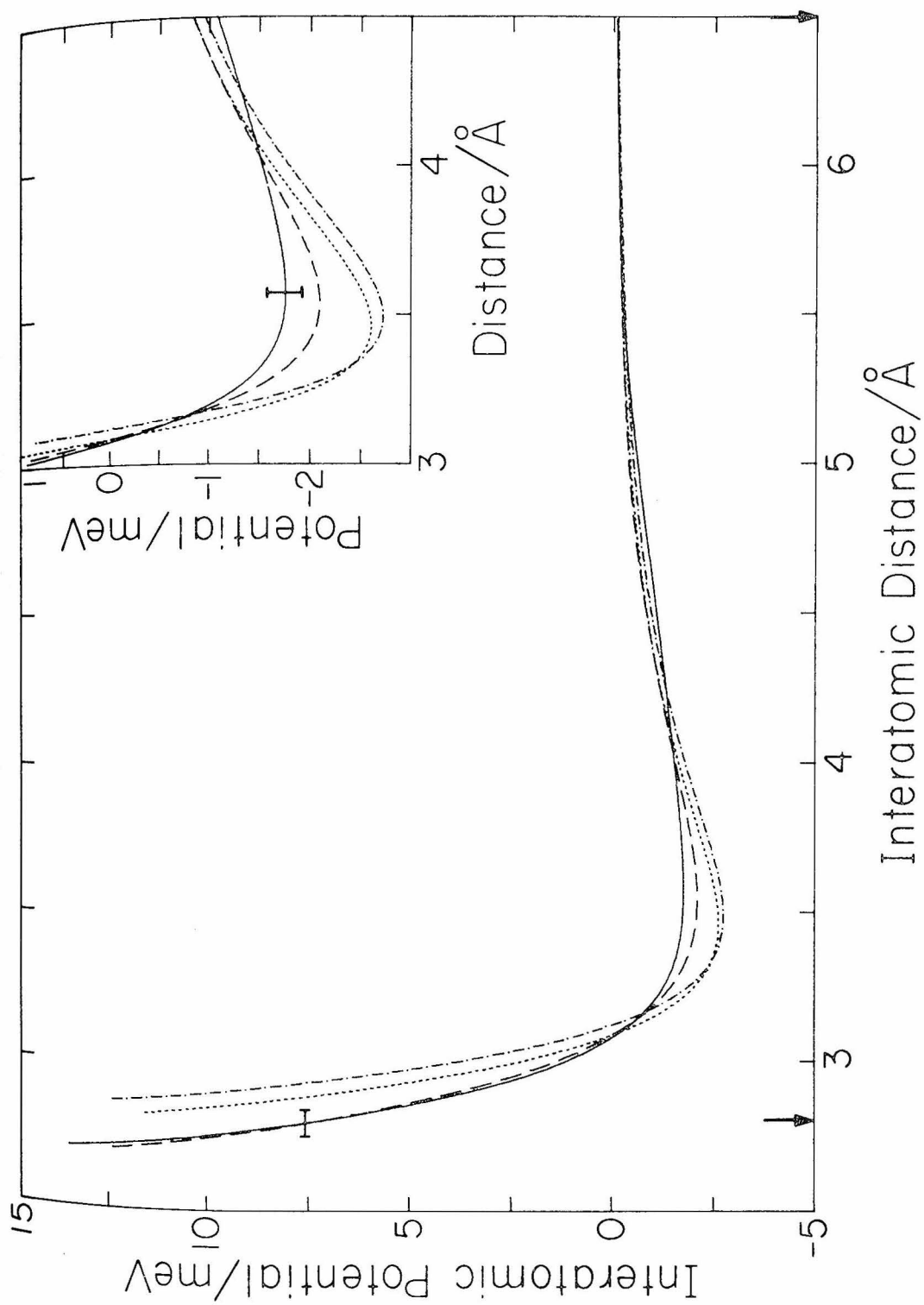


Figure 10

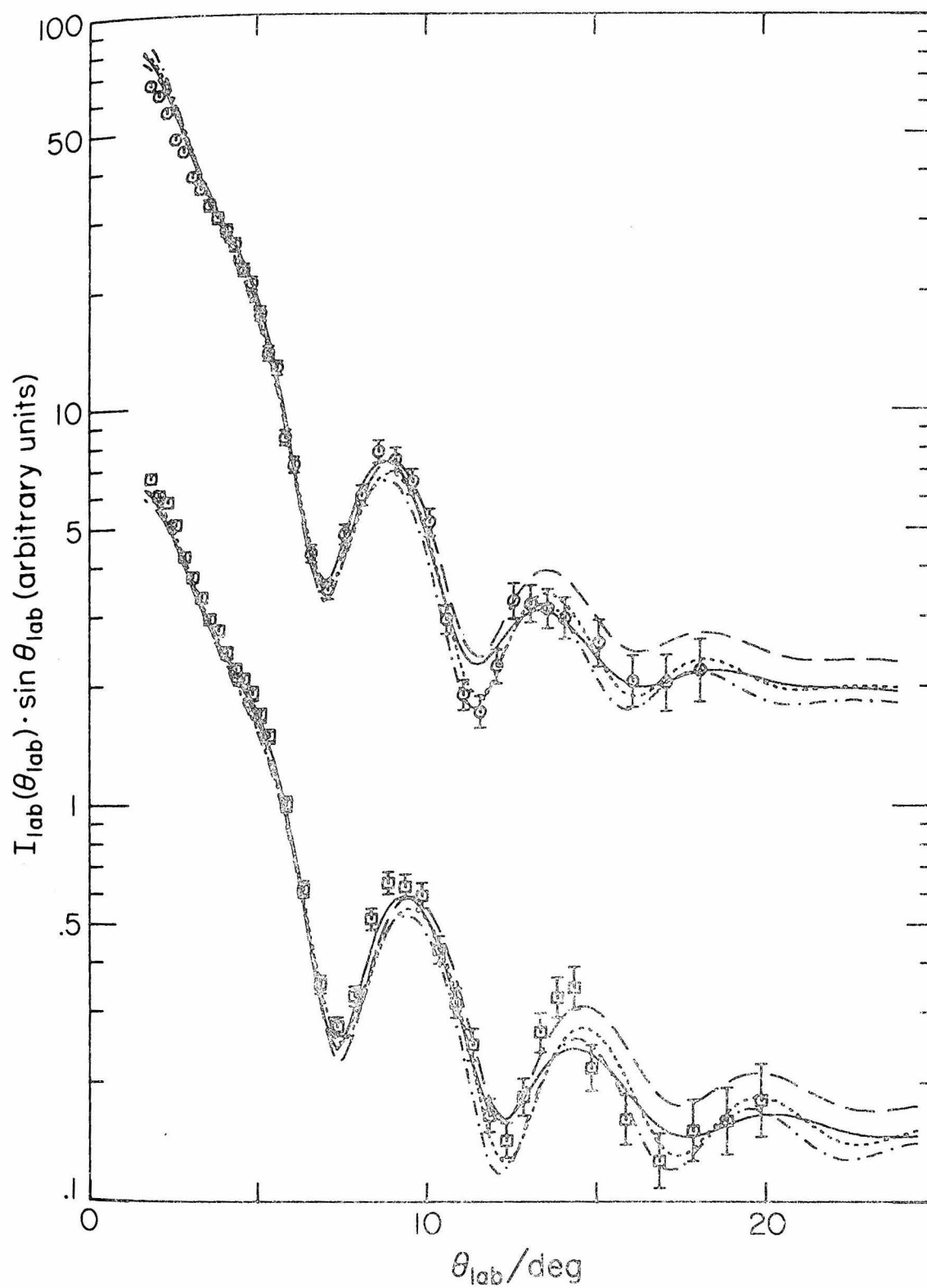


Figure 11

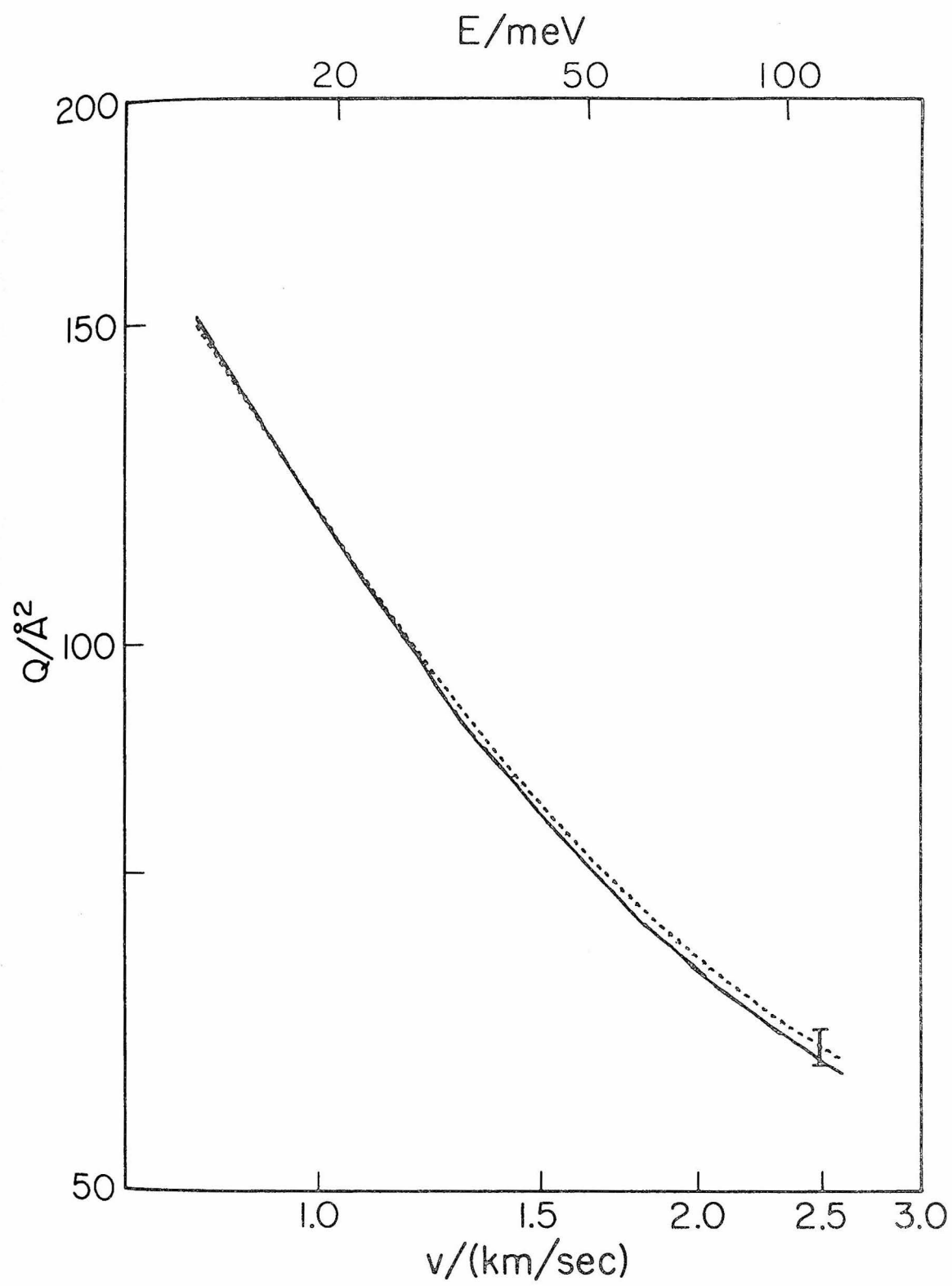


Figure 12

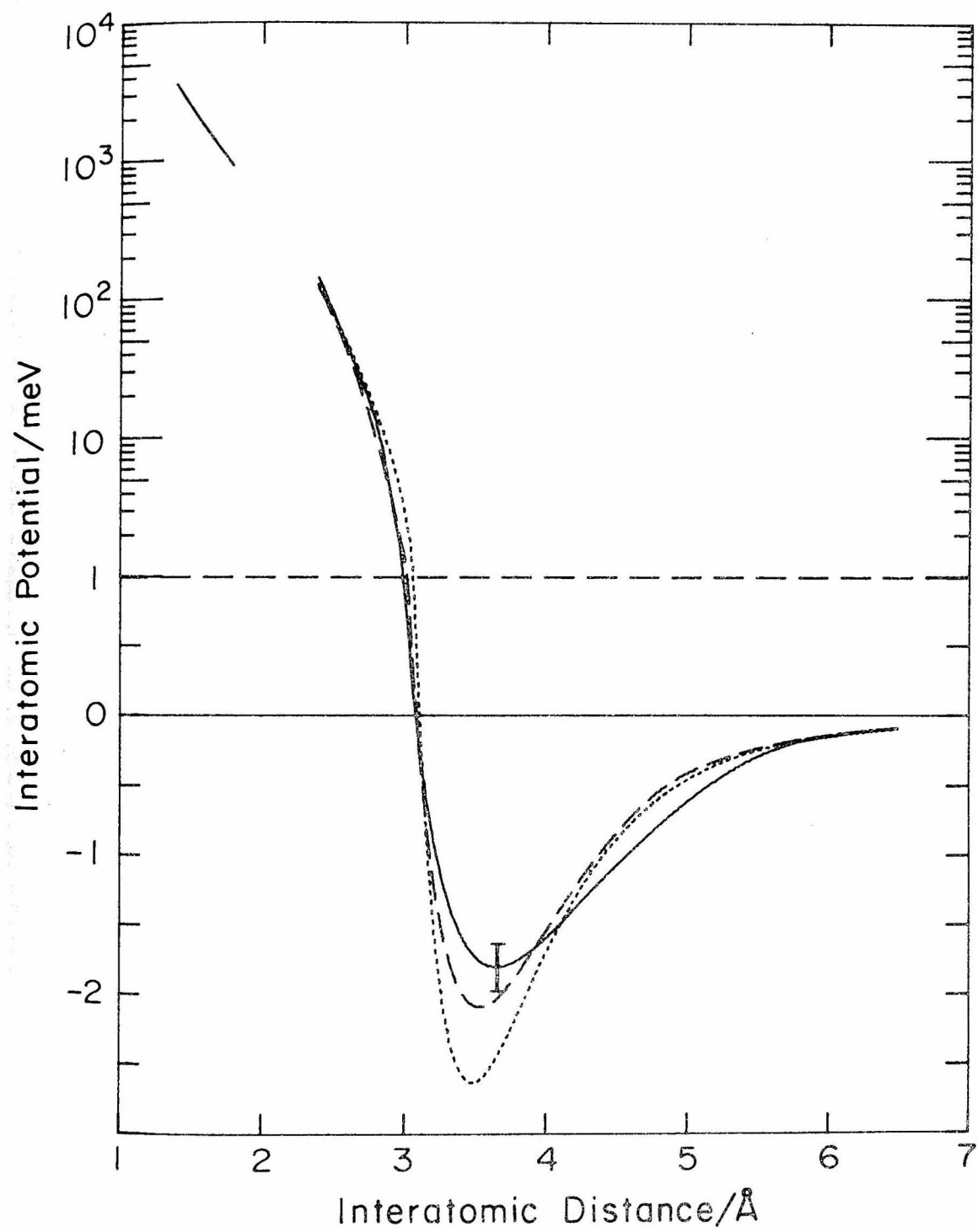


Figure 13

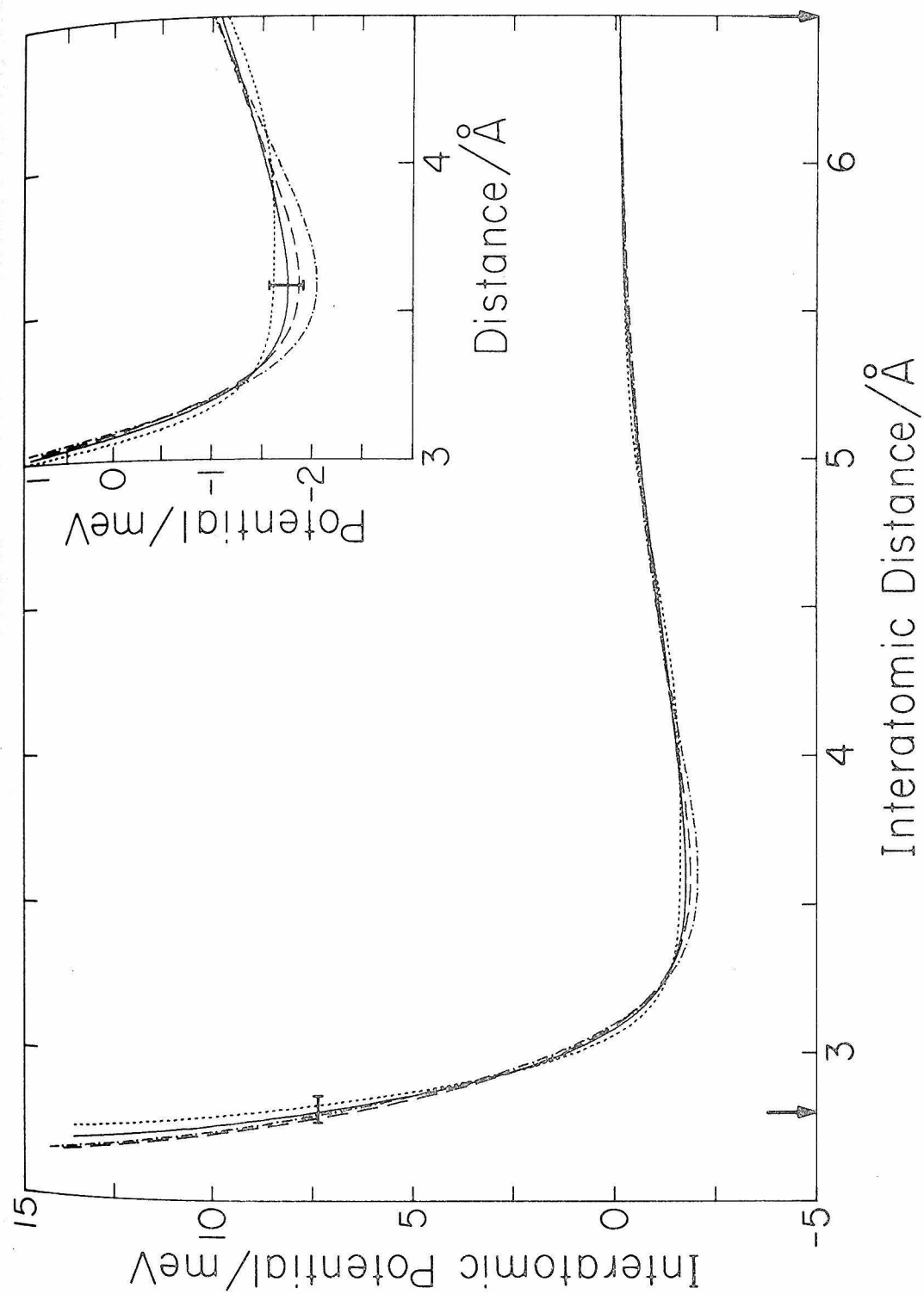


Figure 14

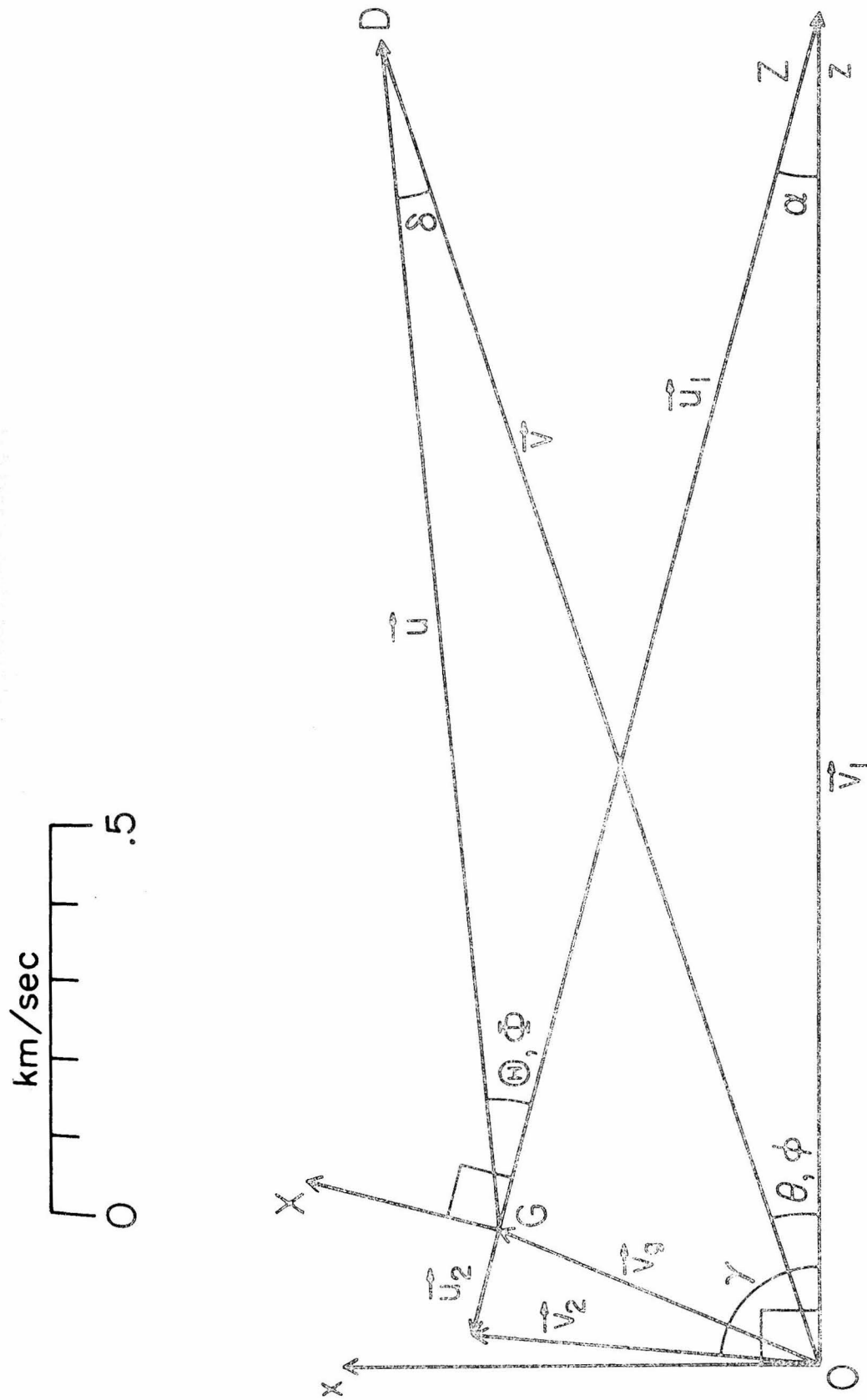


Figure 15

CHAPTER 3

Anisotropic intermolecular potentials

for He-(N₂, O₂, CO, 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.

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c) Contribution No.

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 $\text{He} + \text{N}_2$, O_2 , 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, H_2 , 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

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

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,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., $f(\rho) = Ae^{-b\rho}$, 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 $6.5 \text{ \AA}$ 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 $\sim 5 \text{ \AA}$.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 ($2.8 \text{ \AA} \lesssim r \lesssim 6 \text{ \AA}$).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.

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 $\gamma = \pi/2$.¹¹ 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 ~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 $r_m = 3.30$ Å, $\sigma = 2.98$ Å, and $\epsilon = 2.8$ meV. The theoretical distance parameters appear to be too small by ~0.4 Å, while the well is too deep by perhaps ~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}

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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	$\chi^2_{d,e}$	$\Delta\alpha_{0.95}/\alpha$ (%) ^e
He + N ₂ (29)	MSV	3.67	3.24	2.50	$\beta = 5.82; c_6 = 2.15$	130 (4)	1.74
	M ² SV	3.72	3.24	2.15	$\beta = 5.30; \beta' = 9.09; c_6 = 1.88$	100 (5)	1.58
	SPFD	3.65	3.22	2.27	$b_0 = 31.9; b_1 = -4.72; c_6 = 2.10$	110 (5)	1.64
He + O ₂ (31)	MSV	3.44	3.05	3.05	$\beta = 6.03; c_6 = 1.95$	200 (4)	2.22
	M ² SV	3.49	3.04	2.52	$\beta = 5.35; \beta' = 12.1; c_6 = 1.50$	160 (5)	2.01
	SPFD	3.40	3.03	2.73	$b_0 = 36.3; b_1 = -5.45; c_6 = 1.85$	160 (5)	2.02
He + CO (27)	MSV	3.73	3.32	2.43	$\beta = 6.27; c_6 = 1.62$	190 (4)	1.91
	M ² SV	3.77	3.32	2.09	$\beta = 5.77; \beta' = 10.3; c_6 = 1.29$	160 (5)	1.78
	SPFD	3.70	3.31	2.28	$b_0 = 39.2; b_1 = -5.10; c_6 = 1.52$	160 (5)	1.81
He + NO (26)	MSV	3.69	3.18	2.56	$\beta = 5.03; c_6 = 1.78$	320 (4)	2.55
	M ² SV	3.73	3.17	2.12	$\beta = 4.66; \beta' = 9.33; c_6 = 1.15$	240 (5)	2.23
	SPFD	3.67	3.16	2.16	$b_0 = 19.1; b_1 = -3.98; c_6 = 1.56$	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'_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 higher-order contributions.^dScattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.^eSee 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	$\Delta\alpha'_{0.85}/\alpha$ (%)	spherically averaged anisotropic potential parameters	
	$r_m/\text{\AA}$	r_q	ϵ_0/meV	ϵ_2/meV			$r_m/\text{\AA}$	$\sigma/\text{\AA}$
He + N ₂ (29)	3.60	-0.13	2.43	-0.49	5.75	2.24	130 (5)	1.77
He + O ₂ (31)	3.29	-0.24	2.94	-0.59	5.90	2.13	140 (5)	1.92
He + CO (27)	3.58	-0.22	2.35	-0.47	6.25	1.75	120 (5)	1.59
He + NO (26)	3.45	-0.30	2.45	-0.49	4.98	1.98	100 (5)	1.46

^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 M²SV 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).

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 sections¹⁸ $I(\theta) \cdot \sin\theta$ 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.

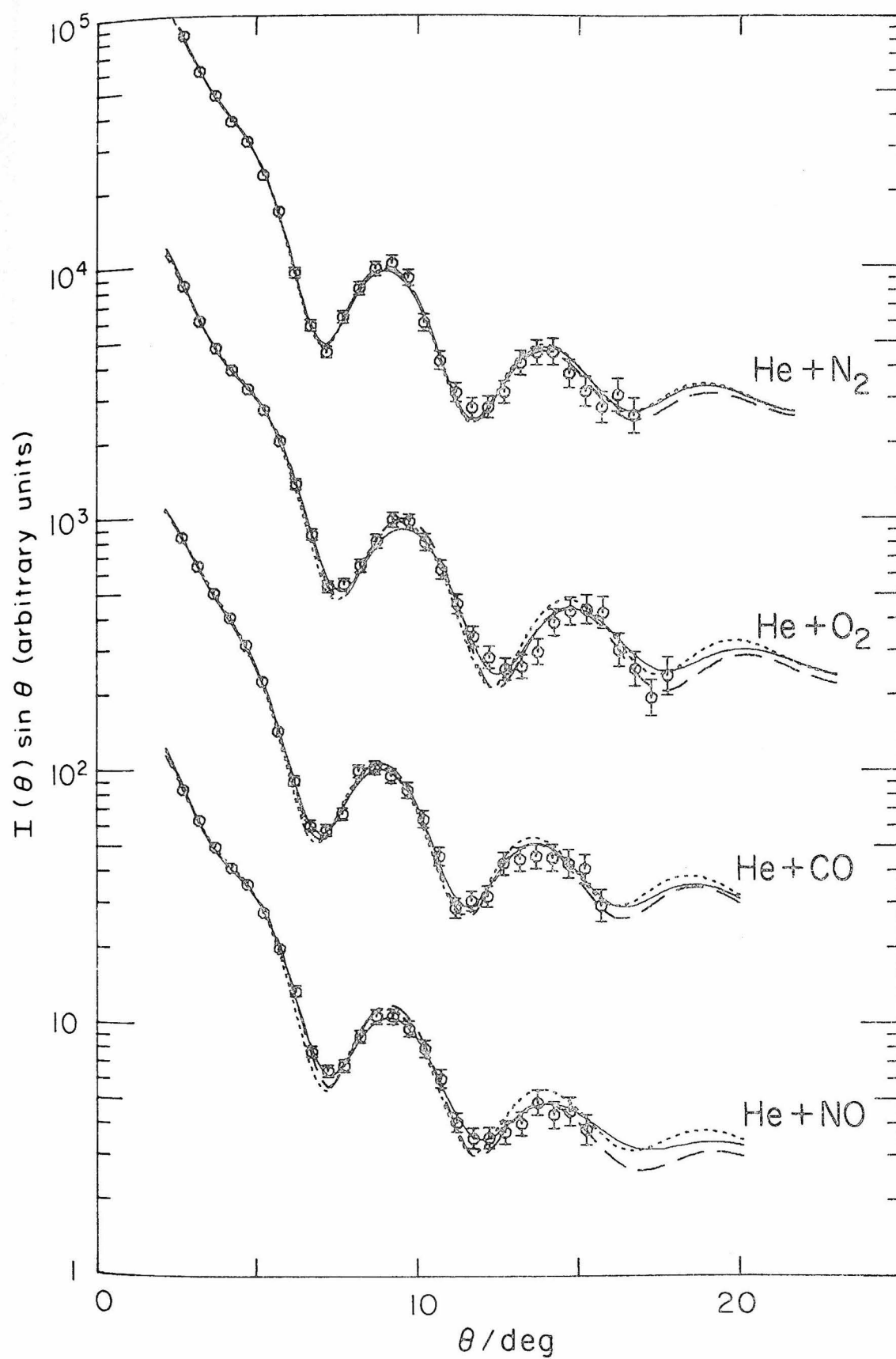


Figure 1

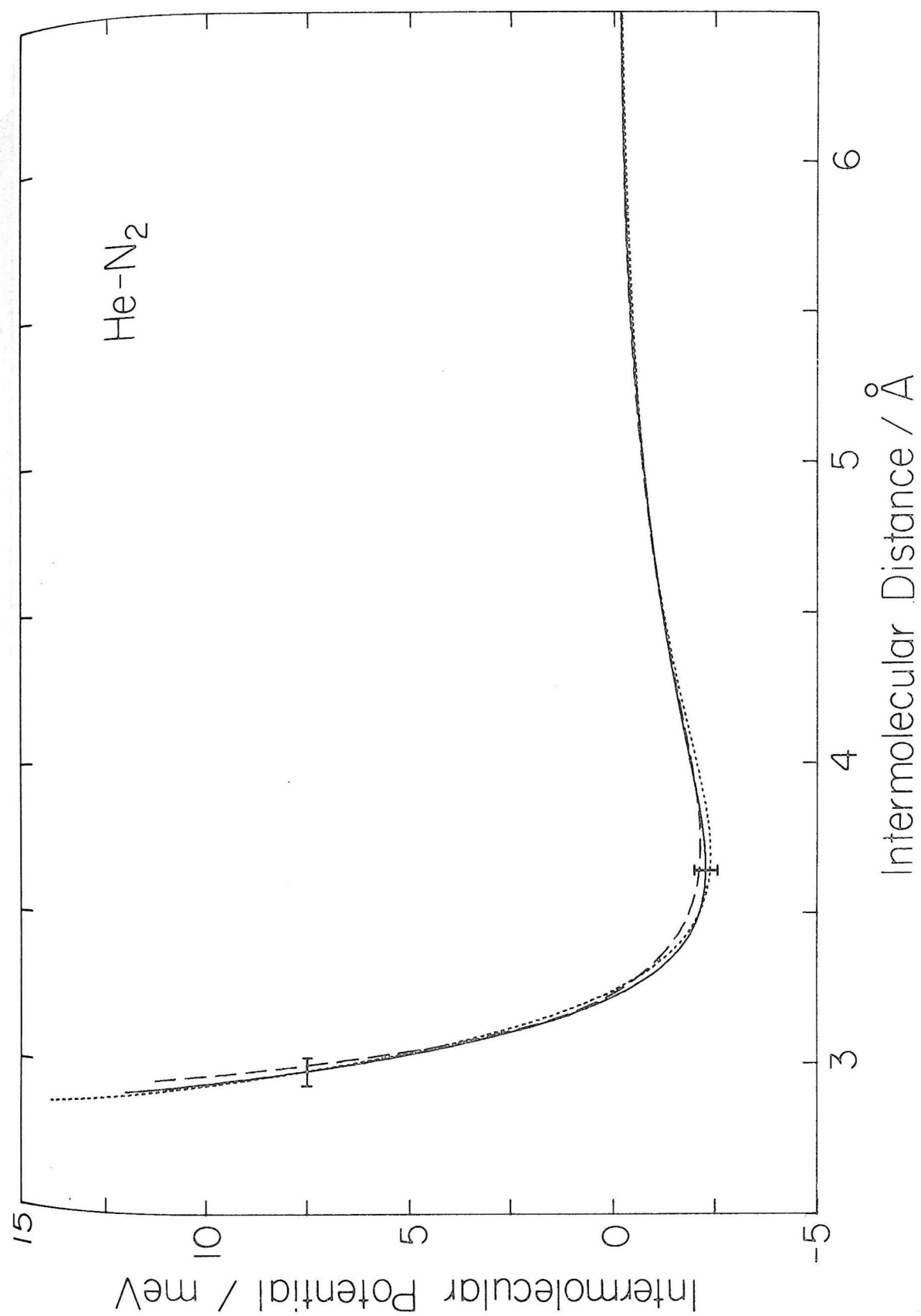


Figure 2

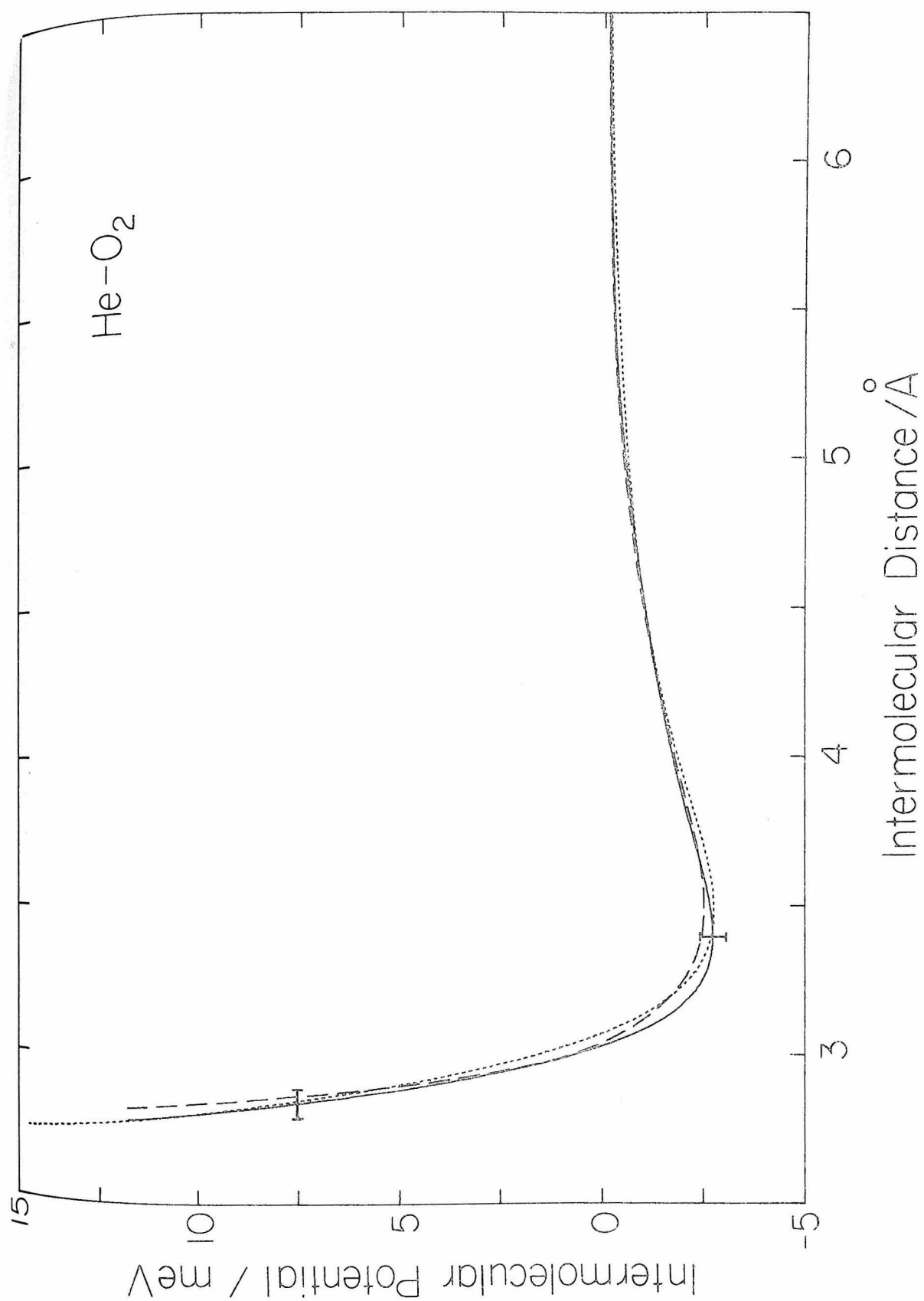


Figure 3

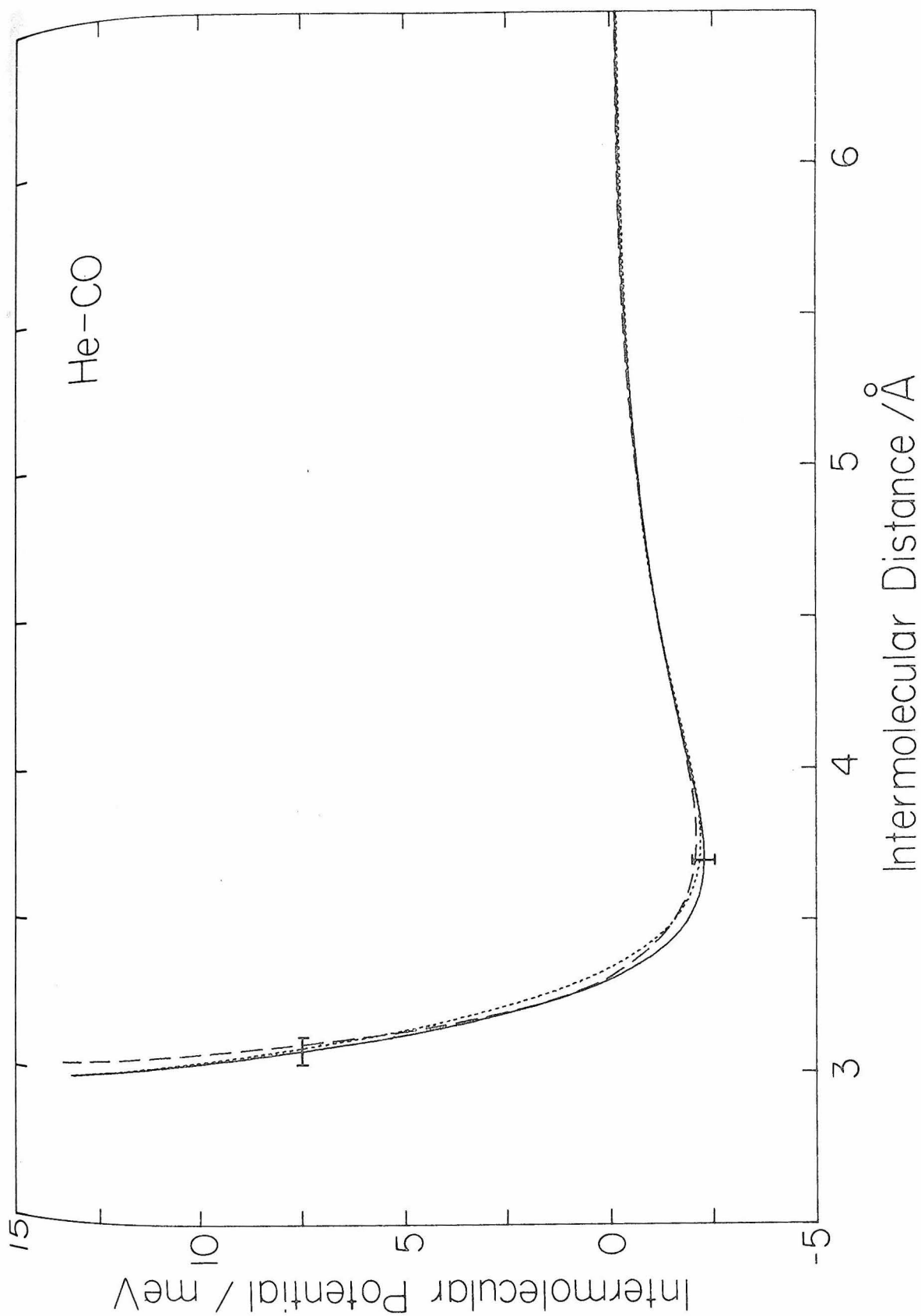


Figure 4

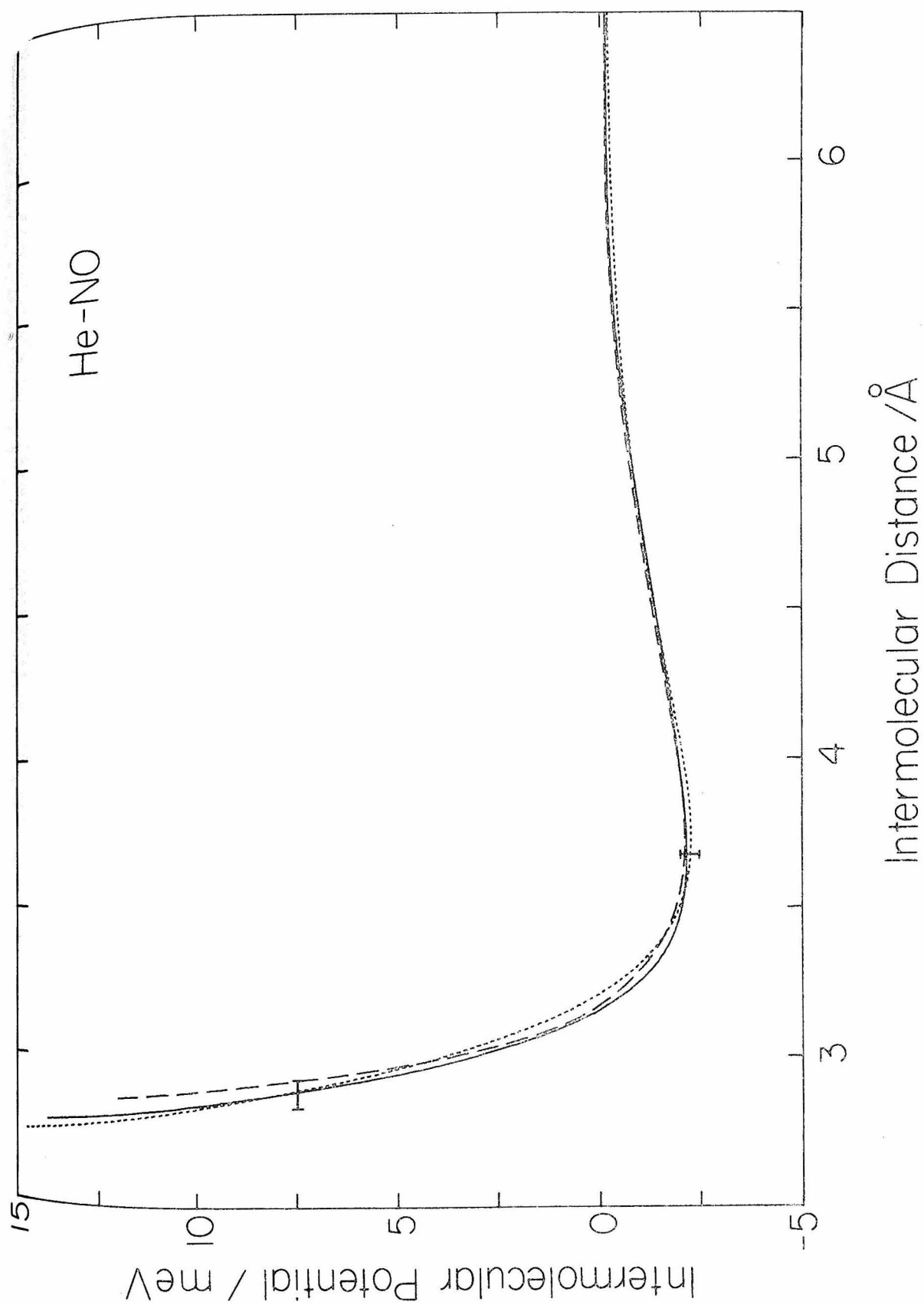


Figure 5

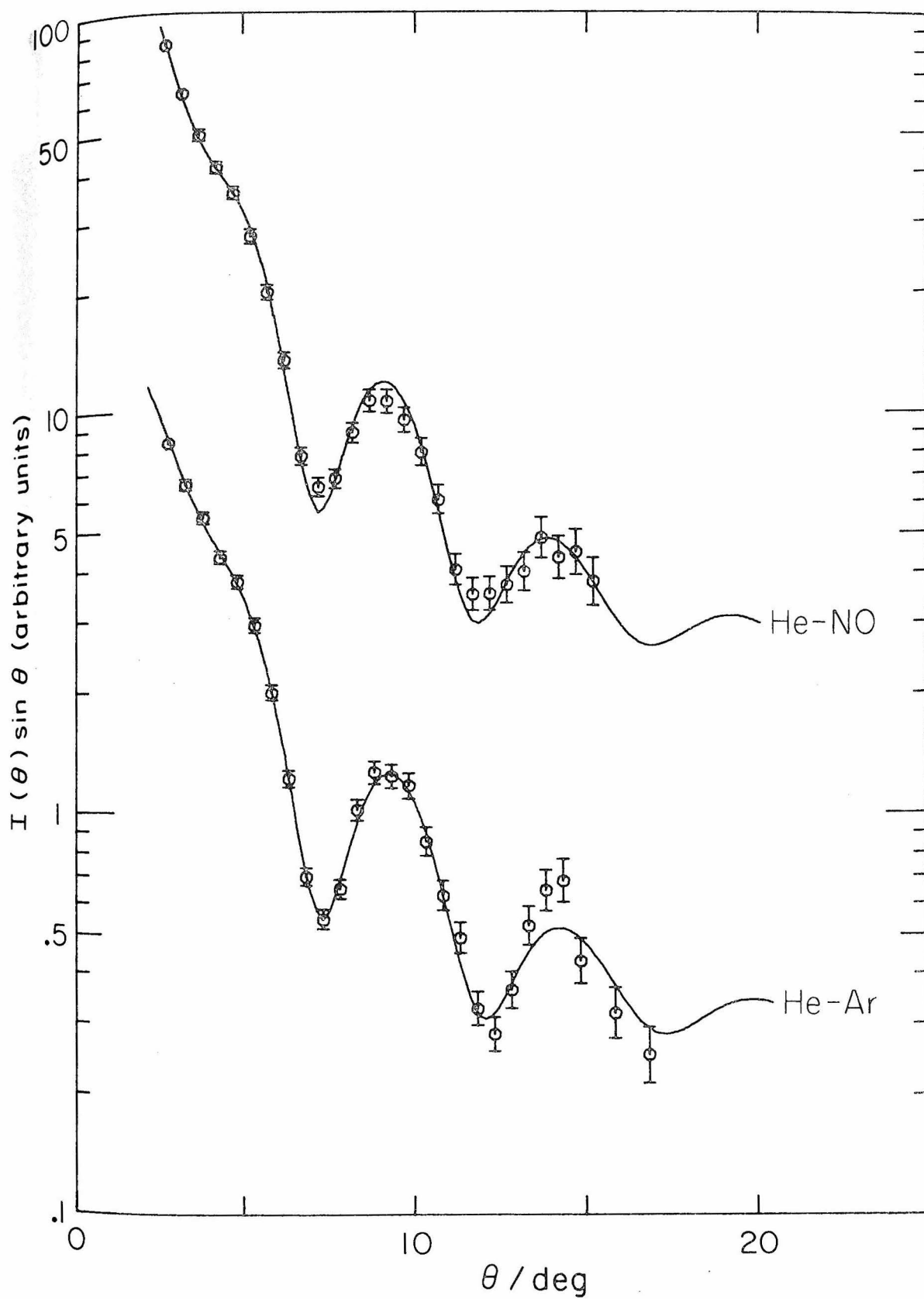


Figure 6

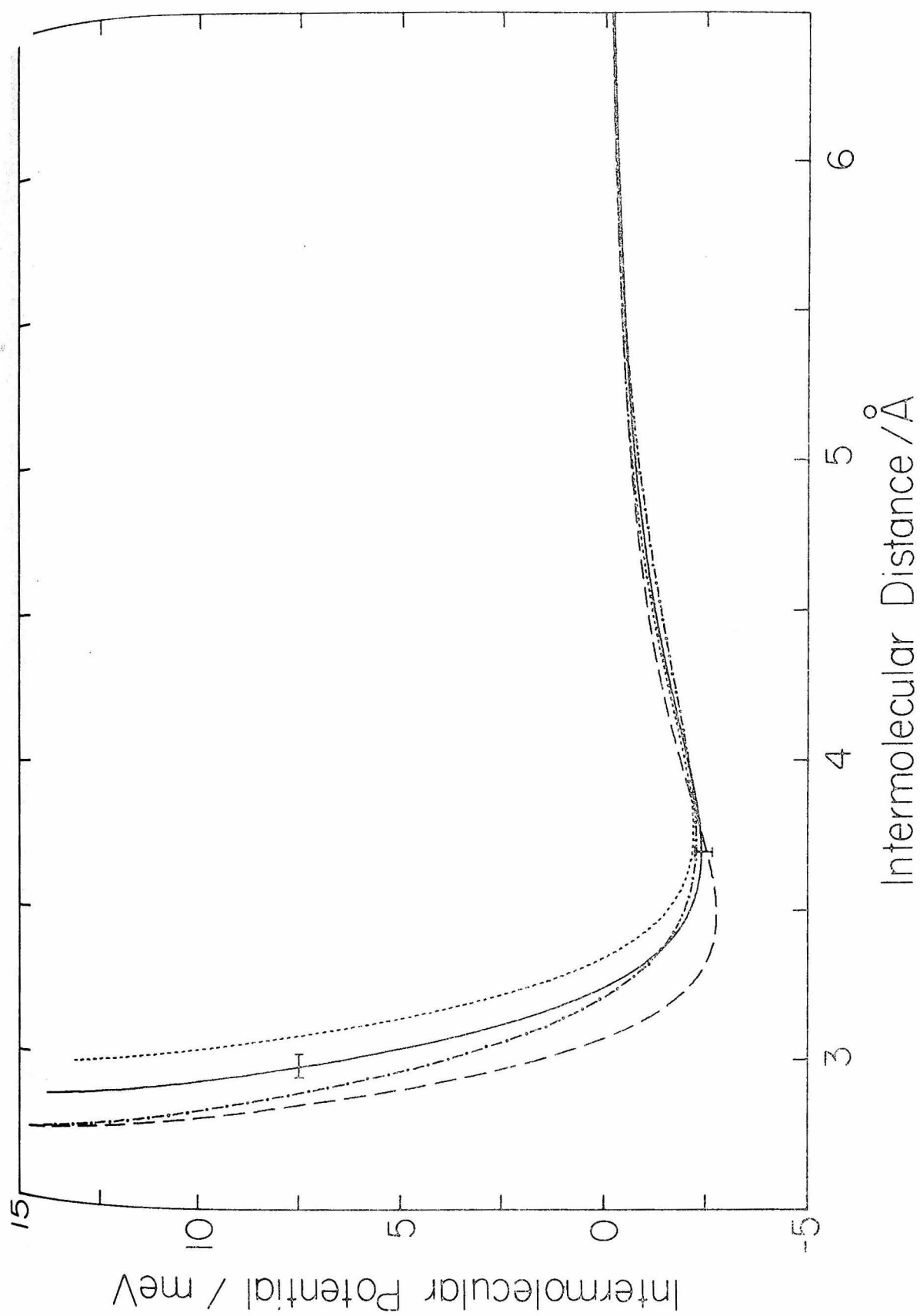


Figure 7

CHAPTER 4

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) correlates with the van der Waals well depth.

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^{c)}Contribution No. .

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 of this paper, 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 is best described by a Mach number of 1.5 and an "effective" specific heat ratio of 1.64,¹³ indicating only a 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. In addition, it 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 non-linear 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 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,

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

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.

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

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 MSV 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, labeled 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, or $\sim 5 \times 10^{10}$ 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 the 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 both semiclassically²⁷ and quantum mechanically,³⁰ and that has recently been observed for scattering in highly anisotropic systems (e.g., He + CO₂).¹¹ This lack of evidence for quenching is equally true 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 these same 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 the perpendicular one. From this it was concluded in Paper III 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 Ref. 10) 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 He + SF₆ interaction somewhat separately later in this section.

A. He + CH₄, NH₃, and H₂O interactions

Potential parameters obtained from central-field analyses of the He + CH₄, NH₃, and H₂O DCS's are presented in Table II. As in previous work, it may immediately be seen that the five-parameter M²SV and SPFD potentials are better able to fit the DCS data for these three systems than is the MSV model, even when 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 (± 0.06 Å for r_m and ± 0.01 Å for σ); however, ϵ values obtained by using the MSV potential model are consistently $\sim 20\%$ greater than for the M²SV 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 M²SV and SPFD values of ϵ for the He + CH₄, NH₃, and H₂O systems are different by only $\sim 2\%$.

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 $\Delta\alpha_{0.95}/\alpha \lesssim 2.2\%$). 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 for the same out-of-plane scattering geometry as the Waterloo group. Nevertheless, the experimental (H₂, He) + NH₃ scattering data 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 d 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 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 $\text{\AA}$ 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 nearly spherically symmetric 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 $\simeq$ 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 30% 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 ϵ is more than twice that for most other molecular interactions with He,^{10,19} having the important consequence of reducing the collision energy from $\sim 30 \epsilon$ to $\sim 13 \epsilon$. (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. 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 ($\sim 9 \epsilon$) 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. It may be more appropriate to introduce greater flexibility into the long-range region (e.g., 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 play 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

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 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.

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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	$\chi^2 d, e$	$\Delta\alpha_{0.95}/\alpha^e$ (%)
He + CH ₄ (30)	MSV	3.86	3.41	2.42	$\beta = 6.01; c_6 = 2.20$	340 (4)	2.73
	M ² SV	3.90	3.40	2.06	$\beta = 5.43; \beta' = 10.2; c_6 = 1.92$	270 (5)	2.46
	SPFD	3.80	3.40	2.00	$b_0 = 36.2; b_1 = -5.96; c_6 = 2.10$	250 (5)	2.39
He + NH ₃ (31)	MSV	3.76	3.29	2.48	$\beta = 5.54; c_6 = 2.23$	200 (4)	2.13
	M ² SV	3.82	3.28	2.03	$\beta = 4.94; \beta' = 9.57; c_6 = 1.86$	140 (5)	1.83
	SPFD	3.73	3.28	2.08	$b_0 = 27.5; b_1 = -4.98; c_6 = 2.19$	150 (5)	1.89
He + H ₂ O (30)	MSV	3.46	3.03	2.71	$\beta = 5.54; c_6 = 2.40$	210 (4)	2.53
	M ² SV	3.50	3.01	2.31	$\beta = 5.02; \beta' = 10.6; c_6 = 2.01$	160 (5)	2.24
	SPFD	3.38	3.01	2.27	$b_0 = 31.4; b_1 = -6.15; c_6 = 2.30$	150 (5)	2.16
He + SF ₆ (26)	MSV	4.24	3.75	4.68	$\beta = 6.10; c_6 = 1.25$	100 (4)	1.46
	M ² SV	4.23	3.76	4.68	$\beta = 6.15; \beta' = 5.07; c_6 = 1.29$	90 (5)	1.43
	SPFD	4.23	3.77	4.79	$b_0 = 39.8; b_1 = -4.62; c_6 = 1.31$	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 $\rho_2 = 1.60$; 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 $C'_6 = \epsilon r_6^6 c_6$. The prime denotes an effective dispersion coefficient, obtained by neglecting contributions from higher-order multipole terms.

^dScattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.

^eSee 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 ($r \lesssim 5 \text{\AA}$) 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, $\sigma = 2^{-1/6} r_m$.

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 , proceeding downwards by one decade for each system in this sequence. 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 Section 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 Section III for a discussion of the definition of this distance). The error with which this potential has been determined is discussed in Sec. IVB. The range of validity of this potential is approximately $3.7 \text{ \AA}$ ($V \gtrsim 5 \text{ meV}$) to $7 \text{ \AA}$.

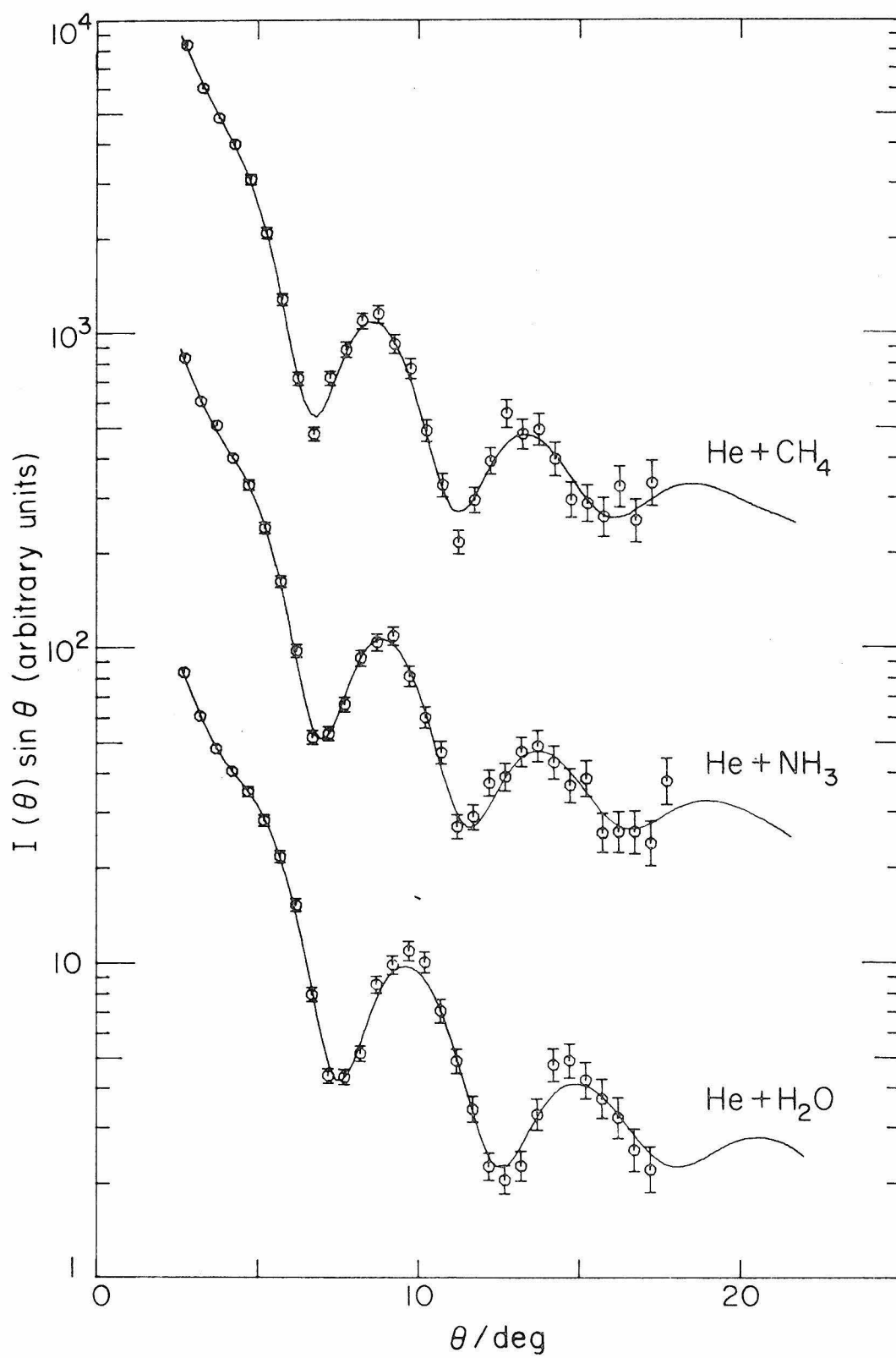


Figure 1

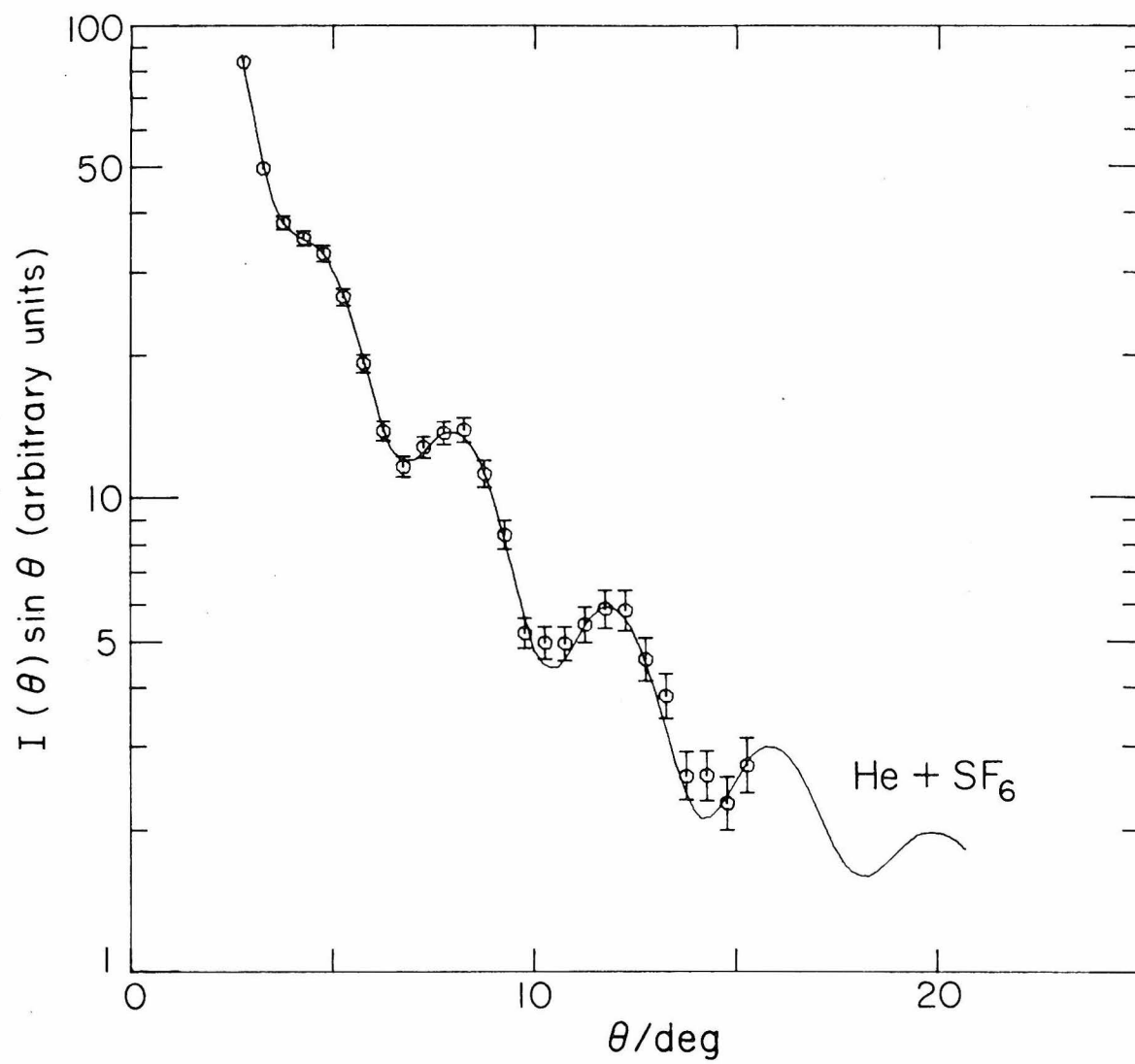


Figure 2

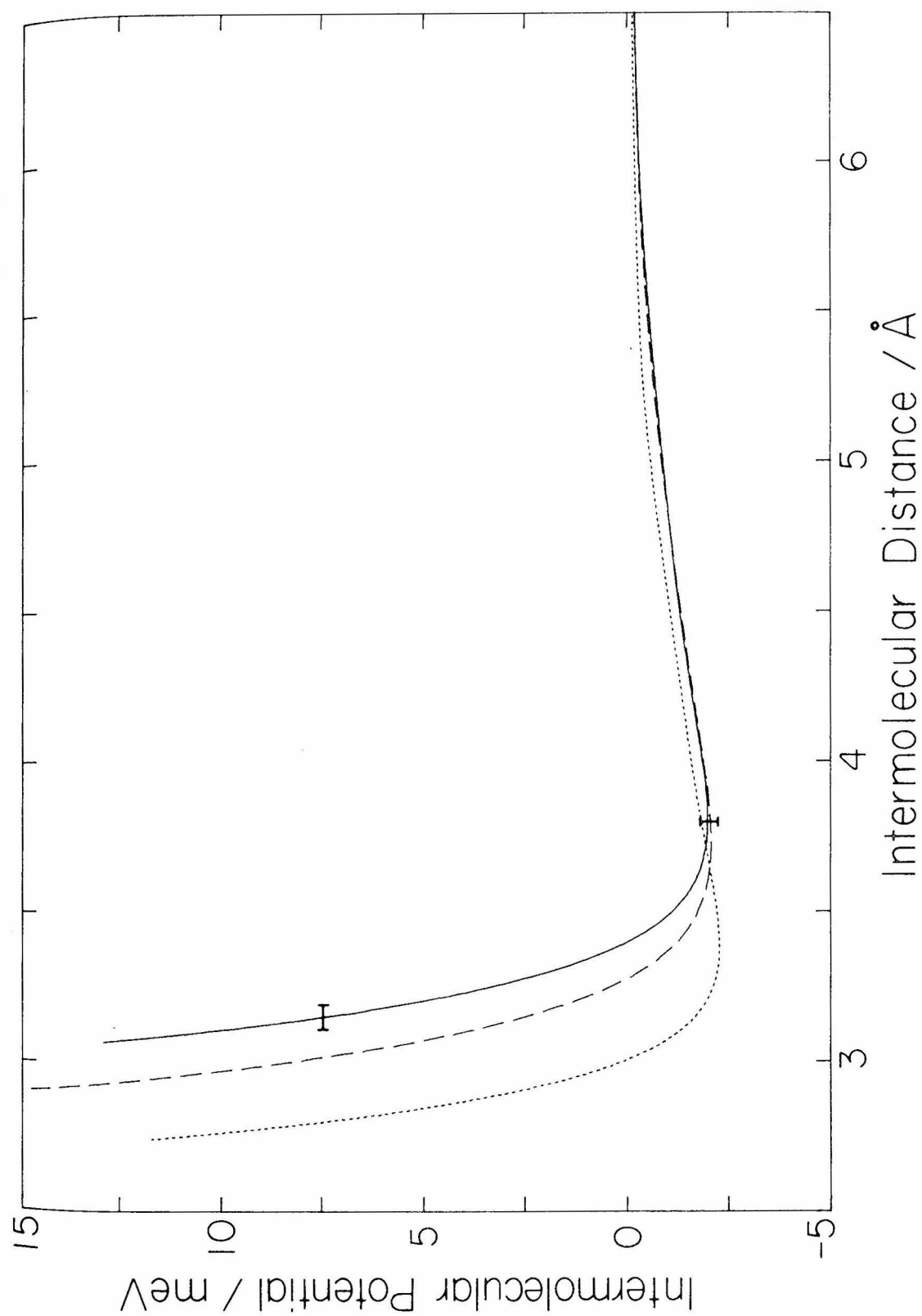


Figure 3

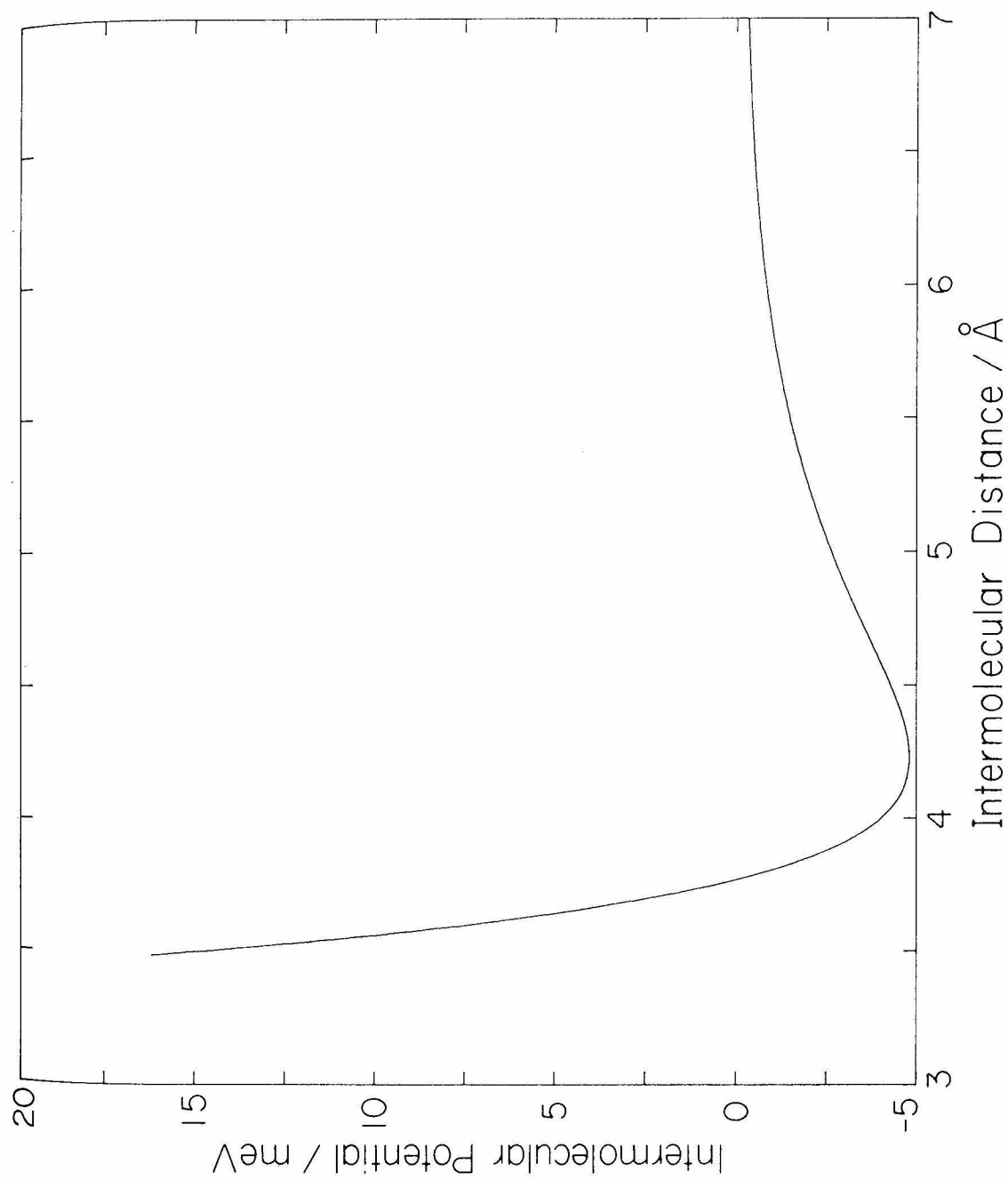


Figure 4

CHAPTER 5

An anisotropic intermolecular potential
for He-CO₂

An anisotropic intermolecular potential for He-CO₂^{a)}

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Despite fundamental interest in anisotropic effects in molecular scattering, detailed experimental investigations of such effects have only recently been fruitful.¹⁻⁵ Semiclassical calculations have been used to predict⁶ quenching of glory, supernumary, and rapid oscillations⁷ in scattering cross sections. Although the semiclassical prediction has been borne out for heavy-particle (e.g., Ar-N₂)⁸ differential cross section (DCS) scattering, this theory is inapplicable for highly quantum systems (e.g., thermal scattering of He, H₂ or D₂).⁹ Strong anisotropic effects in the DCS for such systems¹⁰ have not yet been substantiated;¹¹ indeed, molecular scattering results are most often interpreted by using the central-field approximation.^{9,11-15} We report herein the first unambiguous experimental indication of the effects of anisotropic potentials on the total DCS for atom-molecule scattering in highly quantum systems. We find that even highly

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^{c)}Contribution No. 5767.

flexible central-field potentials¹⁶⁻¹⁸ are unable to fit such DCS data for He-CO₂. Conversely, a physically reasonable anisotropic potential model with the same number of adjustable parameters, in conjunction with the infinite-order sudden approximation (IOSA),¹⁹ yields a high quality fit to the DCS.

Recently, it has become possible to calculate DCS curves for atom-molecule anisotropic potentials, without having to perform elaborate (and expensive) close-coupling calculations.^{19, 20} The particularly successful IOSA should be accurate when the collision energy is substantially greater than the rotational spacings of the molecular partner.^{19, 21} This condition is amply satisfied in the present case, with a collision energy of 64 meV and a rotational spacing for the most probable level ($j = 16$) of 1.5 meV.

Our model for the He-CO₂ anisotropic potential $V(r, \gamma)$ is given by an elliptical modification to central-field types of potentials:²²

$$\left. \begin{aligned} V(r, \gamma) &= \epsilon(\gamma) \cdot f[\rho(r, \gamma)] ; & \rho(r, \gamma) &= \frac{r}{r_m(\gamma)} ; \\ r_m(\gamma) &= r_{m\perp} \cdot \left(\frac{1 + r_q \sin^2 \gamma}{1 + r_q} \right)^{\frac{1}{2}} ; & \epsilon(\gamma) &= \epsilon_0 + \epsilon_2 P_2(\cos \gamma) . \end{aligned} \right\} \quad (1)$$

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 an arbitrary γ , $r_m(\gamma)$ is the value of r for the potential minimum and $-\epsilon(\gamma)$ is the corresponding potential energy. Any central-field reduced potential energy function $f(\rho)$ may be used, since Eq. (1) introduces anisotropy into the potential through the elliptically shaped $r_m(\gamma)$ and the Legendre polynomial representation

for $\epsilon(\gamma)$. We use the MSV potential form²³ for $f(\rho)$; its Morse function is joined smoothly to the known anisotropic dispersion series for He-CO₂²⁴ at $r = 1.6 r_m(\gamma)$.¹⁶ The fitted parameters are the Morse shape parameter β , the anisotropy parameters r_q and ϵ_2 , as well as $r_{m_\perp}$ and ϵ_0 . Simultaneous adjustment of up to five such statistically independent parameters to room-temperature DCS measurements has been shown to be appropriate for highly quantum systems.¹⁶

The present experiments are most sensitive to the attractive well region of the potential, and somewhat sensitive to adjacent regions.¹⁶ The experimental measurements were made using a crossed molecular beams apparatus, described elsewhere.^{9,25} No scattered beam velocity analysis was performed in our measurements.

In Fig. 1 we display the measured He-CO₂ DCS data, and DCS curves calculated (including appropriate velocity and angular averaging) from the least-squares fitted anisotropic and central-field potentials, as well as from the spherical average of the former potential. It is clear that the anisotropic model of Eq. (1) is much more realistic than the highly flexible central-field Simons-Parr-Finlan Dunham (SPFD) potential,¹⁶⁻¹⁸ for which we also adjusted five parameters. Both spherically symmetric potentials produce pronounced oscillatory structure, whereas for both the experimental and IOSA DCS's this structure is appreciably attenuated. We find that, for the highly anisotropic He-CO₂ system, the central-field SPFD potential does not yield the spherical average of the anisotropic potential.^{9,11-13}

The empirical anisotropic potential energy surface obtained from these fits is shown in Fig. 2 over its approximate range of validity.¹⁶

It may be possible to extend this potential to the highly repulsive wall region by combining measurements of gas-phase transport properties¹⁵ with electron-gas calculations.²⁶ Such an extended potential should be useful for the calculation of rotationally inelastic cross sections.

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FIGURE CAPTIONS

Fig. 1. Laboratory differential cross sections $I(\theta)$ for out-of-plane scattering of He by CO_2 at a relative collision energy of 64 meV. Points with error bars are experimental measurements of $I(\theta) \cdot \sin\theta$ vs. the scattering angle θ ; curves are DCS's calculated using potentials extracted from the data. Solid line: anisotropic MSV potential of Eq. (1); dashed line: central-field SPFD potential^{16,17} ($r_m = 3.58 \text{ \AA}$, $\epsilon = 4.51 \text{ meV}$); dotted line: spherical average of the anisotropic MSV potential ($r_m = 3.93 \text{ \AA}$, $\epsilon = 2.98 \text{ meV}$).

Fig. 2. He- CO_2 empirical potential energy surface, calculated from the anisotropic MSV potential of Eq. (1), with best-fit parameters of $r_{m\perp} = 3.31 \text{ \AA}$, $\epsilon_0 = 2.98 \text{ meV}$, $\epsilon_2 = -1.91 \text{ meV}$, $r_q = -0.52$, and $\beta = 4.59$. Potential energy contours (in meV) are displayed for $V(r, \gamma) \leq 10 \text{ meV}$; the polar coordinates of points in this diagram are r (in $\text{\AA}$) and γ . Solid lines: $V(r, \gamma) > 0$; dashed line: $V(r, \gamma) = 0$; dotted lines: $V(r, \gamma) < 0$. The absolute minimum on the potential surface is -3.93 meV and occurs at $\gamma = \pi/2$; $r = 3.31 \text{ \AA}$. Saddle points occur for the collinear configurations $\gamma = 0, \pi$; $r = 4.77 \text{ \AA}$, where the potential energy is -1.07 meV . The minimum and saddle point positions are denoted by crosses. The position of the C and O atoms are also shown for reference. The slight unevenness of some of the contours is caused by the crudeness of the potential model [Eq. (1)].

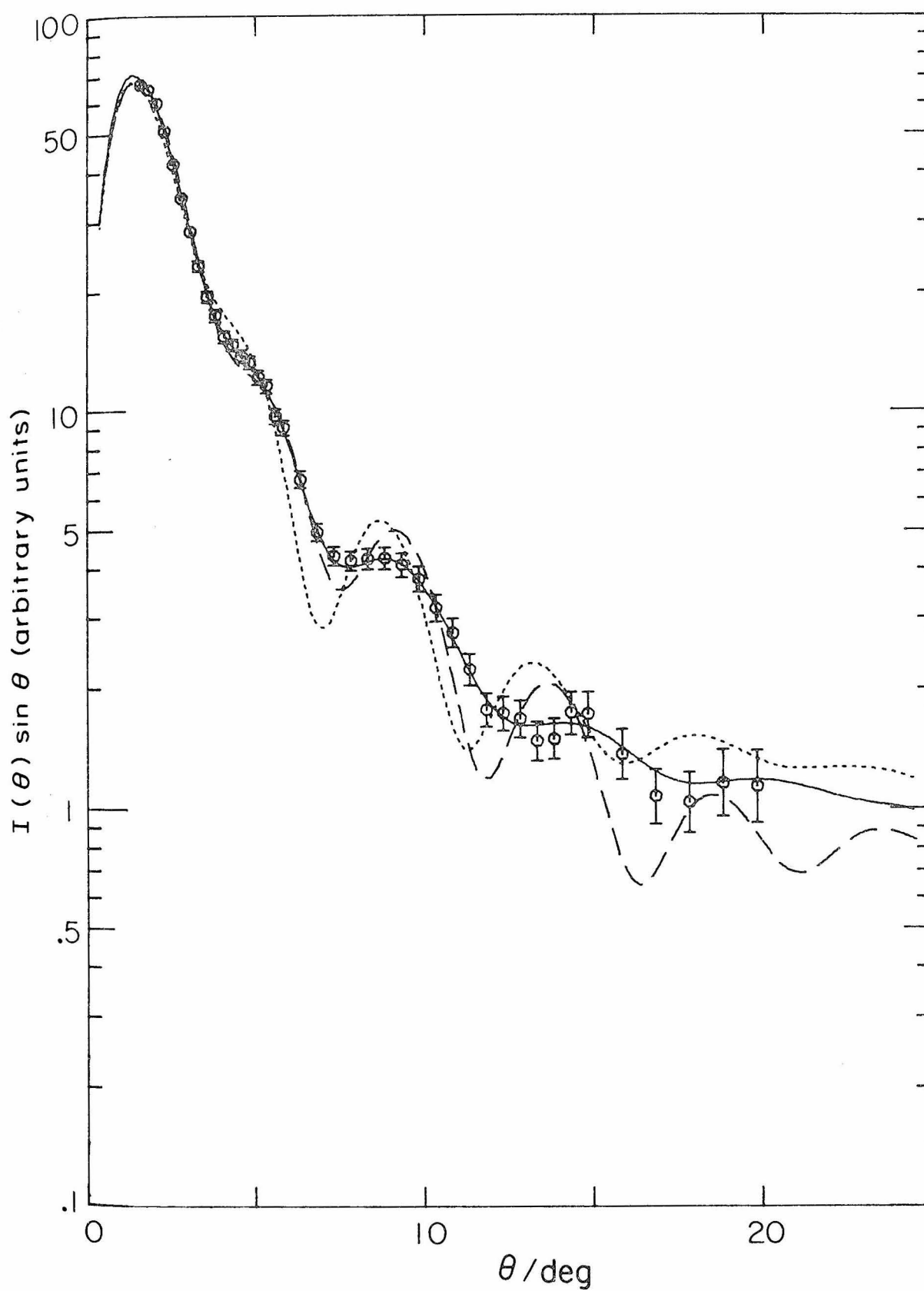


Figure 1

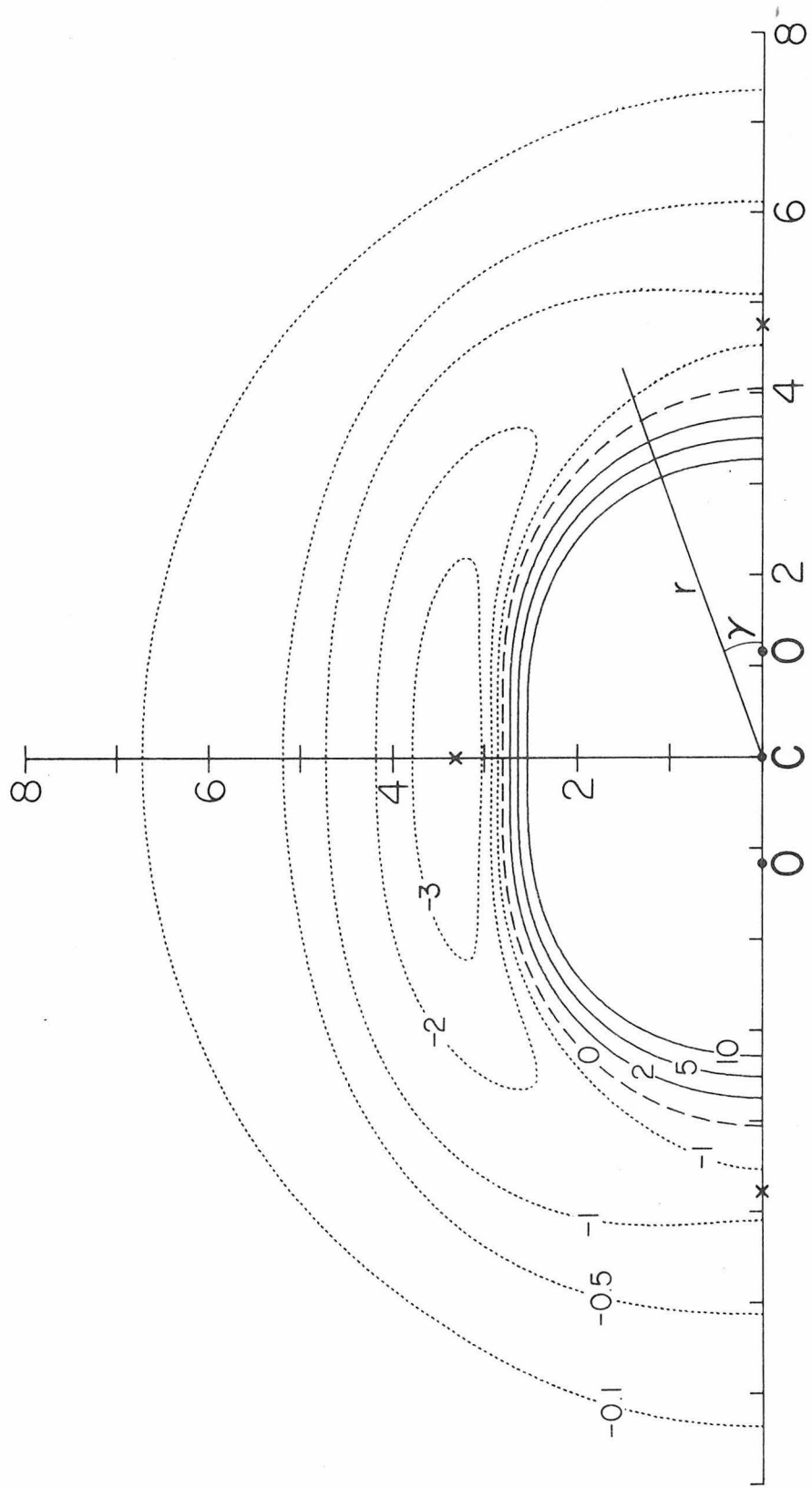


Figure 2

APPENDIX A

An accurate determination of the He-Ar
van der Waals potential

AN ACCURATE DETERMINATION OF THE
He-Ar VAN DER WAALS POTENTIAL^{*}

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ABSTRACT

A new van der Waals potential for He-Ar is constructed from a systematic analysis of differential cross section scattering data. The significant discrepancies between this potential and those based on similar experiments in other laboratories are shown to be due primarily to biases present in the mathematical parameterizations used previously. The new potential is valid for interatomic separations between 2.4 Å and 6.5 Å, and provides an excellent description of all available He-Ar data, including transport and virial coefficients. This potential, which has a well depth of 1.78 meV, is parameterization-independent and accurate to 10%.

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[‡]Contribution No. 5713.

I. Introduction

Despite considerable attention devoted to determining heteronuclear interatomic potentials for rare gas pairs, they have heretofore resisted definitive characterization. This is especially true of He-containing pairs, whose shallow well depths and highly quantum nature limit the usefulness of many of the techniques often used for studies of the important van der Waals attractive minimum. For example, only the repulsive part of the potential may accurately be determined from bulk properties [1-3]. On the other hand, even spectroscopic measurements, which are as yet providing accurate data only for the minima of the heavier rare gas pairs, would provide only a constraint on weakly-bound interatomic potentials, since several vibrational levels are required for an accurate determination of the well depth [4, 5]. On the theoretical front, accurate ab initio results have been obtained for He_2 [6], but such calculations for asymmetric He pairs are still very difficult. Conversely, electron gas models have been applied successfully to heavy rare-gas pairs, but He- (and to a lesser extent Ne-) containing systems have often been regarded as anomalous from the point of view of these statistical theories [7].

As a consequence of the above experimental and theoretical difficulties, thermal scattering experiments have provided the most detailed knowledge yet available for the attractive well region of the He - rare gas pairs. Integral cross section measurements have been employed for accurately deducing the He_2 interaction, and differential cross section (DCS) measurements have been used for the determination of all the He - rare gas interatomic potentials [9-11].

These DCS measurements, however, have yielded significantly different values from one another for the well depths ϵ of the van der Waals attractive minima (especially for He-Ar). These discrepancies of 10% to 25% appear despite the equivalence of the data from different laboratories [10] and the experimental sensitivity to ϵ of about $\pm 10\%$ [12].

Recent computer simulation results have shown that this apparent discrepancy may be caused by the use of insufficiently flexible mathematical parameterizations for the interatomic potential, or by insufficiently accurate long-range behavior. These shortcomings introduce significant biases into the potentials previously extracted from thermal-energy DCS data [12]. Such systematic biases are not exposed exclusively by comparison with the DCS data. Instead, we must first determine the appropriateness of the various potential forms proposed, using an independent method for assessing this bias.

In Sec. II we describe briefly the experimental arrangement used for acquisition of the He-Ar DCS data presented in this study. In Sec. III, we discuss an extensive series of computer simulation calculations which were used to analyze the systematic biases introduced into potentials extracted from DCS data by various commonly assumed representations for the potential energy curve. In Sec. IV the equivalence of the present data with those of earlier DCS measurements in other laboratories is analyzed. Two potential forms, shown on the basis of the simulation calculations to be substantially free of systematic bias, are used to generate He-Ar potentials from our DCS measurements. These potentials are accurate in the attractive minimum region to within $\pm 10\%$, and are compared with those obtained in the earlier analysis of DCS

scattering data [9,10]. In Sec. V, the suitability of our potentials for describing other properties of the He-Ar system is discussed; these properties are then used to extend the range of distances for which the He-Ar potential is accurately known [2,12]. Finally, we present our conclusions in Sec. VI.

II. Experimental

The crossed molecular beam apparatus used in this study is an improved version over earlier ones, which have been described elsewhere [14]. Briefly, a modulated He primary beam is formed in a supersonic nozzle expansion, and is then angularly well collimated in two stages of differential pumping. The Ar beam emerges from a glass capillary array directly into the scattering chamber, and is intense but only slightly supersonic. Background signal subtraction at each scattering angle is performed by remotely uncrossing the beams and remeasuring the modulated signal.

The detector is a doubly-differentially pumped quadrupole mass spectrometer with an electron-bombardment ion source, and has two angular degrees of freedom. In the present experiments this detector was moved either in the plane of the beams, or in a plane perpendicular to it and containing the primary beam. This is done to reduce the possibility of systematic errors in the apparatus relating to detector alignment, angular position measurements, etc. Ion detection after mass filtering utilizes a continuous-dynode electron multiplier, and digital up-down counting techniques, with the gates being synchronized to the primary beam mechanical modulator.

Operating conditions most significant in the present study are a relative collision energy of 64 meV, with a full width at half maximum (FWHM) velocity resolution of 11%. The overall apparatus angular resolution is $\sim 2^\circ$ FWHM. Scattering intensities at angles between 2° and 20° are measured, with signal-to-noise ratios of between about 50 and 5, respectively. Experimental details of the present version of the apparatus will be published elsewhere [15].

III. Computer Simulations

The computer simulations described here are extensions of Bickes and Bernstein's earlier studies [16]. The simulation involves assuming arbitrary but realistic potentials (with parameters typical for He - rare gas interactions) to generate DCS's, to which instrumental averagings and data scatter are added to yield "experimental" data. These are then used in a regression analysis, together with potential forms different from those assumed in generating the simulated data, to obtain "experimental" potentials. Comparing these to the "correct" assumed potentials, we determine the accuracy of the different "experimental" potentials, as well as the sensitivity of the DCS to the potential. These simulation calculations provide a more objective evaluation of the accuracy of different potentials than do goodness-of-fit (to experimental DCS's) statistical criteria, because of their ability to detect any systematic bias inherent in the assumed potential models.

Although the collision energy used here is 64 meV, which is much greater than well depths typical of He-containing systems (~ 2 meV), the simulations also show that the DCS's are sensitive to changes in the van der Waals "attractive well" region ($3.1 \text{ \AA} \lesssim r \lesssim 5.0 \text{ \AA}$) of $\sim 10\%$. On the other hand, sensitivity to the weakly "repulsive wall" region ($2.8 \text{ \AA} \lesssim r \lesssim 3.1 \text{ \AA}$) is limited to $\sim 30\%$; the DCS's are rather insensitive to changes in the potential above ~ 8 meV. Sensitivity to the "attractive tail" region ($5.0 \text{ \AA} \lesssim r \lesssim 6.5 \text{ \AA}$) is $\sim 20\%$. Therefore, under conditions equivalent to those considered here, the DCS measurements permit a determination of the potential energy curve between $2.8 \text{ \AA}$

and 6.5 Å [12]. The corresponding classical range of sensitivity is 2.9 Å to 4.8 Å.

We have made fits to the simulated DCS's using a Buckingham-Corner (BC) potential form [17], given by

$$V(r) = Ae^{-br} - e^{-[4(r_m/r - 1)^3]} (C_6 r^{-6} + C_8 r^{-8}) \quad \text{for } r < r_m$$

$$V(r) = Ae^{-br} - (C_6 r^{-6} + C_8 r^{-8}) \quad \text{for } r > r_m,$$

where r_m is the radius of the attractive minimum. These fits showed that a high statistical parameter correlation exists between the long-range attractive and short-range repulsive regions of the potential, precluding an accurate description for these two regions independently of one another, within the framework of the BC parameterization. We did indeed find that this potential is unable to accurately reproduce the potentials assumed for the simulations. Generalized forms of the BC potential have been proposed recently as convenient means of combining short-range Hartree-Fock calculations for repulsive interactions with long-range dispersion calculations for attractive interactions [18,19]. One of these, termed the HFD potential, has been used in an analysis of He-Ar DCS measurements [10]. Many of its parameters were obtained from the Hartree-Fock and dispersion calculations; we will therefore refer to the resulting potential, which has even less flexibility than does the BC parameterization, as "constrained".

More flexible parameterizations than that of the BC potential include the ESMSV one [20]. The simulation calculations showed that

it provides a better representation of the interatomic potential, but yields a slight overestimation of the well depth. This overestimation of ϵ by the MSV potential for room temperature beam conditions (collision energy of 64 meV) is caused by requiring its single Morse β parameter to simultaneously describe the van der Waals attractive and weakly repulsive regions of the potential. Interference between scattering off these two regions is primarily responsible for the rapid diffraction oscillations in highly quantum systems.

To overcome the limitation mentioned above, we also analyzed the suitability of a modified version of the MSV potential, which has a second Morse function joined smoothly at σ , the zero of the potential. This M^2SV potential uses the additional parameter β' for describing repulsive interactions [21]. Finally, our simulation analysis included the Simons- Parr-Finlan Dunham (SPFD) potential [22,23], given as

$$V(r) = \epsilon b_0 \lambda^2 \left(1 + \sum_{i=1}^N b_i \lambda^i \right) - \epsilon, \quad \text{for } \lambda = 1 - (r_m/r).$$

Using $N = 3$, we fix b_2 and b_3 by smoothly joining the resulting "third-order" SPFD potential to the theoretical multipole expansion at $r = 1.6 r_m$ [24]. The four-parameter M^2SV and SPFD potentials recovered from the simulation calculations are indistinguishable (within error limits) from each other and from the "correct" assumed potential, demonstrating their convergence to it under realistic conditions. The ability of these M^2SV and third-order SPFD potentials to reproduce both the simulated "experimental" data and the assumed "correct" potentials strongly indicates their lack of bias in extracting interatomic potentials from the present DCS scattering data.

Furthermore, since their mathematical parameterizations are significantly different, the potential energy curves obtained are model-independent, and hence accurate, to within the sensitivity limits established by the simulations as given earlier in this section.

IV. Results and Discussion

The DCS scattering data measured in this study were analyzed using the MSV, M^2SV and third-order SPFD parameterizations [20-23]. Although the collision energy used in the present experiments (64 meV) is appreciably different from that of two other laboratories (~ 20 meV) [9,10], the range of interatomic distances that are sampled at these different collision energies overlaps in the attractive well region. However, the lower energy results are more sensitive to the attractive tail region, thereby requiring accurate values for the dispersion coefficients (or fitted values if accurate ones are unavailable), as well as an appropriate choice of an interatomic distance beyond which the multipole expansion is valid. Inaccurate long-range behavior may introduce a bias in the resulting attractive minimum region. Conversely, the higher energy results allow a better determination of the weakly repulsive wall of the potential. For either of these collision energies, the potential form used should have sufficient flexibility to accurately represent the attractive minimum region.

In order to determine the consistency of the experimental measurements of the three laboratories, we compare the potentials obtained from them, using the same mathematical form [25]. Otherwise, if different forms were used, this comparison could be masked by the different associated biases. Consequently, in Fig. 1 we compare our MSV potential with the (ES)MSV potentials [20] obtained in other laboratories [9-11], even though this form is insufficiently flexible for obtaining accurate potentials from our 64 meV data. It can be seen that the potentials obtained are identical, to within the experimental error, throughout the

range of interatomic distances to which the data are sensitive. This demonstrates the consistency, and hence the reliability, of the present and previous DCS measurements.

In Fig. 2 we display the potential energy curves obtained, for $V(r) \lesssim 8$ meV, from the same DCS measurements as those used to obtain the (ES)MSV curves of Fig. 1, but using the parameterizations preferred in the three different laboratories [9,10,15]. These potentials are quite similar in the weakly repulsive region ($r \gtrsim 3.1$ Å), and also in the attractive tail region ($r \gtrsim 5$ Å). However, we note sizeable discrepancies from the present M^2SV and SPFD potentials in the attractive well region. The three well depths ϵ are 1.78 meV (present results), 2.09 meV (ES MSV of ref. [9]) and 2.60 meV (constrained HFD of ref. [10]). The differences among these values are significantly beyond the uncertainty with which ϵ may be obtained from our room temperature DCS measurements using unbiased mathematical forms, shown by the computer simulation calculations (Sec. III) to be about ± 0.18 meV. Since the M^2SV and third-order SPFD potentials are unbiased, also as shown by the simulation calculations, we must attribute the observed discrepancies in ϵ to biases in the ESMSV and constrained HFD potentials.

Accurate theoretical values for the dispersion coefficients have recently become available [24], and differ appreciably from those used by Chen et al. [9]. In addition, the distance at which the multipole expansion was introduced ($r = 5.0$ Å) [9] may be too small [15]. Since the low collision energy experiment (at ~ 20 meV) is particularly sensitive to long-range interactions, the above shortcomings may be

responsible for the (relatively small) differences between the attractive regions of the ESMSV and M^2SV curves of Fig. 2.

The differences between the constrained HFD and M^2SV curves of Fig. 2 are more pronounced. The flexibility of the M^2SV and SPFD forms would permit them, however, to retrieve from the DCS experiments the constrained HFD potential, if the latter provided an accurate representation of the He-Ar potential (in spite of the constrained HFD potential's lack of flexibility; see Sec. III). In such an event, the SPFD, M^2SV , and constrained HFD potentials of Fig. 2 would agree within experimental error. Since this is not the case, we must conclude that the HFD model [18] does not provide an accurate representation of the He-Ar van der Waals potential for intermediate interatomic separations. Its deviation from the M^2SV or SPFD potentials is a measure of its inaccuracy [10].

V. Extensions of the M^2SV and SPFD Potentials

Up to this point, we have relied solely on DCS scattering data to obtain the He-Ar interaction potential. Other properties are also sensitive to this potential, and can therefore be used for its characterization. Integral cross section measurements at thermal energies have been shown to be consistent with the ESMSV potential [26], and are reproduced well by the present M^2SV and SPFD potentials [15]. Spectroscopic measurements of the zero-point dissociation energy D_0 of He-Ar are not yet available [4], but predictions based on the M^2SV and SPFD potentials give $D_0 = (0.72 \pm 0.04)$ meV. A similar prediction is derived from the ESMSV potential [9], but the constrained HFD potential [10] yields $D_0 = 0.83$ meV. Spectroscopic measurements of D_0 may therefore provide another means of distinguishing between some of these potentials, at least in their respective attractive regions.

Gas phase bulk properties are related to the interaction potential less directly than are scattering or spectroscopic quantities. For heteronuclear He - rare gas pair interactions, the bulk properties are sensitive primarily to the repulsive wall regions of the potential [1-3]. Thus, transport properties have been used to accurately determine the He-Ar potential between approximately 2.4 and 2.6 Å [2]. Since this range of distances is beyond that to which the DCS data are sensitive, the potentials determined by the respective studies are complementary. Joining them at about 2.7 Å yields the curves of Fig. 2. We thus obtain extended M^2SV and SPFD potentials over the range of interatomic separations from 2.4 Å to 6.5 Å. These extended

potentials describe the DCS measurements as well as do the original ones, and simultaneously describe the bulk property data very well. This is true even of virial coefficient data [27], even though they were not used at all in obtaining the extended potentials.

Finally, we may consider the results of high-velocity integral cross section measurements [13]. These are shown in Fig. 2 for $1.4 \text{ \AA} \lesssim r \lesssim 1.8 \text{ \AA}$; the gap between $1.8 \text{ \AA}$ and $2.4 \text{ \AA}$ remains because of the inconsistency among independent measurements of this region [28]. If, in Fig. 2, a smooth interpolation between the high-velocity scattering results and the dilute gas and DCS results given by the extended M^2SV potential is appropriate, the resulting potential energy curve would provide a good characterization for the He-Ar interaction for all distances $r \gtrsim 1.4 \text{ \AA}$. This potential describes all the available data for the He-Ar system, and is essentially model-independent throughout its range of validity.

VI. Conclusion and Summary

The appropriateness of different mathematical parameterizations for the accurate analysis of thermal energy DCS data has been discussed on the basis of detailed computer simulation calculations [12]. These simulations showed that many of the parameterizations heretofore used introduce significant biases into the potential energy curves extracted from DCS measurements; such biases are not exposed exclusively by comparison with the DCS data. We have used two forms shown to be substantially free of bias in our analysis of new measurements of He-Ar DCS scattering data. Despite the demonstrated consistency of these measurements with those of two other laboratories [9,10], the potential models used for iteratively inverting the results of these earlier experiments yielded attractive minima 17% or 45% deeper than the present ones. The latter have values of $\sigma = (3.08 \pm 0.03)\text{\AA}$ and $\epsilon = (1.78 \pm 0.18)\text{ meV}$, unbiased because appropriately flexible parameterizations were employed in the present analysis. By using transport and virial coefficient data, these potentials were extended to the highly repulsive region, to which the DCS data are insensitive. The resulting potentials provide an excellent description of all the available data for the important heteronuclear rare gas pair He-Ar. A fuller account of this work will be given in forthcoming publications [12,15].

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Figure Captions

Figure 1. He-Ar interatomic potentials of the MSV shape as a function of interatomic separation. The inset magnifies the vertical scale of the potential energy minimum region by a factor of 2.5. Solid curve: this work; dashed curve: ref. 9; dotted curve: ref. 10. The vertical error bar in the inset indicates the estimated precision of $\pm 10\%$ in the potential energy at the van der Waals minimum, while the horizontal error bar at 8 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 approximate range of sensitivity of the experiments to the DCS [12].

Figure 2. He-Ar potentials, plotted semilogarithmically for energies above 1 meV, and linearly below 1 meV. Solid curve in the upper left is obtained from the high-velocity integral cross section measurements of ref. 13. Other curves are constructed from an amalgam of DCS and gas-phase transport 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. 9; dotted curve: HFD potential of ref. 10. The horizontal error at $r = 2.6$ Å is ± 0.01 Å and is about the same as the horizontal displacements among the three potentials there [2]; at the attractive minimum, the error bar of $\pm 10\%$ represents the accuracy of the M^2SV potential [12].

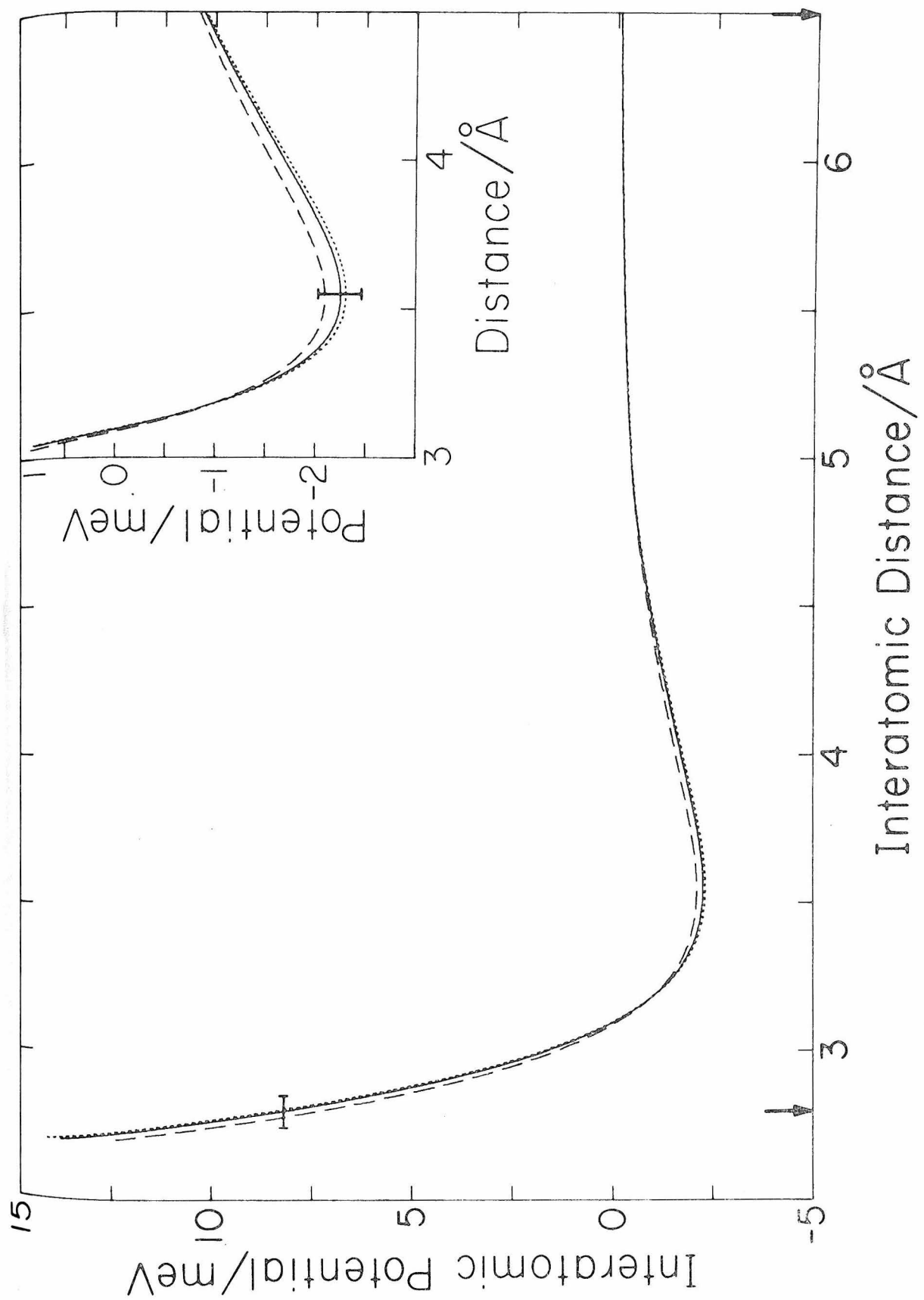


Figure 1

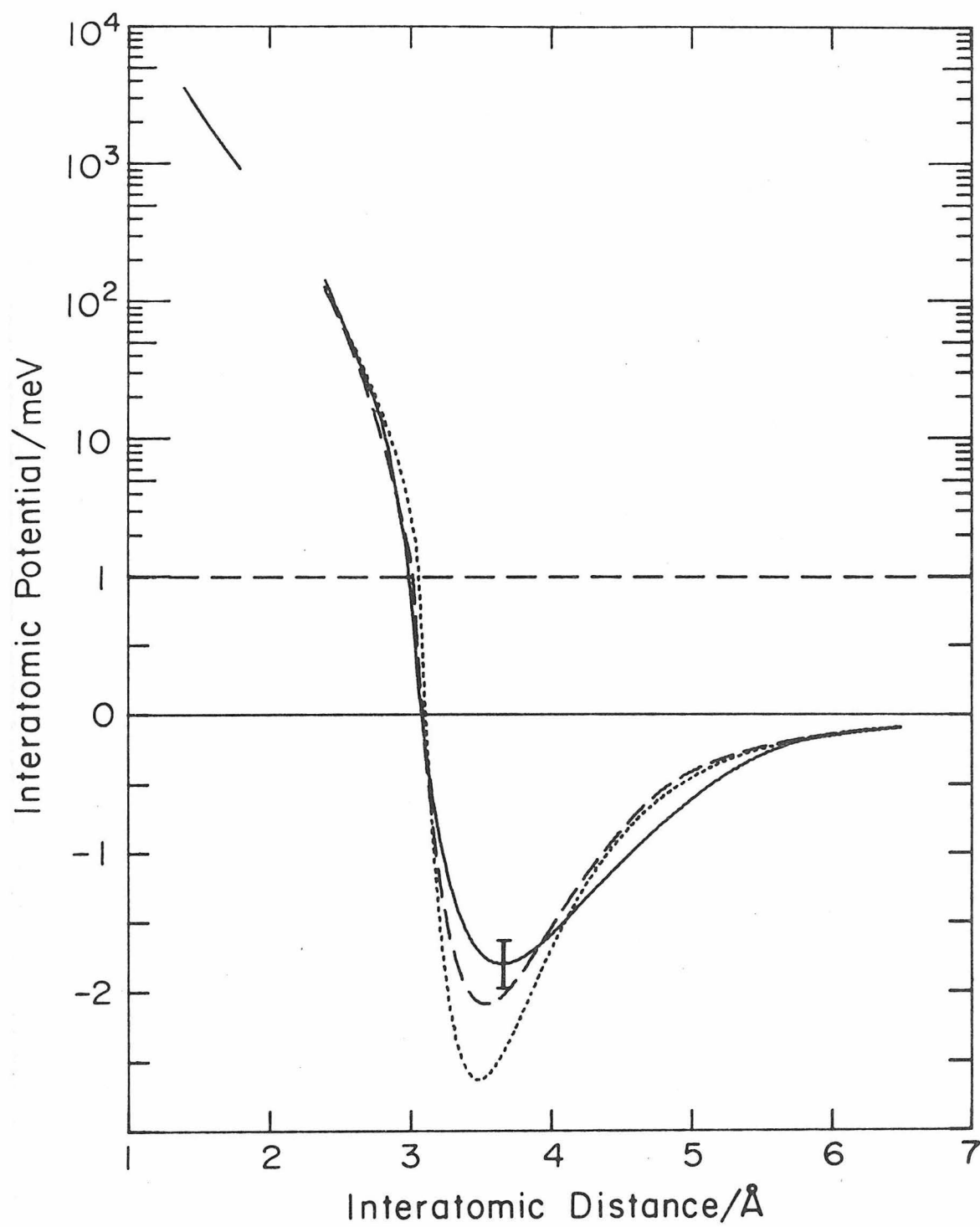


Figure 2

APPENDIX B

Anisotropic intermolecular potentials

for He-(CO₂, N₂O, C₂N₂)

Scattering of thermal He beams by crossed atomic and molecular beams.

V. Anisotropic intermolecular potentials for He + CO₂, N₂O, C₂N₂^{a)}

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Abstract

Experimentally measured differential cross sections are presented for the interactions of He with the linear molecules CO₂, N₂O, and C₂N₂. These data, which are most sensitive to the van der Waals attractive minimum region, show pronounced dampening of the diffraction oscillations. This is an indication that the intermolecular potentials have large anisotropies. Indeed, central-field analysis of the experimental data, even in terms of very flexible models, is shown to be inadequate. However, an infinite-order sudden approximation analysis yields physically reasonable anisotropic intermolecular potentials, and provides excellent fits to the scattering data. The spherical averages of the empirical anisotropic potentials are quite different from the spherically symmetric potentials obtained by the central-field analysis of the experimental data. For He + CO₂, the anisotropic potential is extended to highly repulsive interactions, to which the present data are insensitive, by combining theoretical calculations and measurements of gas-phase bulk properties.

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I. INTRODUCTION

Molecular scattering data have been very useful in the determination of intermolecular potentials, particularly if the species are spherically symmetric, or nearly so.¹⁻⁵ However, using central-field potentials to analyze experimental data for systems with large anisotropies is inappropriate.^{6,7} Semiclassical⁸ and quantal^{7,9} theories have been used to predict quenching of the glory, supernumary, rainbow, and rapid quantal oscillatory structure¹⁰ in molecular scattering cross sections; these effects have also been observed experimentally.^{4,6,11,12} Despite fundamental interest in molecular anisotropies, detailed experimental investigations have only recently been successful in investigations of interaction asphericities.¹³⁻¹⁷

With the recent success of rotational decoupling approximations,¹⁸⁻²¹ it is now possible to routinely determine a wide variety of phenomenological cross sections,^{4,22-24} without having to perform elaborate close-coupling calculations.²⁵ In particular, the infinite-order sudden approximation (IOSA), which totally decouples the rotational from the vibrational degrees of freedom, gives rise to simplified expressions for these phenomenological cross sections.^{7,18,22,23,26-28} This approximation is valid when the relative incident energy is substantially greater than the rotational energy level spacing, and when the cross sections are dominated by relatively small values of the orbital angular momentum.

In the present paper, we analyze experimental measurements of the differential cross sections (DCS) for the highly quantum and aniso-

tropic systems $\text{He} + \text{CO}_2$, N_2O , and C_2N_2 , obtained using room temperature crossed molecular beams. In Sec. II, we show how the IOSA can be used, with existing central-field data reduction programs,^{3b} to determine anisotropic intermolecular potentials. In Sec. III, we present our experimental results, and the procedures used in the data reduction. Both central-field and anisotropic potential forms used for the data analyses are given in Sec. IV. In Sec. V, we present empirical anisotropic intermolecular potentials, and discuss the inappropriateness of the central-field analysis for the systems considered in this study. Finally, we summarize our results in Sec. VI.

II. THEORY

A detailed description of the infinite-order sudden approximation (IOSA) has been given elsewhere,⁷ and we will only briefly discuss the theory to show how it can be used to obtain anisotropic intermolecular potentials. Using the coordinates shown in Fig. 1, the Hamiltonian for an S-state atom interacting with a Σ -state rigid rotor is

$$H = -\frac{\hbar^2}{2\mu r} \frac{\partial^2}{\partial r^2} r + \frac{\tilde{L}^2}{2\mu r^2} + \frac{\dot{L}^2}{2I} + V(r, \gamma), \quad (1)$$

where μ and $\tilde{L}$ are the reduced mass and orbital angular momentum respectively, of the atom relative to the molecule. Since the molecular angular momentum is $\dot{J}$,

$$\tilde{J} = \dot{J} + \tilde{L} \quad (2)$$

is the total angular momentum operator. The moment of inertia of the rigid rotor is I and $V(r, \gamma)$ is the interaction potential. In the IOSA, one makes both the centrifugal sudden^{18,19}

$$\tilde{L}^2 \simeq \hbar^2 \ell (\ell + 1) \quad (3)$$

and energy sudden²⁹

$$\dot{L}^2 \simeq \hbar^2 j(j + 1) \quad (4)$$

replacements of the angular momentum operators. For a rigid rotor, this results in the uncoupled set of ordinary differential equations

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2} - \frac{2\mu}{\hbar^2} V(r, \gamma) \right] g_\ell(r; \gamma) = 0, \quad (5)$$

to be solved for the radial wavefunctions $g_\ell(r; \gamma)$, subject to the usual scattering boundary conditions

$$g_\ell(0; \gamma) = 0 \quad (6)$$

and

$$g_\ell(r; \gamma) \xrightarrow{r \rightarrow \infty} k^{-\frac{1}{2}} \left[e^{-i(kr - \ell\pi/2)} - e^{i(kr - \ell\pi/2 + 2i\eta_\ell(\gamma))} \right], \quad (7)$$

where $\eta_\ell(\gamma)$ is the phase shift for a fixed orientation angle γ . Although this procedure appears tantamount to assuming that the angle γ remains fixed during the collision, the IOSA has been derived elsewhere in less offensive terms:³⁰⁻³² the IOSA formulation need assume only that the rotational energy level spacing, and differences in the centrifugal potentials for adjacent orbital angular momentum channels, are small. The wavenumber

$$k^2 = \frac{2\mu}{\hbar^2} \left[E - \frac{\hbar^2 j(j+1)}{2I} \right] \quad (8)$$

is a measure of the incident relative kinetic energy.

As shown elsewhere,^{7,33} the "total" (elastic plus inelastic) DCS is simply the weighted orientation average

$$\sigma(\theta) = \frac{1}{2} \int_0^\pi I(\gamma, \theta) \sin \gamma \, d\gamma \quad (9)$$

of the central-field DCS's

$$\sigma(\gamma, \theta) = \frac{1}{4k^2} \left\{ \left[\sum_{\ell=0}^{\infty} (2\ell + 1) \sin[2\eta_{\ell}(\gamma)] P_{\ell}(\cos\theta) \right]^2 + \left[\sum_{\ell=0}^{\infty} (2\ell + 1) (\cos[2\eta_{\ell}(\gamma)] - 1) P_{\ell}(\cos\theta) \right]^2 \right\} . \quad (10)$$

In deriving this simplified expression, it was necessary to neglect the velocity changes of rotationally inelastic collisions, which is consistent with the IOSA. Pack and Preston³⁴ have shown that with this assumption, the center-of-mass to laboratory coordinate transformation is identical to that for central-field elastic scattering. We could thus adapt the central-field data reduction procedure (Sec. III), with only the relatively minor modifications needed to include anisotropic effects [Eq. (9)], to perform the appropriate incident velocity and beam angle averaging, for direct comparisons with the experimental DCS's presented below.

III. EXPERIMENTAL AND DATA REDUCTION

The crossed molecular beam apparatus has been described previously,³ so that only a brief outline of its major features is given here. A modulated He 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 directly into the scattering chamber through a glass capillary array. The secondary beam source may be tilted upwards, thus uncrossing the beams, for measurements of background scattering intensity. Beam operating characteristics are summarized in Table I. Due to the slightly supersonic nature of the secondary beam, its internal temperature (particularly the rotational temperature) may not be the ambient one (298 K). We note that its velocity distribution is best characterized by a Mach number of 1.5 (Table I) and an "effective" specific heat ratio of 1.64, the latter indicating cooling of only the transverse translational degrees of freedom.³⁵ Because the secondary beam particles are much heavier than those of the primary for all the scattering experiments considered in this study, the rather wide velocity distribution of the secondary beam does not contribute significantly to the distribution of relative collision velocities; the overall apparatus velocity resolution is about the same as that of the highly supersonic He beam.

As in earlier work, a quadrupole mass spectrometer is used to detect out-of-plane scattering of He atoms as a function of the scattering angle (with the in-plane scattering angle fixed at 0°). Ion detection and signal processing utilizes a Spiraltron continuous dynode

electron multiplier. Its pulses are sufficiently fast ($\lesssim 1 \mu\text{sec.}$) to allow use of digital counting techniques; the gates of an up-down counter are synchronized with the primary beam chopper.

Differential pumping in the mass spectrometer is provided by a small (5 ℓ/sec) ion pump in the detector entrance buffer chamber, followed by a larger (25 ℓ/sec) ion pump in the ionizer region. During experiments, we also use a liquid helium cryopump (400 ℓ/sec), which provides effective pumping, even for He! ^{3b} The pressure in the ion source region was $\sim 1 \times 10^{-9}$ torr during the course of these experiments.

Rapid cryopumping of the CO_2 and C_2N_2 beams on liquid-nitrogen cooled surfaces kept the scattering chamber pressure at $\sim 3 \times 10^{-7}$ torr, while use of the less condensable N_2O beam raised this pressure to $\sim 1 \times 10^{-6}$ torr. These pressures, coupled with a primary beam attenuation due to scattering by the secondary beam of only $\sim 5\%$, easily ensure that the single-collision conditions essential for DCS measurements prevail. 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 $\sim 1.7^\circ$ and $\sim 20^\circ$ 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 $\sim 0.03^\circ$). ^{3b} Long-

term drifts in beam intensities and detection efficiency were compensated for by periodic measurements of the scattered signal at a reference angle near 5° . The experimental DCS's are shown in Fig. 2 for He + CO₂, He + N₂O and He + C₂N₂.³⁶ Data points represent the average of three or four independent angular scans performed in several days' experimentation for each scattering pair. Total counting times at each angle ranged from ~ 3 min near 2° , to ~ 30 min at 20° . Signal-to-noise ratios over the same angular range were between about 50 and 5, respectively.

The data reduction procedure used to obtain the fits shown in Fig. 2 has also been described previously.^{3b} We use Marquardt's³⁷ weighted least-squares prescription to fit the parameters of mathematical functions chosen to represent the intermolecular potential, as discussed in Sec. IV. DCS's in the center-of-mass coordinate frame are calculated from partial wave phase shifts of high accuracy, and are then averaged extensively over both beams' angular and velocity spreads in the transformations to the out-of-plane laboratory coordinate frame. The overall apparatus velocity resolution is $\sim 11\%$ FWHM for the systems included in this study. Averaging also is used to account for the overall apparatus angular resolution, of 1.9° FWHM.

The fitting quality for the calculated DCS's (relative to the experimental ones) are expressed as χ^2 or as $\Delta\alpha_{0.95}/\alpha$ statistical indices.^{3b} The former is the sum of weighted residuals squared, which is the quantity minimized by the weighted least-squares fits. The latter gives the 95% confidence level³⁸ for the scaling factor α

necessary to bring the calculated (absolute) cross sections into vertical register with the experimental (arbitrarily normalized) intensities.³⁶

The $\Delta\alpha_{0.95}/\alpha$ goodness-of-fit index is statistically adjusted both for the number of data points, and for the number of parameters adjusted in the fits. Furthermore, it is independent of the arbitrary normalization used in the experiments, and is a more useful index than χ^2 for comparing fitting quality between different experiments or potential fits.^{3b}

IV. DATA ANALYSIS AND INTERMOLECULAR POTENTIALS

The experimental DCS's obtained as described in Sec. III and displayed in Fig. 2, were fitted by weighted least-squares optimization of the parameters of the various intermolecular potentials described below. These included both central-field and anisotropic models.

A. Central-field potential models

The van der Waals interactions for the atom-molecule systems considered in this study are anisotropic. As such, central-field potentials, represented generically by

$$V(r) = \epsilon \cdot f(\rho), \quad \rho = \frac{r}{r_m}, \quad (11)$$

where r_m is the radius of the attractive minimum and ϵ is its depth, provide at best an approximate description of these interactions.⁴

Central-field analyses were performed herein to test the validity of the approximation of Eq. (11). For a thermal rigid rotor at 300 K, representative of the secondary beams used in the present studies (Sec. III), a typical rotation frequency is $\sim 3 \times 10^{11}$ Hz. Since the collision interaction time (to traverse ~ 10 Å) is $\sim 6 \times 10^{-13}$ sec, the molecule rotates too slowly to establish an "effective" isotropic potential.

The central-field potential energy forms used in this study are the highly flexible double-Morse-spline-van der Waals (M^2SV)³⁹ and third-order Simons-Parr-Finlan Dunham (SPFD)^{40, 41} parameterizations. Both of these have three adjustable shape parameters, as

well as the well position and depth parameters r_m and ϵ , respectively [Eq. (11)]. Other parameters govern the strength of the multipole expansion for the long-range attraction (c_6 for both the M^2SV and SPFD forms), and the attractive well and weakly repulsive wall regions (β and β' of the M^2SV potential; b_0 and b_1 of the SPFD one). It has been shown⁴² that both these parameterizations successfully decouple the attractive minimum from the adjacent regions of the intermolecular potential, and that all five of their parameters may be determined by fitting them to room-temperature DCS data from highly quantum isotropic interactions. The five-parameter M^2SV and SPFD potential forms are highly flexible, without inducing unduly large statistical parameter correlations. They are able to accurately describe (spherically symmetric) weak van der Waals potentials within the range of intermolecular distances sampled by DCS data of the present type (reduced distances ρ between ~ 0.8 and ~ 1.8).^{3,42} We also used the four-parameter Morse-spline-van der Waals (MSV)⁴³ potential form to fit just the low-angle ($\theta \lesssim 6^\circ$) portion of the DCS's presented here (see Sec. V). The MSV form is quite similar to the M^2SV one, but has only a single Morse β parameter to describe the shape of both the attractive well and weakly repulsive wall regions of the potential.

B. Anisotropic potential models

For a more appropriate analysis of the experimental DCS's, we used two anisotropic potential forms having rather different mathematical parameterizations. In addition to these two anisotropic potential forms, we further analyzed the He + CO₂ DCS using a

modification to the existing He + CO₂ electron gas potential.⁴⁴ These physically reasonable potential forms were used in an effort to gain an indication of the uniqueness and reliability of the resulting anisotropic intermolecular potentials.

The first potential form is an elliptical modification to central-field types of potentials

$$\left. \begin{aligned} V(r, \gamma) &= \epsilon(\gamma) f[\rho(r, \gamma)], \text{ where } \rho(r, \gamma) = \frac{r}{r_m(\gamma)} \\ \text{and} \\ r_m(\gamma) &= r_{m\perp} \left[\frac{1 + r_q \sin^2 \gamma}{1 + r_q} \right]^{\frac{1}{2}}; \quad \epsilon(\gamma) = \epsilon_0 + \epsilon_2 P_2(\cos \gamma). \end{aligned} \right\} \quad (12)$$

For an arbitrary γ , $r_m(\gamma)$ is the distance to the potential minimum, and $-\epsilon(\gamma)$ is the corresponding potential energy, with r and γ being defined in Fig. 1. Any central-field reduced potential energy function may be used for $f(\rho)$ since the anisotropy is introduced through the Legendre polynomial expansion of the well depth and the elliptically shaped well position. A particularly useful and fairly reliable form for $f(\rho)$ is the Morse-Spline-van der Waals (MSV) potential,⁴³

$$\left. \begin{aligned} f(\rho) &= e^{\beta(1-\rho)} [e^{\beta(1-\rho)} - 2] && \text{for } \rho < \rho_1 \\ f(\rho) &= (\rho_2 - \rho_1) [s_1 (\rho_2 - \rho_1)^2 + s_3] \\ &\quad + (\rho - \rho_1) [s_2 (\rho - \rho_1)^2 + s_4] && \text{for } \rho_1 < \rho < \rho_2 \\ f(\rho) &= - \sum_{i=1}^3 c_{2i+4} \rho^{-(2i+4)} && \text{for } \rho > \rho_2. \end{aligned} \right\} \quad (13)$$

The cubic spline coefficients ($i = 1 - 4$) are fixed by smoothness conditions at the spline points ρ_1 and ρ_2 . The first spline point is the inflection point of the Morse function,⁴² while the second spline point is fixed at $\rho_2 = 1.6$.^{3b} The reduced c_n coefficients ($n = 6, 8, 10$) are related to the known⁴⁶ long-range dispersion coefficients by

$$c_n = \frac{C_n(\gamma)}{\epsilon(\gamma) r_m^n(\gamma)} . \quad (14)$$

This anisotropic potential has 5 adjustable parameters: the Morse shape parameter β , the anisotropy parameters r_q and ϵ_2 , as well as $r_{m\perp}$ and ϵ_0 . As predicted by Pack,⁹ the experimental data are more sensitive to the well position anisotropy parameter r_q than to the well depth anisotropy parameter ϵ_2 . The remaining parameters are also sensitively determined by the experimental DCS's. It is important to note that these five adjusted parameters are statistically independent^{38,42} of one another (see Sec. V), thus allowing physically meaningful values to be obtained for them.

The second potential form used in this study is a sum of one central-field potential, located at the molecular center-of-mass, and two additional central-field potentials, located at distances of z_0 and $-z_0$ along the molecular axis. The latter two potentials are constrained to be identical. Using Lennard-Jones potentials, this anisotropic potential model is given by

$$\begin{aligned}
 V(r, \gamma) = & \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \\
 & + \epsilon_0 \left[\left(\frac{r_{m_0}}{r_1} \right)^{12} - 2 \left(\frac{r_{m_0}}{r_1} \right)^6 \right] \\
 & + \epsilon_0 \left[\left(\frac{r_{m_0}}{r_2} \right)^{12} - 2 \left(\frac{r_{m_0}}{r_2} \right)^6 \right],
 \end{aligned} \tag{15}$$

where $r_1 = [r^2 + z_0^2 - 2rz_0 \cos \gamma]^{\frac{1}{2}}$,
and $r_2 = [r^2 + z_0^2 + 2rz_0 \cos \gamma]^{\frac{1}{2}}$.

The positions of the middle and peripheral central-field attractive minima are r_m and r_{m_0} respectively, with corresponding well depths ϵ and ϵ_0 . An asymptotic expansion of this potential gives

$$\begin{aligned}
 V(r, \gamma) \xrightarrow{r \rightarrow \infty} & - \frac{1}{r^6} [2\epsilon r_m^6 + 4\epsilon_0 r_{m_0}^6] \\
 & - \frac{1}{r^8} \{4\epsilon_0 r_{m_0}^6 z_0^2 [5P_0(\cos \gamma) + 16P_2(\cos \gamma)]\}.
 \end{aligned} \tag{16}$$

Since this does not have a P_2 anisotropy in the C_6 coefficient, the potential does not have the correct long-range behavior. This deficiency is eliminated by letting

$$\begin{aligned}
 V(r, \gamma) = & \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] - \frac{C_6(2)}{r^6} P_2(\cos \gamma) \\
 & + \epsilon_0 \left[\left(\frac{r_{m_0}}{r_1} \right)^{12} - 2 \left(\frac{r_{m_0}}{r_1} \right)^6 \right] + \epsilon_0 \left[\left(\frac{r_{m_0}}{r_2} \right)^{12} - 2 \left(\frac{r_{m_0}}{r_2} \right)^6 \right],
 \end{aligned} \tag{17}$$

where $C_6(2)$ is the known⁴⁶ long-range van der Waals coefficient for P_2 .

The third potential form that we used for the He + CO₂ data reduction is a modification of the He + CO₂ electron-gas potential,⁴⁴

$$\left. \begin{aligned} V(r, \gamma) &= D_1 V^{\text{HF}}(r, \gamma) + D_2 V^{\text{cor}}(r, \gamma) \\ &+ (1 - D_2) \bar{V}^{\text{cor}}(r, \gamma) + D_3 V_{\text{EG}}^{\text{cor}}(r, \gamma), \\ \text{where } V^{\text{HF}}(r, \gamma) &= \sum_{n=0,2,\dots} P_n(\cos \gamma) A_{n1} \exp(A_{n2} r + A_{n3} r^2), \\ \text{and } V_{\text{EG}}(r, \gamma) &= - \sum_{n=0,2,\dots} P_n(\cos \gamma) B_{n1} \exp(B_{n2} r + B_{n3} r^2) \end{aligned} \right\} \quad (18)$$

are the electron-gas estimates of the Hartree-Fock and correlation interaction energies.⁴⁹⁻⁵² The notation and numerical values are those of Ref. 44, except for the adjustable parameters D_1 , D_2 and D_3 . As noted elsewhere,⁵² the electron-gas model does not have the correct long-range van der Waals tail. To remedy this deficiency, it is necessary to smoothly join the short-range electron-gas correlation energy and the known long-range van der Waals tail. There have been two ways^{44, 53} of doing this; the first one assumes that the long-range potential has the correct anisotropy at the position where the logarithmic derivatives of the corresponding Legendre components are equal. This is the procedure used by Parker, Snow and Pack,⁴⁴ giving

$$V^{\text{cor}}(r, \gamma) = \sum_{n=0,2,\dots} v_n^{\text{cor}}(r) P_n(\cos \gamma)$$

where

$$v_n^{\text{cor}}(r) = \left\{ \begin{array}{ll} -B'_{n1} \exp(B_{n2} r + B_{n3} r^2) & r \leq r_n \\ -C_6(n) r^{-6} - C_8(n) r^{-8} & r > r_n \end{array} \right\} \quad (19)$$

The point at which the logarithmic derivatives of the two forms are equal is r_n , and B'_{n1} is chosen to make v_n^{cor} continuous. The second method assumes that the short-range electron-gas correlation energy has the correct anisotropy, giving⁵³

$$\bar{V}^{\text{cor}} = \sum_{n=0,2,\dots} \bar{v}_n(r) P_n(\cos\gamma),$$

where

$$\bar{v}_n(r) = \left\{ \begin{array}{ll} -B_{n1} \exp(B_{n2} r + B_{n3} r^2) & r \leq r_n \\ -C_6(n) r^{-6} - C_8(n) r^{-8} + (B_{n1} - B'_{n1}) \exp(B_{n2} r + B_{n3} r^2) & r > r_n \end{array} \right\} \quad (20)$$

There is no a priori way of determining which of these methods is more appropriate; it is probable that a linear combination of these methods would be best.

Since the electron-gas correlation energy is only a crude estimate of the actual correlation energy, it is usually necessary to scale it in order to obtain potentials having accurate well depths.⁴⁴ This potential form then has the three adjustable parameters D_1 , D_2 and D_3 of Eq. (17). The parameter D_1 scales the repulsive wall. D_2 mainly affects the well depth anisotropy, and to a lesser extent affects the

well position anisotropy. D_3 determines the overall well depth. The adjustable parameters, with the exception of D_1 , mainly affect the attractive well region, to which the experimental DCS's are most sensitive.⁴² This is also the region where the electron-gas potential is most likely to be inaccurate.

Unfortunately, the $D_{\infty h}$ symmetry of our "cigar-shaped" anisotropic potential models is inappropriate for the He + N₂O interaction. A "pear-shaped" model having the appropriate $C_{\infty v}$ symmetry would, however, require at least one additional parameter. We would expect this further refinement to have a rather small effect. We note for example, that the dipole moment of N₂O is only 0.167 D,⁵⁴ which is too small to produce the large distortions in the overall electronic cloud distribution that would presumably necessitate a model with $C_{\infty v}$ symmetry.

Using the anisotropic potential models described above, we calculated DCS's in the center-of-mass coordinate frame for the orientation angles γ_i of a 12-point Gauss-Legendre quadrature, and then obtained the IOSA DCS's by evaluating Eq. (9). Since the potential (and hence the scattering) is symmetric about $\gamma = \pi/2$, this actually required calculations at only 6 values of γ . These results differed insignificantly from a 24-point Gauss-Legendre quadrature. The IOSA DCS's are then averaged extensively over both beam's angular and velocity spreads, identically as in the central-field calculations (Sec. III).

V. DISCUSSION

The first question to be addressed is the validity of the usual assumption that central-field fits to molecular scattering data yield the spherically symmetric (orientation averaged) component of the intermolecular potential.^{2, 11, 12} For weakly anisotropic interactions in highly quantum systems, this central-field assumption has quantitatively been shown to be valid,⁴ although use of an anisotropic potential parameterization may yield a better description of the data. However, in preliminary work on He + CO₂, it was found that the central-field assumption breaks down for this highly anisotropic interaction.⁶

Interpretations of scattering results for anisotropic interactions have been based for some time on semi-classical calculations.⁸ These showed that the effect of anisotropic potential scattering on integral elastic cross sections is primarily to dampen, or quench the glory undulations.¹⁰ Similar results were obtained for the supernumary rainbow and rapid quantum oscillatory structure of elastic DCS's.¹⁰ 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 being sensitive only to the spherical average of the intermolecular potential.^{2, 11, 12} Such a straightforward application of the semi-classical theory for DCS's is, however, inappropriate for the highly quantum systems under discussion here.⁴ More recently, quantum mechanical calculations have been performed for scattering from anisotropic potentials;²⁵ due to the complexity of this scattering problem, it has usually been necessary to employ approximation techniques.¹⁸⁻²¹ The IOSA has

been used, with reasonable theoretical potentials,⁴⁴ to predict quenching in the DCS of both highly quantum and semi-classical systems.^{7,9} This approximation should be valid for the systems under consideration, because the collision energy (~ 64 meV) is substantially larger than the separation between adjacent rotational energy levels (1 or 1.5 meV at 300 K).

By comparing the experimental DCS's and the central-field fitted ones of Fig. 2, it is quite evident that the He + CO₂, N₂O, and C₂N₂ scattering patterns exhibit significantly quenched oscillatory structure. Central-field potential parameters are presented in Table II for fits to the entire DCS's, and to just the low scattering angle measurements ($\theta \lesssim 6^\circ$). Classically, the latter measurements should be due primarily to long-range interactions, which are more nearly isotropic than are short-range ones. Consequently, it is possible that the central-field assumption may be more appropriate for low-angle DCS's than for ones including scattering at relatively wide angles. We see from Table II that the potential parameters obtained from these central-field fits to each of the systems considered are quite different, despite the appropriateness of their parameterizations for fitting isotropic potential scattering.⁴² The large differences are substantiated graphically by referring to the potentials plotted in Figs. 3-5 for He + CO₂, N₂O, and C₂N₂, respectively, and provide another clear indication that anisotropic effects are important for these systems.

DCS's calculated from best-fit anisotropic potentials of Eqs. (12) and (13) fit to the data are also shown in Fig. 2. It is quite apparent from the figure, and from the statistical indices of Tables II and IV,

that the elliptical anisotropic potential model is much better able to reproduce the entire experimental DCS than is the highly flexible SPFD potential model, for which the same number of parameters were adjusted. In Tables III and IV we give parameters for these elliptical potentials, as well as well position and depth parameters for the spherical averages. By comparing the latter parameters with the corresponding ones of Table II, we see that there are substantial differences, especially for ϵ , between the spherical averages of the anisotropic potentials and the central-field fitted ones. Referring again to Figs. 3-5, it is apparent that central-field analyses of the present DCS's do not yield the orientation average of the anisotropic intermolecular potential, even when only low-angle scattering is considered. The central-field assumption is thus invalid for the highly anisotropic interactions being considered herein.

The empirical anisotropic potential energy surfaces obtained from the fits to the elliptical potential model of Eqs. (12) and (13) are shown in Figs. 6 and 7 for He + CO₂ and He + N₂O, respectively. We do not show the corresponding potential energy surface for He + C₂N₂; the elliptical parameterization is inadequate to realistically model the very large anisotropy of this system. Nevertheless, the anisotropic potential does yield an improved fit to the DCS over the best central-field fits. It may be necessary to introduce a second parameter for the $r_m(\gamma)$ function of Eq. (12), or to allow the Morse parameter β to vary with γ as well. However, it is probably inappropriate to adjust six potential parameters to the present data.^{4, 42}

Finally we present in Fig. 8 the fits to the He + CO₂ DCS using the triple-LJ parameterization of Eq. (17), and using the electron-gas model of Eqs. (18)-(20).⁴⁴ Unfortunately, significant difficulties were encountered in fitting the parameters of both these models to the DCS data. For the triple-LJ fit, the parameter ϵ [Eq.(15)] became very small, thereby effectively eliminating the effect of the central LJ potential and reducing it to a three-parameter fit. The parameters were highly statistically correlated, and hence their numerical values may not be very realistic.⁴² Moreover, the non-coincidence of the peripheral LJ functions' origins with the O atoms ($z_0 = 1.97 \text{ \AA}$, compared with the bond length of $1.16 \text{ \AA}$) is unphysical. Nevertheless, the triple-LJ anisotropic potential obtained does fit the experimental DCS reasonably well ($\Delta\alpha_{0.95/\alpha} = 1.18\%$). The electron-gas parameterization also yielded fits with highly statistically correlated potential parameters. The D_2 parameter obtained was very close to zero, indicating that it may be more appropriate to join the short-range electron-gas potential to the long-range van der Waals attractive tail by the second of the methods suggested in Sec. IV [Eq.(20)]. The best-fit electron-gas potential, however, yielded a DCS in substantially poorer agreement with the experimental one ($\Delta\alpha_{0.95/\alpha} = 1.99\%$) than did either the elliptical or triple-LJ parameterizations (Fig. 8).

Contour diagrams for the He + CO₂ triple-LJ and electron-gas empirical intermolecular potentials are shown in Figs. 9 and 10, respectively. Both these potentials are qualitatively different from the one obtained by using the elliptical model (Fig. 6). The latter gave a "T-shaped" equilibrium He-CO₂ configuration, whereas the former two

yield linear ones. The triple-LJ potential has a much larger well depth anisotropy than does the elliptical one, while the electron-gas well depth is nearly angle-independent. It seems that without supplementary information, it would be difficult to decide whether the potential energy surface has an absolute minimum for $\gamma = 0, \pi$ or for $\gamma = \pi/2$. Fortunately, such supplementary information is available for some van der Waals interactions, indicating that the T configuration is more stable than the linear one for non-polar or weakly polar interactions (e.g., $\text{He} + \text{I}_2$, $\text{Ar} + \text{H}_2$, $\text{Ar} + \text{OCS}$), but is linear for highly polar ones (e.g., $\text{Ar} + \text{HCl}$, $\text{Ar} + \text{HF}$).¹⁵ It is quite likely that the systems considered in this study also have T-shaped equilibrium configurations, and that the elliptical potentials shown in Figs. 6 and 7 are more reasonable than the empirical triple-LJ or electron-gas ones.

VI. SUMMARY AND CONCLUSIONS

By measuring the differential cross sections (DCS) for scattering of a room-temperature nozzle beam of He by crossed beams of CO_2 , N_2O , and C_2N_2 , we have determined physically realistic intermolecular potentials for these systems. These potentials have large anisotropies, both in the well depth and in the position of the attractive minimum. Central-field analyses of the scattering data yield potentials that are not the orientation averages of the anisotropic intermolecular potentials.⁴ The central-field assumption fails even when only that part of the DCS least sensitive to repulsive interactions is considered in the analysis.

For the $\text{He} + \text{CO}_2$ interaction, several empirical anisotropic parameterizations were fitted to the DCS data. Most successful of these was an elliptical modification of central-field types of potentials. A model utilizing the sum of three central-field potentials (triple-LJ), centered on the molecular center-of-mass and along the molecular axis, yielded a good fit to the DCS, but gave a qualitatively different potential energy surface than did the elliptical one. Finally, the attractive well region of the electron-gas $\text{He} + \text{CO}_2$ potential⁴⁴ was adjusted empirically to the data. It also provided a qualitatively different anisotropic intermolecular potential, but yielded much poorer fits to the DCS data. The triple-LJ and electron-gas models suffer from highly statistically correlated potential parameters, while the lack of such correlations for the elliptical model may indicate that it is more physically reasonable. The equilibrium configurations for

the interactions being considered are probably "T"-shaped rather than linear.¹⁵ This behavior is shown by the elliptical parameterization, whereas the triple-LJ model yields a strongly favored linear configuration, and the well depth of the empirically adjusted electron-gas potential is nearly isotropic. We conclude that the elliptical parameterization is appropriate for the He + CO₂, N₂O, and C₂N₂ van der Waals interactions.

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TABLE I. Beam operating conditions

Characteristic	Primary beam	Secondary beams		
Beam gas	He	CO ₂	N ₂ O	C ₂ N ₂
Inlet pressure/torr	1300	4.1	4.1	4.1
Inlet temperature/K	298	298	298	298
Angular FWHM ^a /deg.	1	4	4	4
Most probable velocity/(km/sec)	1.757	0.478	0.478	0.440
Velocity FWHM, ^a $\Delta v/v$	0.10	0.75	0.75	0.75
Mach number ³⁵	18	1.5	1.5	1.5

^a) Full width at half maximum.

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

System ^a	Potential Type ^b	$r_m/\text{\AA}$	$\sigma/\text{\AA}$	ϵ/meV	Shape Parameters ^b	χ^2 c, d	$\Delta\alpha_{0.95/\alpha}$ d (%)
He + CO ₂ (41)	SPFD	3.58	3.26	4.51	$b_0 = 60.7$; $b_1 = -6.57$; $c_g = 0.89$	2100 (5)	2.79
	(18)	3.73	3.24	3.33	$b_0 = 28.6$; $c_g = 1.14$	3300 (4)	1.02
He + N ₂ O (40)	SPFD	3.70	3.34	4.23	$b_0 = 49.1$; $b_1 = -5.73$; $c_g = 0.81$	2300 (5)	3.01
	(17)	3.32	2.94	3.81	$b_0 = 39.1$; $c_g = 2.69$	400 (4)	0.41
He + C ₂ N ₂ (41)	SPFD	3.79	3.33	3.77	$b_0 = 31.9$; $b_1 = -3.94$; $c_g = 1.06$	1900 (5)	2.68
	(18)	3.24	2.89	3.39	$b_0 = 42.5$; $c_g = 4.25$	2200 (4)	0.83

^a Experimental conditions given in Table I; the number of experimental data points is given in parentheses. For each

system, the first row gives a five-parameter fit to the entire DCS (between $\sim 1.7^\circ$ and 20°); the second row gives a four-parameter fit to just the low-angle portion of the DCS (between $\sim 1.7^\circ$ and 6°).

^b Discussed in Sec. III and Ref. 42. See also Eqs. (11) and (13).

^c Scattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.

^d Goodness-of-fit statistical indices; discussed in Sec. III and in Ref. 42. Note that despite the large χ^2 statistical indices, $\Delta\alpha_{0.95/\alpha}$ indicates that the fits to the low-angle DCS's are quite good. This is due to the larger absolute (but same relative) weights required for normalized weighted χ^2 to be obtained for the low-angle fits. The $\Delta\alpha_{0.95/\alpha}$ statistical index is more appropriate for judging the goodness-of-fit than is the χ^2 one.

TABLE III. Van der Waals asymptotic dispersion constants.^a

System	$C_6(0)/\text{eV} \cdot \text{\AA}^6$	$C_6(2)/\text{eV} \cdot \text{\AA}^6$	$C_8(0)/\text{eV} \cdot \text{\AA}^8$	$C_8(2)/\text{eV} \cdot \text{\AA}^8$
He + CO ₂	9.98	2.31	46.4	48.4
He + N ₂ O	11.33	3.17	52.5	54.9
He + C ₂ N ₂	18.92	4.42	88.0	94.4

^a See Ref. 46.

TABLE IV. Intermolecular potential parameters from anisotropic fits to the experimental DCS.

System ^a	anisotropic potential parameters ^b				χ^2 c, d	$\Delta\alpha_{0.95/\alpha}$ x (%)	parameters for the spherically averaged anisotropic potentials	
	$r_{m_L}/\text{\AA}$	r_q	ϵ_0/meV	ϵ_2/meV			$r_m/\text{\AA}$	ϵ/meV
He + CO ₂ (41)	3.31	-0.52	2.98	-1.91	170 (5)	0.82	3.93	3.34
He + N ₂ O (40)	3.35	-0.56	2.95	-2.49	220 (5)	0.95	4.40	3.42
He + C ₂ N ₂ (41)	3.52	-0.61	2.76	-2.65	770 (5)	1.75	4.29	3.55

^a Experimental conditions given in Table I; the number of experimental data points is given in parentheses.^b Potential form defined by Eqs. (12) and (13); symbols have the same meanings as in these equations. The MSV potential of Eq. (13) has $\rho_2 = 1.60$. Dispersion coefficients calculated from Eq. (14) and the values given in Table III.^c Scattering intensity normalized to 500 at $\theta = 4.8^\circ$; the number of parameters varied is given in parentheses.^d Goodness-of-fit statistical indices; discussed in Sec. III and in Ref. 42.

FIGURE CAPTIONS

Fig. 1. Center-of-mass coordinate system for (e.g.) the He + CO₂ interaction. r is the length of the position vector $\underline{r}$ of the He atom with respect to the molecular center of mass, and θ is the angle between $\underline{r}$ and the molecular axis.

Fig. 2. Laboratory differential cross sections for out-of-plane scattering of He by CO₂, N₂O, and C₂N₂, 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 $^{36} I(\theta) \cdot \sin \theta$ 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 elliptical potential of Eqs. (12) and (13); dashed lines: central-field SPFD potential; dotted lines: spherical average of the anisotropic elliptical potential. The potential parameters are given in Tables II, III, and IV.

Fig. 3. Spherically symmetric intermolecular potentials for He + CO₂ as a function of intermolecular distance. Solid curve: spherical average of the anisotropic elliptical potential; dashed curve: central-field SPFD potential; dotted curve: central-field SPFD potential fit to only the low-angle scattering data ($\theta \lesssim 6^\circ$). The error bar on the spherically averaged anisotropic potential indicate the accuracy with which potentials may be determined from isotropic DCS data.⁴²

Fig. 4. Spherically symmetric intermolecular potentials for He + N₂O; symbols as in Fig. 3.

Fig. 5. Spherically symmetric intermolecular potentials for He + C₂N₂; symbols as in Fig. 3.

Fig. 6. He + CO₂ empirical potential energy surface, calculated from the elliptical anisotropic potential of Eqs. (12) and (13). Potential energy contours (in meV) are displayed for $V(r, \gamma) \leq 10$ meV; the polar coordinates in this diagram are r (in Å) and γ . Solid lines: $V(r, \gamma) > 0$; dashed line: $V(r, \gamma) = 0$; dotted lines: $V(r, \gamma) < 0$. The absolute minimum on the potential surface is -3.93 meV and occurs at $\gamma = \pi/2$; $r = 3.31$ Å. Saddle points occur for the collinear configurations $\gamma = 0, \pi$; $r = 4.77$ Å, where the potential energy is -1.07 meV. The minimum and saddle point positions are denoted by crosses. The positions of the C and O atoms are also shown for reference. The slight unevenness of some of the contours is caused by the crudeness of the potential model.

Fig. 7. He + N₂O empirical potential energy surface, calculated from the elliptical anisotropic potential of Eqs. (12) and (13). Symbols as in Fig. 6; the absolute minimum is -4.20 meV and occurs at $\gamma = \pi/2$; $r = 3.45$ Å; saddle points occur at $\gamma = 0, \pi$; $r = 5.05$ Å, where the potential energy is -0.46 meV.

Fig. 8. Laboratory differential cross sections for out-of-plane scattering of He by CO₂. Points with error bars are the experimental measurements of the scattering cross sections $^{36} I(\theta) \cdot \sin\theta$ 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

line: anisotropic elliptical potential of Eqs. (12) and (13); dashed line: empirical electron-gas potential of Eqs. (18-20); dotted line: triple-LJ potential of Eq. (17).

Fig. 9. He + CO₂ empirical potential energy surface, calculated from the triple-LJ potential of Eq. (17). Symbols as in Fig. 6.

Fig. 10. He + CO₂ empirical potential energy surface, calculated from the electron-gas potential of Eqs. (18-20). Symbols as in Fig. 6.

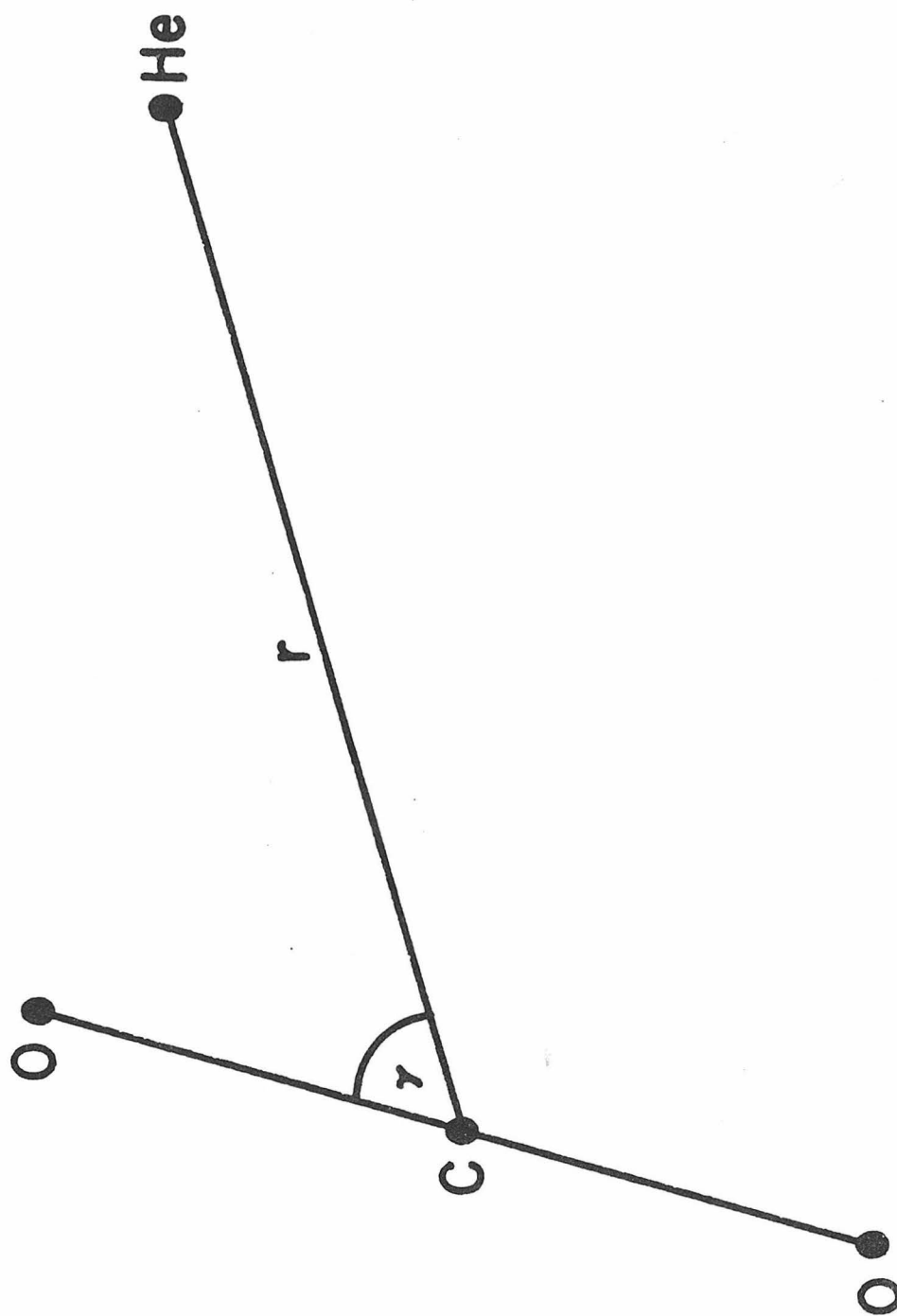


Figure 1

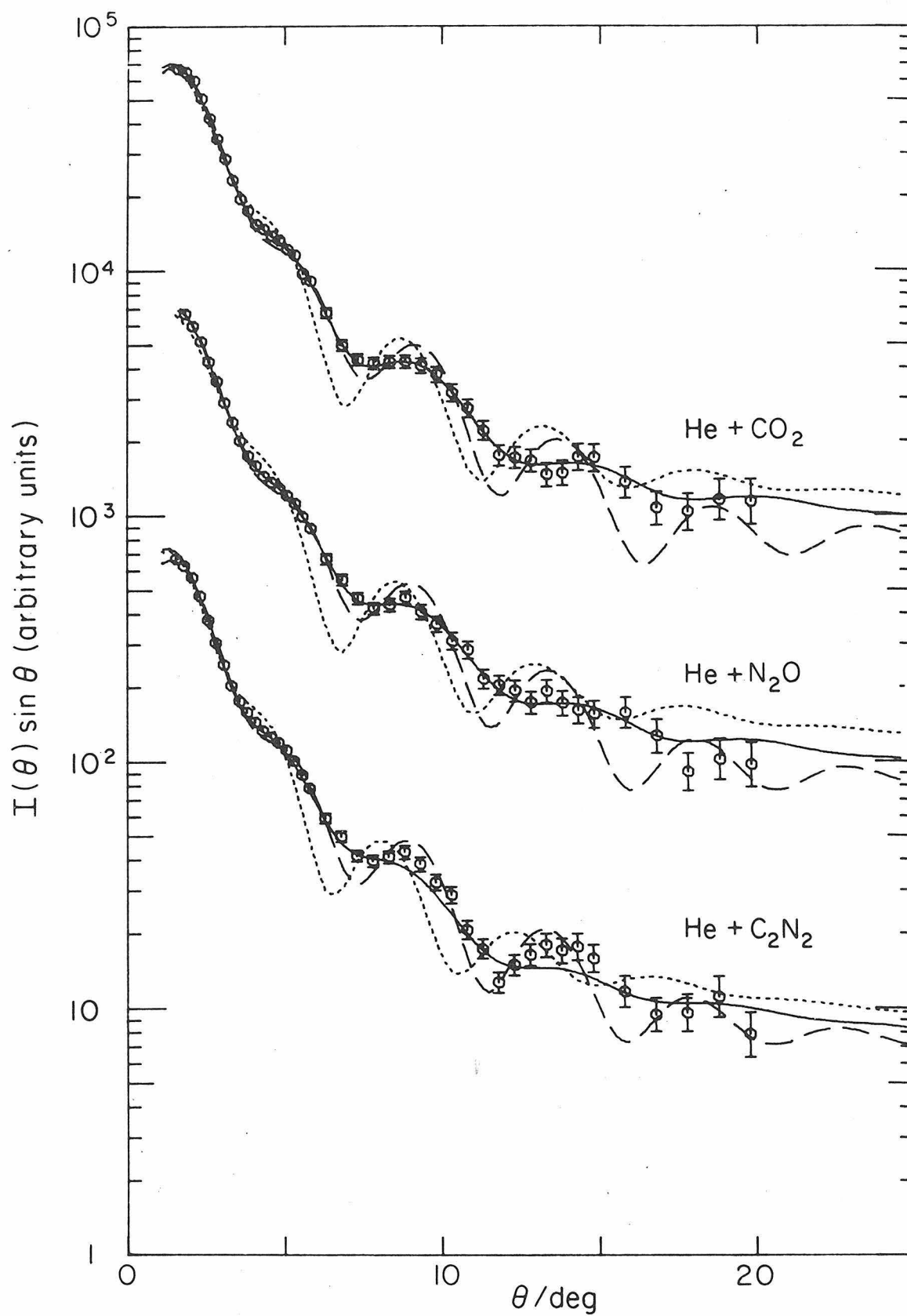


Figure 2

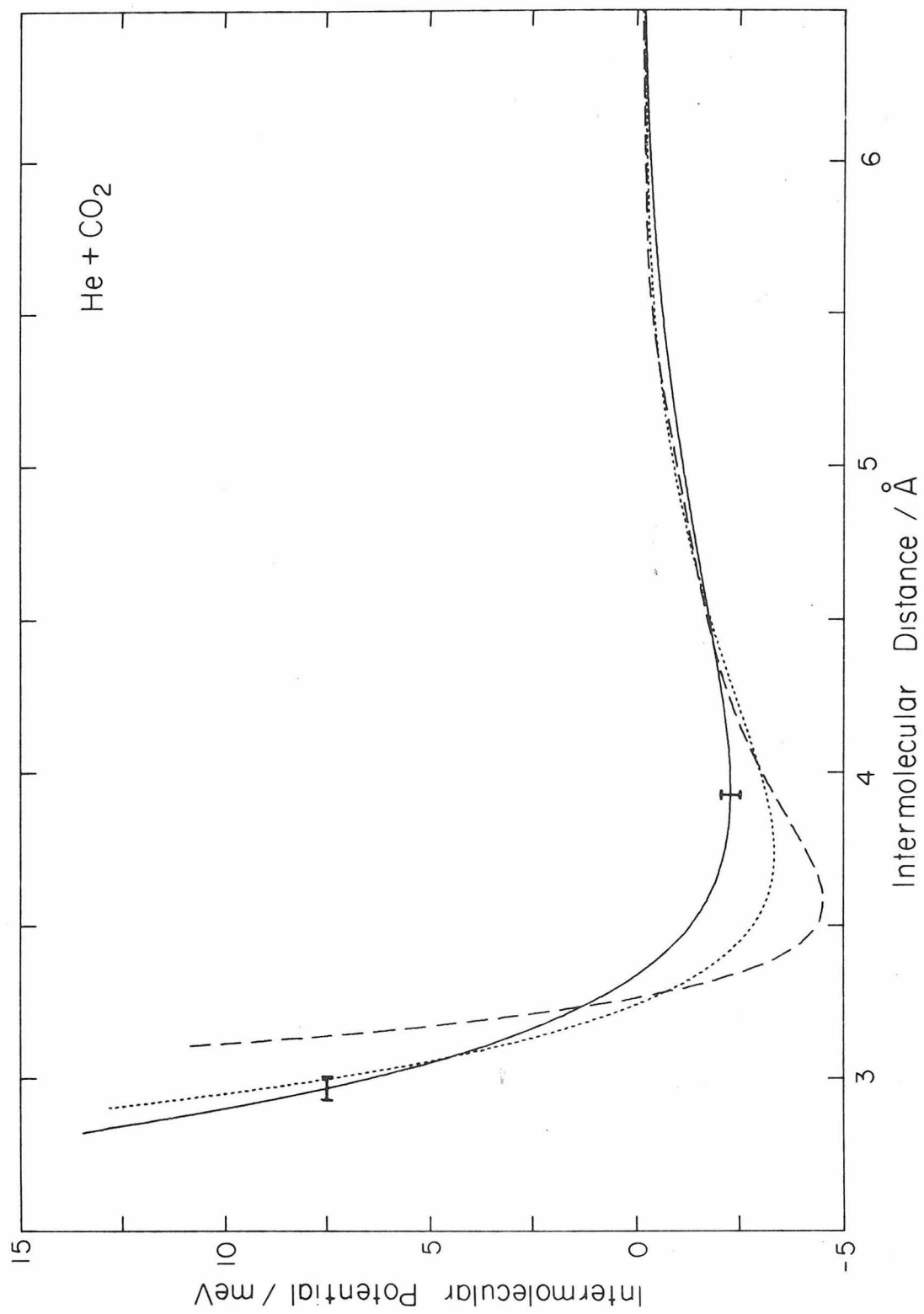


Figure 3

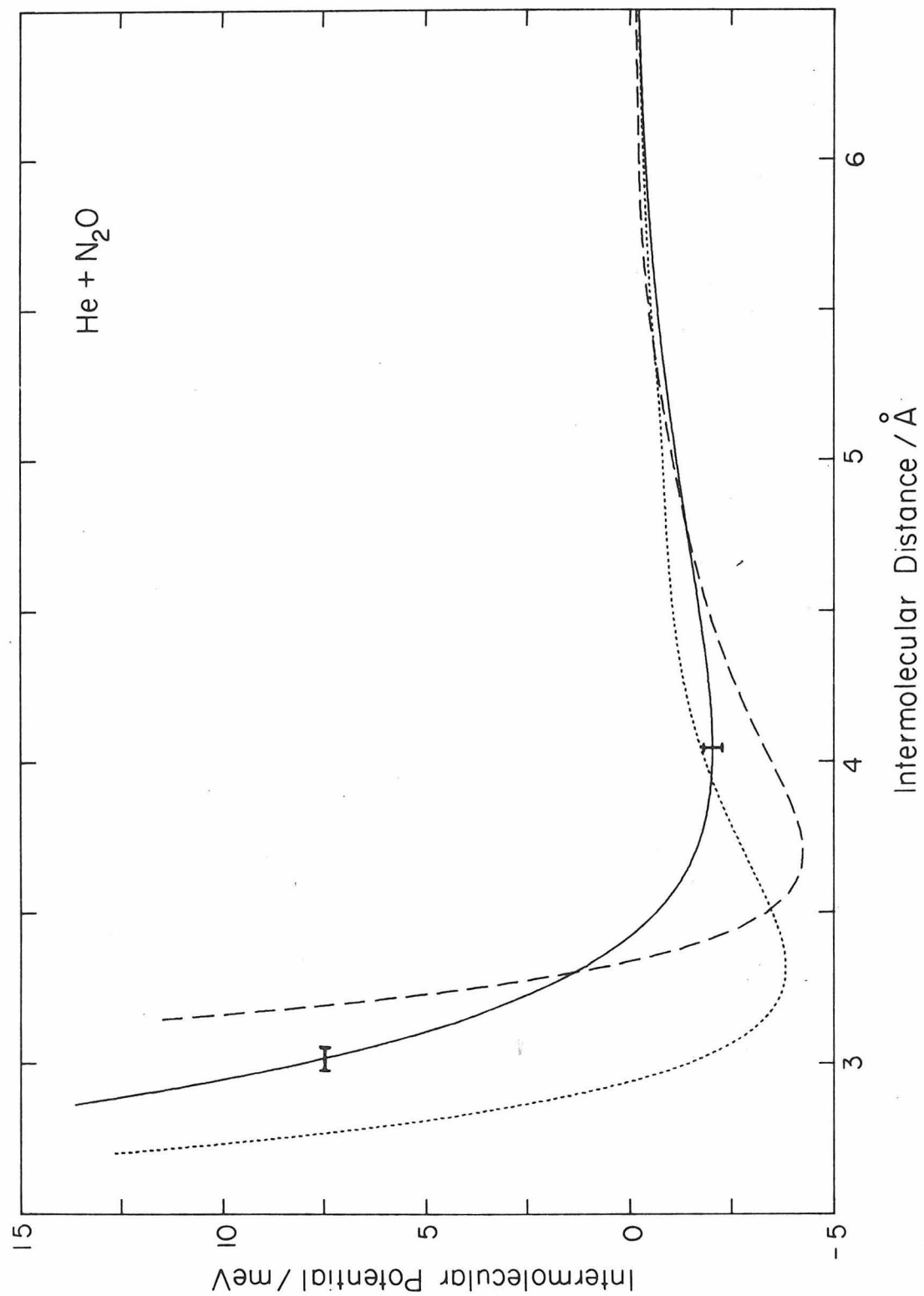


Figure 4

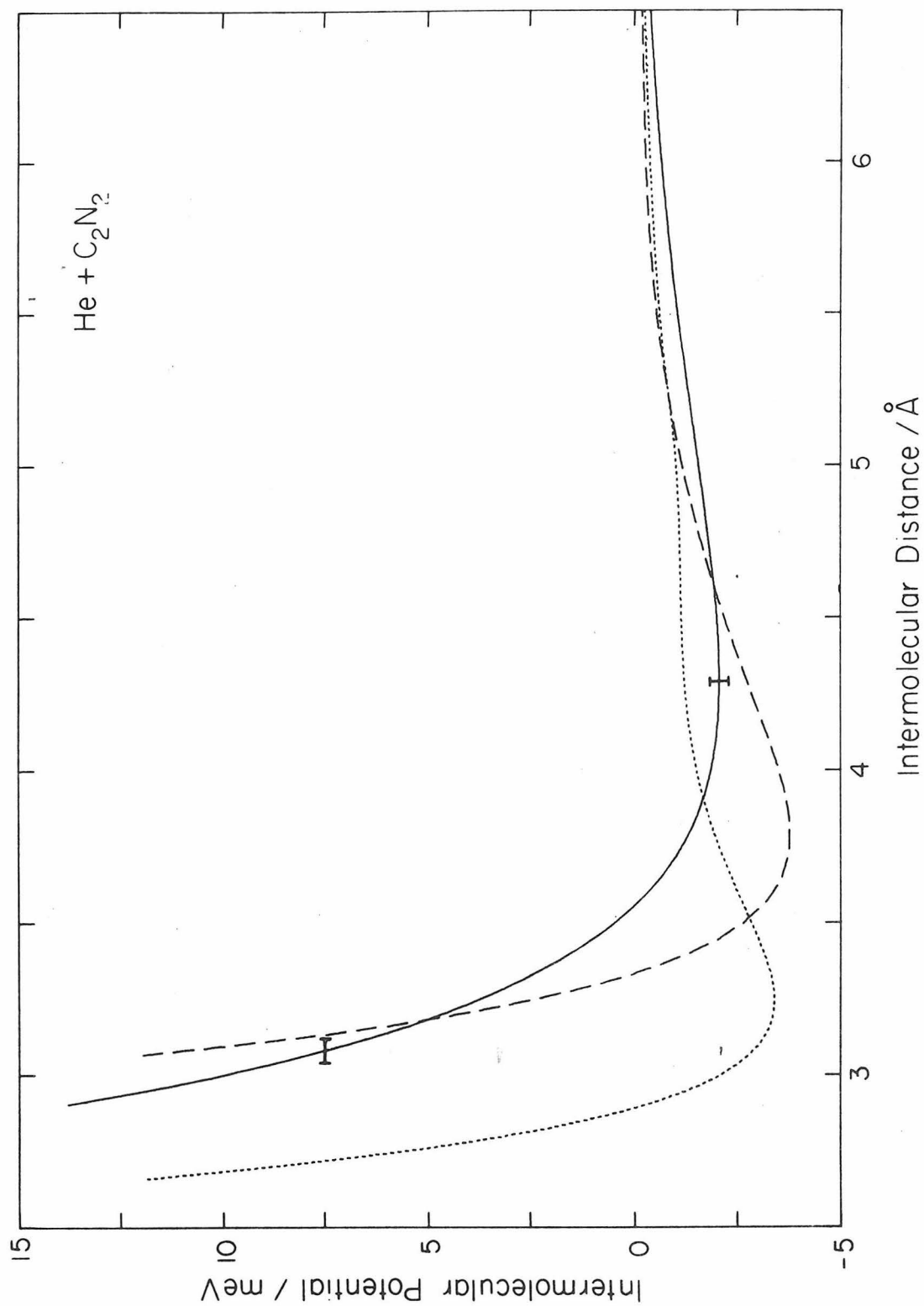


Figure 5

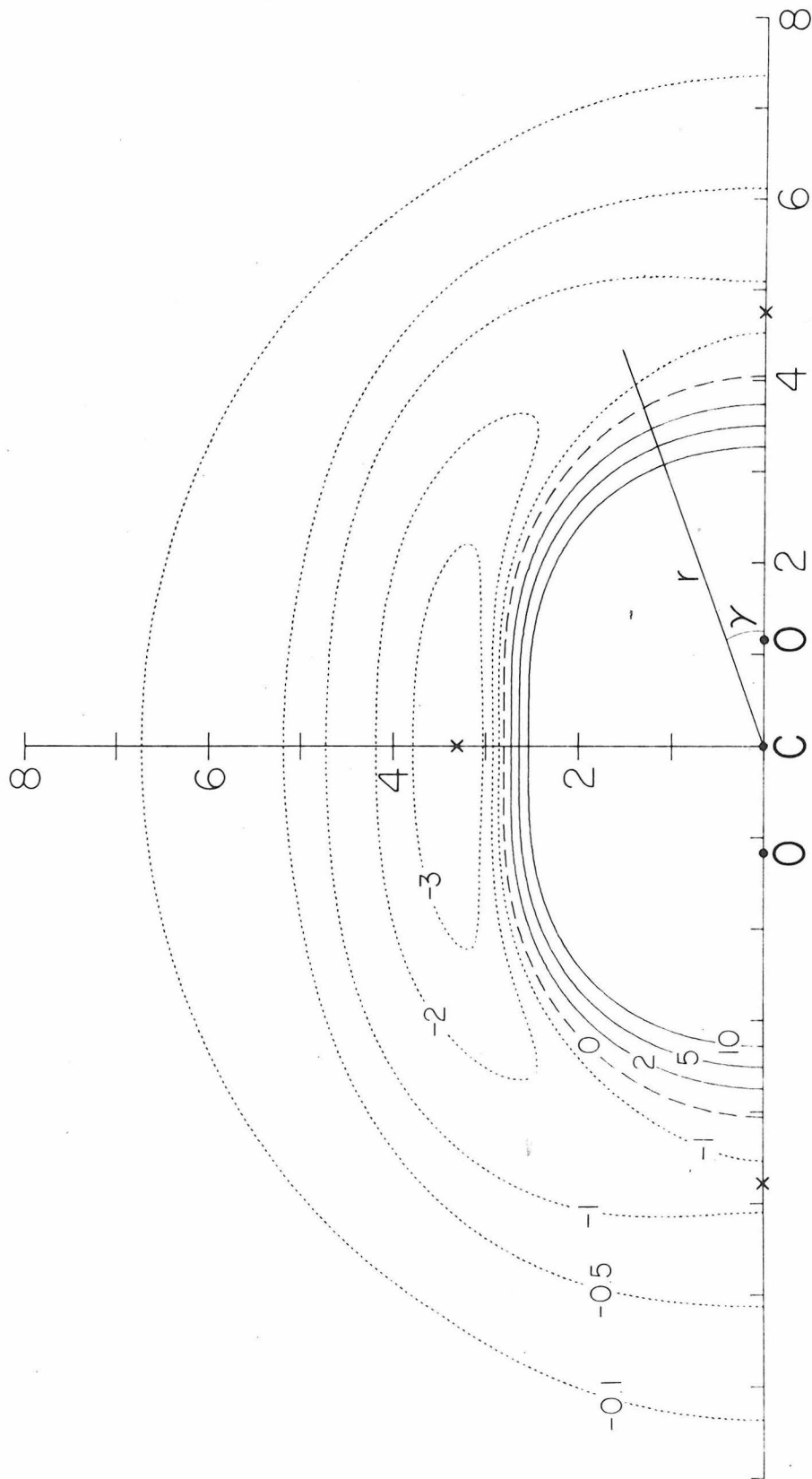


Figure 6

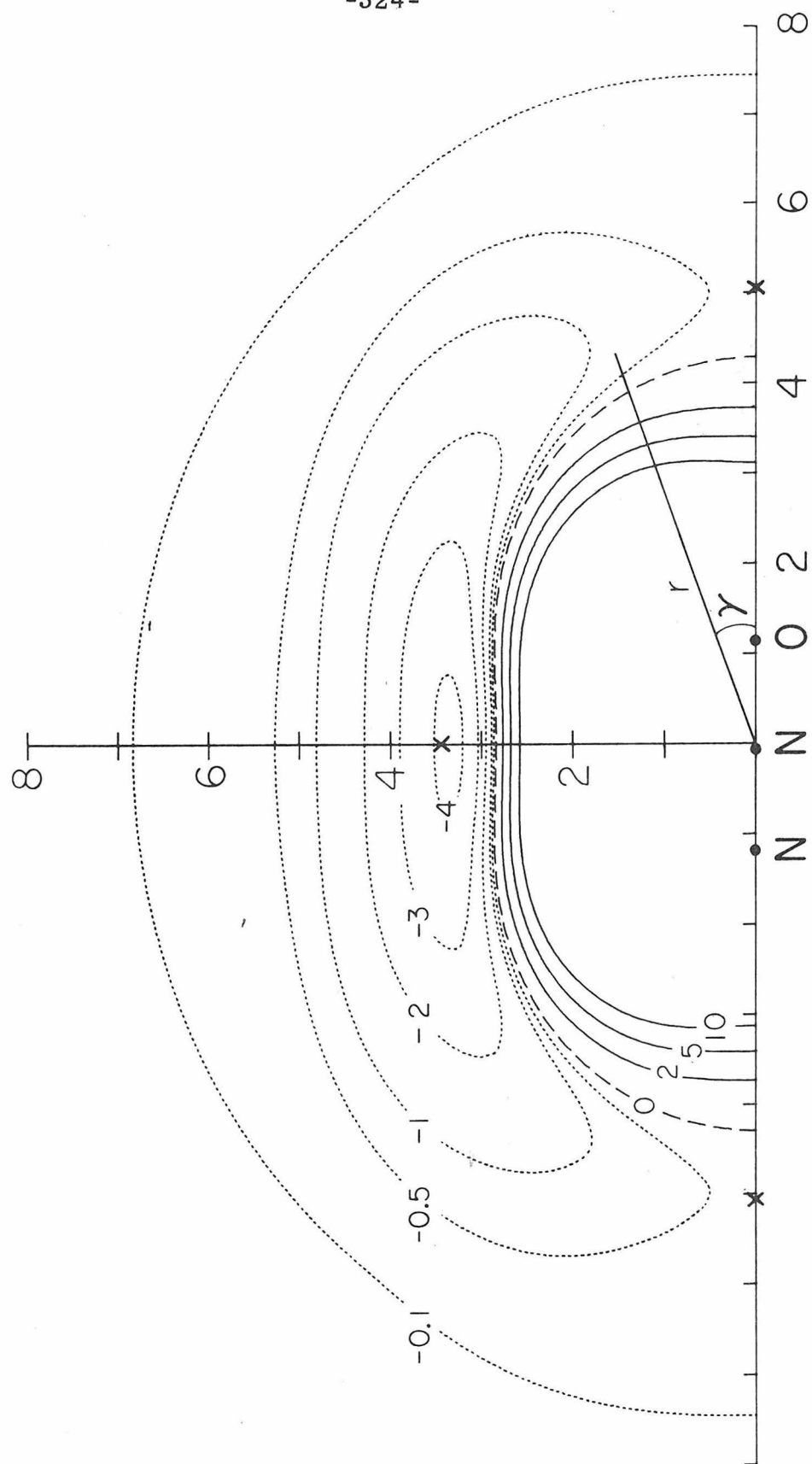


Figure 7

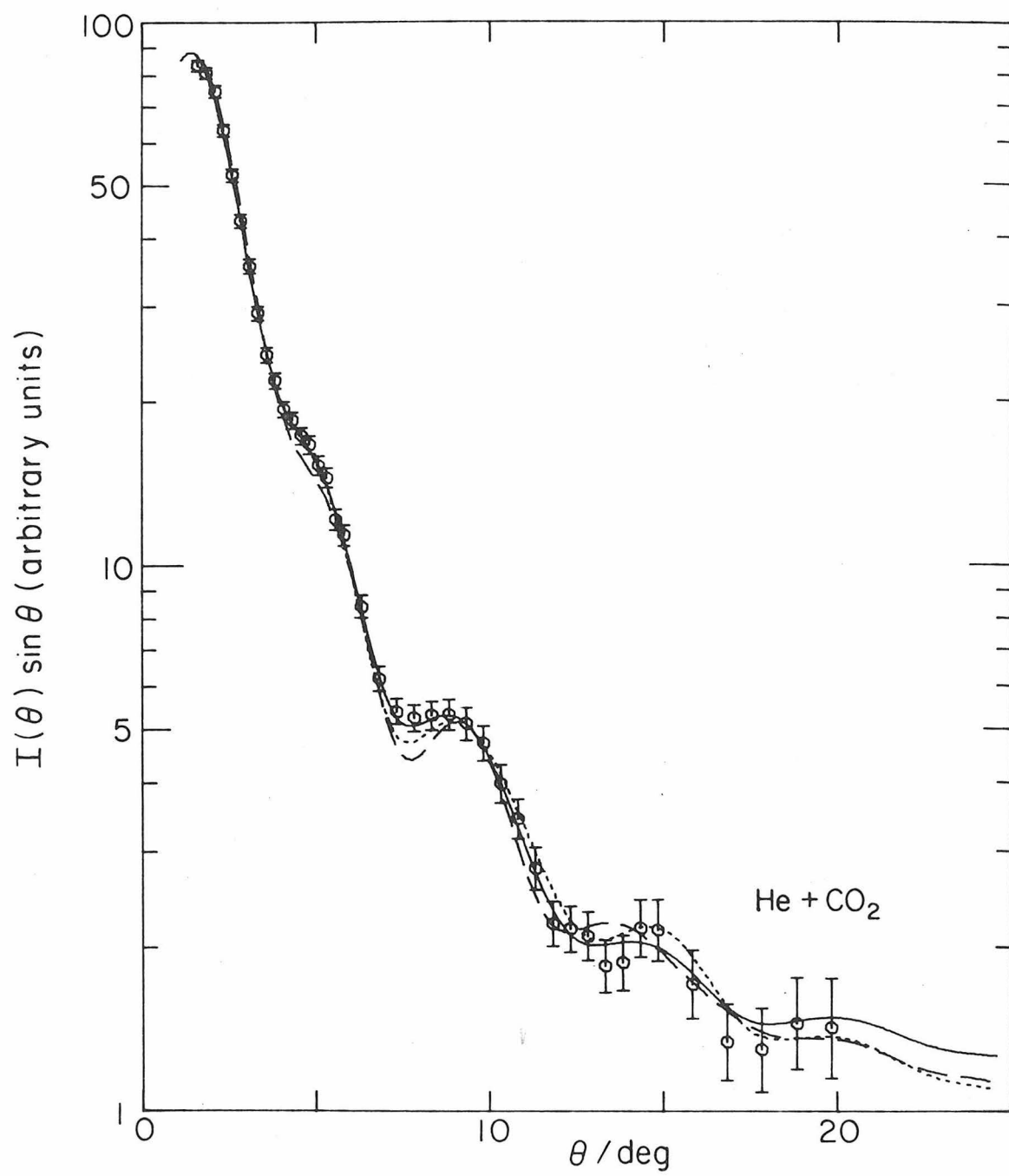


Figure 8

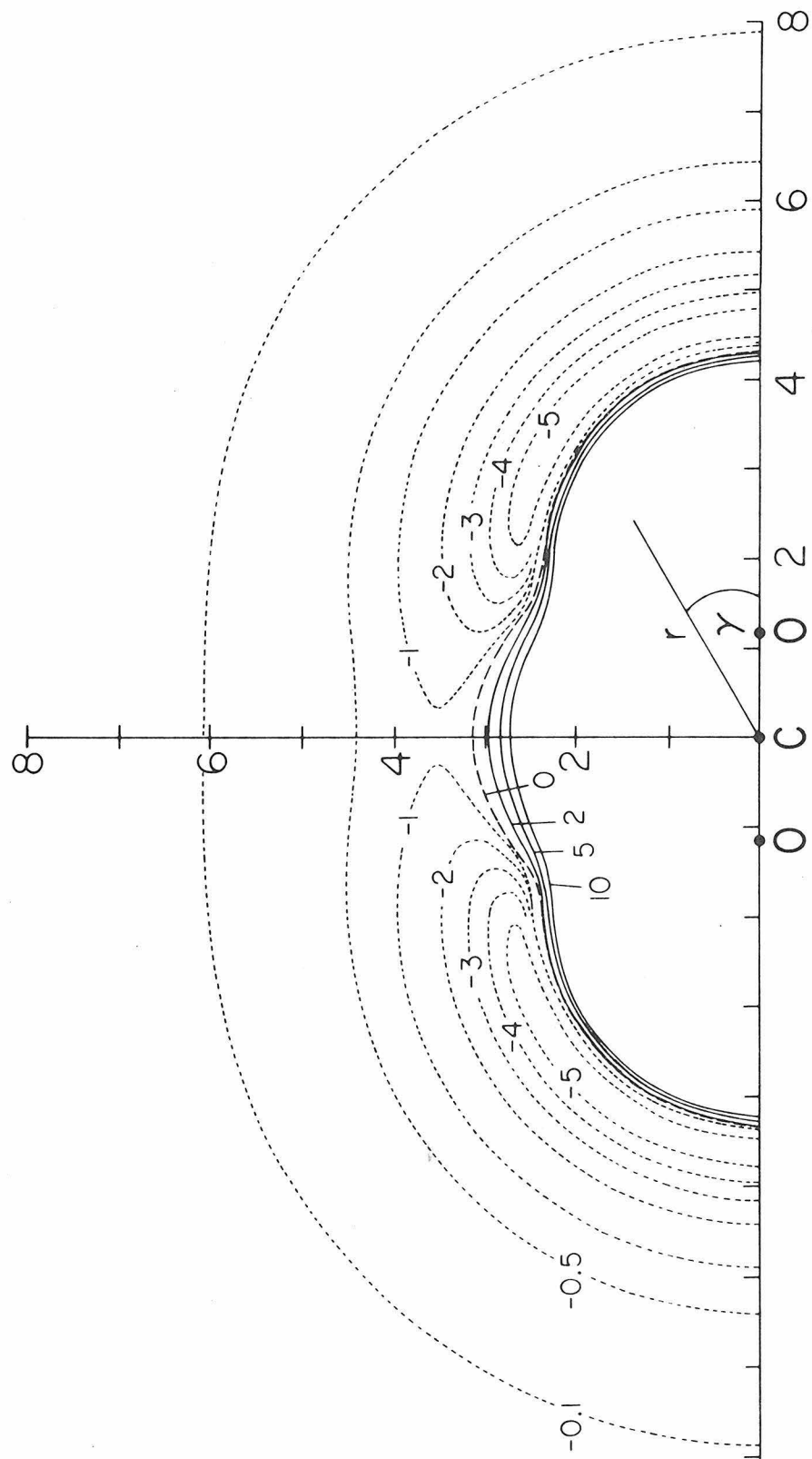


Figure 9

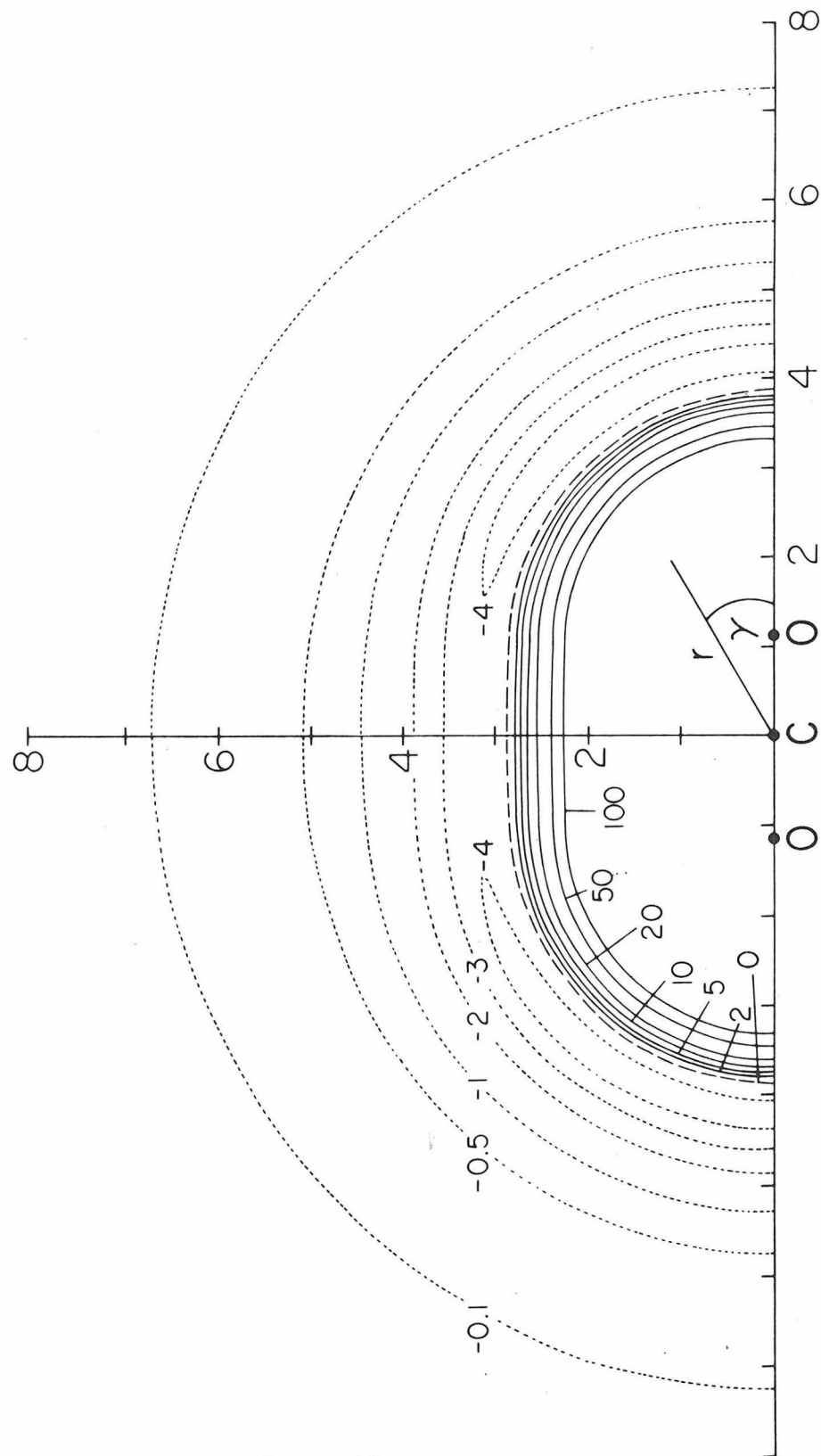


Figure 10

APPENDIX C

Crossed molecular beam experimentation

The apparatus used for the experimental work described in this thesis was discussed in the introduction as a crossed molecular beam device. "Device" is really a misnomer; the apparatus is monstrous, though with care it can be quite wieldy! The ultimate goal of such an apparatus is itself very simple: atoms or molecules are prepared in specified internal states and with specific translational energies. The resulting well-defined collisions between such particles are observed as functions of product internal state, velocity, and scattering direction. The present version of our somewhat more modest apparatus has evolved over several years from those used previously. Our description herein will involve only a broad overview of the experimental techniques and ideas involved. Conditions most relevant to the experimental results have been described in detail earlier in this thesis (Chapter 2, Sec. II). Other aspects of the apparatus have very recently been described in great detail.¹ Another description of an earlier version of the apparatus provides a relevant background for the present discussion.² Late model modifications to the apparatus and procedures are detailed towards the end of this appendix.

Not unexpectedly, practical limitations restrict the amount of specificity that can be attained in the crossed beams apparatus, both in the collision conditions and in detector sensitivity. We first point out that since the experiments performed in this thesis are due primarily to elastic scattering, the internal states of the scattered particles are the same as the initial ones. The remaining degrees of freedom are therefore just the initial velocity vectors of the colliding partners, and the scattering direction. The incident direction of the

colliding partners is best specified by angularly well collimating the particles emerging from a source of the gas, hence the term "molecular beams". Merely allowing a gas to effuse from a region of relatively high pressure into a region of lower pressure, however, results in a poorly defined velocity of the particles. Consequently, we use a "supersonic expansion" (or "nozzle beam") to generate one of the beams, which we will henceforth label as the primary beam. The secondary beam is generated by a source combining some of the advantages of the supersonic expansion, without requiring some of its more elaborate features (such as high speed differential pumping).

In order for the beams' initial conditions to be propagated into the crossed-beams interaction region and result in a well-defined collision, only collisions in that region can be allowed. Consequently, the pressure in regions traversed by the beams, and in the beams themselves, must be sufficiently low to ensure single-collision conditions. We also note that it is only under such circumstances that the scattering angle can be readily determined. For example, if a particle originating from the scattering zone experiences a second collision during its flight to the detector, the initial scattering direction information is lost. Since the crucial aspect of the experiment is to measure the scattered intensity as a function of the scattering angle, it is essential that secondary collisions be avoided. With the present experimental apparatus, single-collision conditions are ensured by working at pressures of $\lesssim 10^{-6}$ torr. These high-vacuum requirements place an upper limit on beam intensities, and thereby place stringent requirements on detector sensitivity.

Since the scattering partners are neutral species, the beam to be analyzed must first be ionized. The electron-bombardment ionizer itself however, hardly discriminates at all against background gas particles in the ionizer region. Consequently, the residual gas at the mass of interest must be reduced to very low levels, since the scattered beam itself is many orders of magnitude less intense than the incident beam. This problem is exacerbated in non-reactive collisions: the scattered beam to be detected has the same mass as one (or both) of the incident beams. Requirements for the detector therefore fall into two categories; vacuum pumps effective for the scattered gas, and discrimination against background in addition to mass filtering. The first requirement is satisfied in our experimental arrangement, by using a combination of high-speed pumps, which function at pressures below even 10^{-10} torr. Furthermore, effectively isolating the detector chamber from the scattering zone (except for small collimators) by two stages of pumping removes most of the background gas before it ever reaches the ionizer. Under the operating conditions currently realized for the detector, its sensitivity limit for a scattered He beam is about 20 ions per second reaching the ion counter. This corresponds to a partial pressure of scattered He in the ionizer region of $\sim 10^{-14}$ torr! To extract this extremely weak signal from the background partial pressure of He in the ionizer region of $\sim 10^{-11}$ torr, we must use modulation techniques. This involves "labeling" the primary beam during its flight time by alternately opening and closing a shutter interrupting its flow at some known frequency. Since the primary beam particles of interest travel directly from the beam

source, and are deflected by the (unmodulated) secondary beam into the detector, they must arrive with the same frequency information as the primary beam shutter. Their arrival must also be phase-shifted by an amount corresponding to the molecular flight time and the detector electronic response time. These AC modulation techniques improve the signal-to-noise ratios by about three orders of magnitude. The weakest signals measured in the experiments described in this thesis require about one hour to gain a signal-to-noise ratio of ~ 5 .

We now turn to the modifications made in the crossed-beams apparatus since the most recent detailed description. We first discuss the alignment procedure. The purpose is to ensure that the intersection of the two beams occurs in a well-defined zone, and that the detector rotates exactly about this zone. A precision-machined pin is placed at the scattering center, which is along the vertical axis of the apparatus. Since the scattering angle is defined by the deflection of primary beam particules into the detector, the most essential part of the alignment is to ensure that these components be in an exact line, for a zero-degree scattering angle. The primary beam axis is defined by three orifices: the nozzle, skimmer, and final collimator. These are adjusted to be collinear (horizontally and vertically) with the pin at the scattering center, thus defining the 0° scattering direction. The two collimators defining the detector axis are then adjusted to be exactly on this 0° scattering direction, and the angular readout system is adjusted accordingly. This part of the alignment is performed with a precision optical surveyor's telescope placed opposite the primary beam, rather than opposite the secondary beam. Earlier practice

utilized a mirror to sight along the 0° axis, but was abandoned when it was realized that this may have introduced distortions in the particularly important 0° alignment. The next step is the alignment of the secondary beam, for which purpose the surveyor's telescope is placed along the 90° axis. With the pin still in place at the scattering center, we need only ensure that the secondary beam axis pass through it. After accomplishing this adjustment, we check the detector's ability to rotate precisely about the scattering center, by measuring the distance between the pin and the detector's entrance collimator. This distance should not change as the detector is rotated throughout its in-plane and out-of-plane angular range. Based on this check, and on the accuracy with which the collimator positions may be measured and adjusted, the overall alignment is accurate to about $\pm 0.2^\circ$. This residual misalignment may be measured and compensated for in the scattering data, as detailed earlier in this thesis (Chapter 2, Sec. IV).

We pointed out earlier that the vacuum requirements of the detector are very stringent. In order to reduce the outgassing rate from detector surfaces during experiments, even after vigorous bakeouts have cleaned them substantially, the entire detector is cooled by liquid nitrogen. This also provides a radiation shield for the liquid helium cryopump, which provides most of the pumping action in the pressure-critical ionizer region. Formerly, the liquid nitrogen cooling was provided merely by flowing the cryogen through cooling jackets on the detector. This flow system was very inefficient however: one 20-hour experiment would require two or three 160-l dewars. Moreover, because of the condensability of background gases, variations in the

cyrogen flow would seriously affect the pressure in the apparatus. To solve both these problems, the detector's cyrogen supply is now held in a large storage dewar. The cyrogen level is the same in this storage dewar as inside the apparatus, and the efficiency of its use has been improved by a factor of two or three. As long as the storage dewar is kept reasonably full, the cyrogenic lines inside the apparatus do not undergo temperature fluctuations, and this source of pressure "bursts" has been eliminated.

Prior to May 1977, scattered beam particles were detected only by analogue devices. This was modified using an ion detector whose high-gain and fast-response characteristics make it suitable for counting individual ions impinging on the detector. Signal processing for this pulse detector system is described in detail in Ref. 1. In principle, pulse counting techniques should allow detection of lower signal levels because the ion current, instead of being time-averaged in its amplification, retains its inherently discrete characteristics. Counting individual pulses also allows their arrival time to be accurately measured, providing an important incentive for the use of these techniques, as discussed below. As with all detectors, the output signal must vary in a known fashion with the input signal. The first ion detector used was a Spiraltron, which loses gain for count rates above $\sim 2 \times 10^4$ Hz. This does not cause a problem until the gain is insufficient for the pulses to pass the discriminator of the counting circuitry. For modulated experiments, this may be a particularly significant problem. During the time that the primary beam is on, the ion count rate is higher than when the primary beam is off. The gain during the beam-

on interval may then be lower than during the beam-off interval, and fewer of the counts occurring during the former interval are recorded. At high signal level, the modulated count rate therefore becomes non-linear. The Spiraltron was carefully checked to determine the upper limit of its linear response with our detection electronics. For a He primary beam, this was found to occur at a background count rate of $\sim 7 \times 10^4$ Hz. The detection system was always kept at a sufficiently low sensitivity to prevent non-linear response. However, operation at the requisite reduced sensitivity required considerable sacrifice in the signal-to-noise ratio of the experiment. Later on, a new ion detector was placed in the mass spectrometer. The gain of this high-current Channeltron is higher than that of the Spiraltron formerly in use, and does not fall off with increasing count rate as quickly. Although it has not yet been used in a scattering experiment, the Channeltron's linearity has been verified for count rates of up to $\sim 3 \times 10^5$ Hz; we anticipate its full dynamic range to be up to $\sim 10^6$ Hz. At this high count rate, the electronic counters lose linearity, and would probably not be reached during scattering experiments. Consequently, the present ion detector is capable of linear operation throughout the entire dynamic range required in the experiment.

To conclude this appendix, we now turn to a discussion of future types of experiments to be performed on the crossed-beams apparatus. In the immediate future, these will involve measurements of energy transfer caused by collisions between the beam particles. At the thermal energies used, the most probable inelasticities are due to rotational transitions of the molecular scattering partner. In

atom-molecule systems, one way to determine these energy transfers is to measure the velocity change of one of the scattering partners. Conservation of energy and momentum then allows a direct evaluation of the number of rotational quanta transferred to or from translational degrees of freedom. The technique to be used in these experiments is time-of-flight velocity analysis of the scattered beam. In order to attain high duty cycles, the time-of-flight pulses are allowed to overlap during their flight to the detector. The time-of-flight distribution is thus convoluted over the chopping function of the velocity analyzer. To recover the original velocity distribution, it is necessary to deconvolute this chopping function from the temporal distribution of the scattered signal. The chopping function's intervals are very short ($\sim 10\mu\text{sec.}$), requiring fast response of the detector; hence pulse counting techniques are essential, as indicated earlier. The deconvolution procedure is described in detail in Ref. 1. Also discussed there are the associated electronics (a multi-channel scaler) required for accumulation of the temporal signal distribution. Currently, the system is designed to operate with the velocity analyzer rotating at 400 Hz, with 255 intervals. The flight path between the analyzer and the mass spectrometer ionizer is 15 cm; for a supersonic He beam at 300 K, the average flight time is thus $\sim 100\mu\text{sec.}$ Consequently, most of the velocity information is contained in the first few intervals of the time-of-flight distribution, and the resolution may be poor. To solve this problem, it may be necessary to increase the flight path somewhat, although this would require extensive hardware modifications. Alternatively, the rotation frequency of the velocity analyzer may be increased. This has been accomplished

for up to 800 Hz (almost 50,000 rpm'), but I'd hate to be around if the bearings go! Even greater rotation frequencies may effectively be attainable by repeating the interval sequence around the velocity analyzer disk while decreasing each interval width accordingly. Of course, the velocity resolution problem can always be lessened by using slower beams. It is hoped that the velocity analysis experiments will provide sufficient resolution to resolve the inelastic differential cross section from the elastic one.

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APPENDIX D

Extraction of interatomic potentials from
elastic differential cross section measurements

As with the experimental aspects of the crossed-beam project, the data reduction procedure is quite involved. Many of its computational features have been discussed earlier in this thesis (Chapter 2, Sec. III). In order to understand the data gathered by the experiment, a thorough understanding of the data analysis is essential. We will begin by providing an outline of the classical and quantal descriptions of central-field elastic scattering. More detailed and general discussions may be found in a number of standard references.¹⁻⁵

In a central-force field, the scattering partners may be considered structureless (even if they are not atoms, internal degrees of freedom are neglected in this approximation), so that there are six coordinates, which classically specify the problem completely. Separating the center-of-mass motion from the relative motion between the two particles of masses m_1 and m_2 simplifies the problem to a three-coordinate one. This may be regarded as the dynamics of a single particle, of "reduced mass" $\mu = \frac{m_1 m_2}{m_1 + m_2}$, in a central-field potential $U(r)$. This "effective potential" is the sum of the interatomic potential $V(r)$ and a centrifugal term $\frac{\ell^2}{2\mu r^2}$. The latter contribution arises from the separation of the angular momentum ℓ , which is a constant of the motion for central-field potentials. The total energy of the system E is also a constant of the motion, and we obtain the two first-order differential equations,

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

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

Here, $U(r) = V(r) + \frac{\ell^2}{2\mu r^2}$ is the effective potential, and $\frac{d\theta}{dt}$ is the rate of change of the relative velocity vector's direction. This classical trajectory may then be integrated, yielding the asymptotic scattering angle as

$$\chi(E, b) = \pi - 2bE^{\frac{1}{2}} \cdot \int_{r_c}^{\infty} \frac{dr}{dr^2} [E - U(r)]^{-\frac{1}{2}} \quad (3)$$

The impact parameter b is what the distance of closest approach of the colliding particles would have been if there were no interaction between them; the classical turning point r_c is the corresponding distance of closest approach in the presence of the interaction potential, and may be obtained from Eq. (1) by setting $\frac{dr}{dt} = 0$. The classical deflection function given by Eq. (3) may be found once the potential $V(r)$ and relative collision energy E are specified.

At this point, it is convenient to introduce the reduction variables r_m and ϵ ; the first is the attractive minimum radius of the interaction potential, and ϵ is its depth. Eq. (3) becomes

$$\chi(K, \beta) = \pi - 2\beta \cdot \int_{\rho_c}^{\infty} \frac{d\rho}{\rho^2} \left[1 - \frac{f(\rho)}{K} - \frac{\beta^2}{\rho^2} \right]^{-\frac{1}{2}}, \quad (4)$$

where $\rho = \frac{r}{r_m}$; $\rho_c = \frac{r_c}{r_m}$; $\beta = \frac{b}{r_m}$ are reduced distances, and $K = \frac{E}{\epsilon}$; $f(\rho) = \frac{V(r)}{\epsilon}$ are reduced energies. A useful quantity in discussing the probability of occurrence of scattering is the (integral) cross section,

$$Q = \frac{\text{total number of scattered particles per unit time}}{\text{incident particle intensity}} \quad (5)$$

The measurements made in this thesis are related to the differential cross section (DCS) for scattering,

$$\sigma(\Omega)d\Omega = \frac{\text{number of particles scattered into } d\Omega \text{ per unit time}}{\text{incident particle intensity}}, \quad (6)$$

where $d\Omega$ is an element of solid angle. The integral cross section is given in terms of the DCS by $Q = \int \sigma(\Omega)d\Omega$. In the present non-polarized beam experiments, the scattering is symmetric about the (relative) beam axis, as that

$$\sigma(\Omega)d\Omega = 2\pi\sigma(\theta)\sin\theta\,d\theta, \quad (7)$$

where θ is the scattering angle. For a particle incident upon a center of force with reduced impact parameter between β and $\beta + d\beta$, the deflection angle will be between χ and $\chi + d\chi$, as given by Eq. (4). The relation between the DCS and the classical deflection function is thus

$$\sigma(\chi) = -\frac{\beta}{\sin\chi} \cdot \frac{d\beta}{d\chi} \quad (8)$$

For potentials with an attractive well, the classical deflection function $\chi(\beta)$ passes through a minimum at the "rainbow angle" θ_r ; for $\theta < \theta_r$ there are three different impact parameters contributing to the scattering at a single $\theta = |\chi|$. Consequently, the classical DCS for van der Waals potentials is given by

$$\sigma(\theta) = -\sum_i \frac{\beta}{\sin\theta} \left| \frac{d\beta_i}{d\theta} \right| \left\{ \begin{array}{ll} i = 1, 2, 3 & \text{for } \theta < \theta_r \\ i = 1 & \text{for } \theta > \theta_r \end{array} \right\} \quad (9)$$

The classical DCS is thus dependent only on the reduced energy K .

Although it may provide useful insights, classical mechanics is often inapplicable to the problem of atomic and molecular scattering. Quantum effects for the systems studied in this thesis are large,

since the van der Waals potential energy changes significantly over the de Broglie wavelength ($\sim 0.5\text{\AA}$). The demise of the classical description is a manifestation of the uncertainty principle, in that both β and χ cannot both be simultaneously well defined. Consequently, the classical trajectory of Eq. (4) cannot be used for such systems; indeed, the concept of a trajectory becomes poorly defined.

As for the classical scattering problem discussed above, the quantum description is given most conveniently in the center-of-mass coordinate frame. Since the effects of scattering can only be observed in a region far removed from the interaction region (as compared to collision dimensions), we treat the quantum mechanical problem by considering the asymptotic behavior of the wavefunction. It may then be described as an incoming plane wave (conventionally chosen incident along the z-axis), and an outgoing spherical wave,

$$\psi_{\mathbf{k}}(\mathbf{r}, \theta, \phi) = e^{ikz} + \frac{f_{\mathbf{k}}(\theta, \phi)}{r} \cdot e^{ikr}, \quad (10)$$

where $k = \frac{\mu v}{\hbar}$ is the wavenumber and v is the relative collision velocity. The scattering amplitude function $f_{\mathbf{k}}(\theta, \phi)$ contains the results of the collision, and is related to the DCS as

$$\sigma_{\mathbf{k}}(\theta, \phi) = \left| f_{\mathbf{k}}(\theta, \phi) \right|^2 \quad (11)$$

As for the classical case, the DCS must be axially symmetric; in further restricting the treatment to central fields, the wavefunction may be expanded in terms of Legendre polynomials $P_{\ell}(\cos\theta)$ and the expansion coefficients a_{ℓ} ,

$$\psi_k(r, \theta) = \sum_{\ell=0}^{\infty} a_{\ell} \cdot \frac{u_{\ell}(r)}{r} \cdot P_{\ell}(\cos \theta) \quad (12)$$

Substituting Eq. (12) into the Schrödinger equation yields equations to be satisfied by the radial wavefunctions $u_{\ell}(r)$ for each ℓ ;

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2 \right] u_{\ell}(r) = 0, \quad (13)$$

where now $U(r) = \frac{2\mu}{\hbar^2} \cdot V(r)$. For $V(r) = 0$, Eq. (13) reduces to Bessel's equation; since we must have $u_{\ell}(0) = 0$ for $\psi(0)$ to be finite, only the regular solution is acceptable,

$$V(r) = 0 \Rightarrow u_{\ell}(r) = kr \cdot j_{\ell}(kr), \quad (14)$$

where $j_{\ell}(kr)$ is the regular ℓ^{th} -order spherical Bessel function. Since the j_{ℓ} are asymptotically sinusoidal, the net effect of a potential $V(r)$ which falls off rapidly as $r \rightarrow \infty$, is to introduce an energy-dependent "phase shift" $\eta_{\ell} = \eta_{\ell}(k)$ in the asymptotic solution,

$$\psi(r, \theta) = e^{ikz} + \frac{f(\theta)}{r} \cdot e^{ikr} = \sum_{\ell=0}^{\infty} \frac{a_{\ell}}{r} \cdot \sin(kr - \frac{\pi\ell}{2} + \eta_{\ell}) P_{\ell}(\cos \theta) \quad (15)$$

We now perform the partial wave expansion of the plane wave component of Eq. (15),

$$e^{ikz} = \sum_{\ell=0}^{\infty} (2\ell+1) \frac{i^{\ell}}{kr} \cdot \sin(kr - \frac{\pi\ell}{2}) P_{\ell}(\cos \theta) \quad (16)$$

The expansion coefficients a_{ℓ} may now be identified by comparing outgoing and incoming spherical waves (the latter must vanish):

$$a_{\ell} = i^{\ell} \frac{2\ell+1}{k} e^{i\eta_{\ell}} \quad (17)$$

The scattering amplitude is then given as

$$f_k(\theta) = \frac{1}{k} \cdot \sum_{\ell=0}^{\infty} (2\ell+1) P_{\ell}(\cos\theta) \sin\eta_{\ell} e^{i\eta_{\ell}} \quad (18)$$

The DCS may be found by substituting Eq. (18) into Eq. (11),

$$\sigma(\theta) = \frac{1}{4k^2} \left\{ \left[\sum_{\ell=0}^{\infty} (2\ell+1) \sin(2\eta_{\ell}) P_{\ell}(\cos\theta) \right]^2 + \left[\sum_{\ell=0}^{\infty} (2\ell+1) [\cos(2\eta_{\ell}) - 1] P_{\ell}(\cos\theta) \right]^2 \right\}. \quad (19)$$

Using the orthonormality relations of Legendre polynomials, the integral cross section attains a particularly simple form:

$$Q(k) = \frac{4\pi}{k^2} \cdot \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \eta_{\ell}. \quad (20)$$

Note that the quantum mechanical cross section depends on both the energy and the wavenumber, while the classical cross section is independent of k .

The only remaining task is to determine the scattering phase shifts η_{ℓ} . This may be accomplished by comparing the asymptotic behavior of the radial wavefunctions [the $u_{\ell}(r)$] satisfying Eq. (13), with the corresponding $V(r) = 0$ solutions. The $u_{\ell}(r)$ may be obtained by direct numerical integration of Eq. (13). Alternatively, approximation methods may be used, one of the most successful of these being the JWKB formulation.^{2, 3, 6} The JWKB phase shifts are not usually of sufficiently high accuracy at low ℓ for our purposes; they

can be corrected by applying the method of Rosen and Yennie, based on a perturbation of the JWKB wavefunctions.⁶

The computational procedure for obtaining DCS's is thus quite straightforward. For an assumed interaction potential $V(r)$, the radial Schrödinger equation [Eq. (13)] is numerically integrated to obtain the partial wave phase shifts as functions of the wavenumber and energy of the colliding partners. These are then used in Eq. (19) to obtain the DCS. Since the dynamics are calculated in the center-of-mass coordinate frame, the calculated DCS must be transformed to the laboratory coordinate frame before comparison to the experimental data. Further complications arise from the finite angular and energy resolution of the apparatus; the calculated lab DCS's must therefore be averaged appropriately over the apparatus angular and relative velocity distributions. Finally, we note that the calculated DCS is in absolute units (e.g., $\text{\AA}^2/\text{steradian}$), whereas the measured DCS is in arbitrary units, since absolute measurements, which are very difficult to obtain, are not made. The calculated DCS must therefore be scaled to the measured one: only the shape of the DCS is used in determining the interaction potential.

Up until now, we have considered only the "forward" part of the data reduction, proceeding from an assumed interaction potential to the measured DCS. The goal of the experiment is, however, just the reverse: determining $V(r)$ from the DCS. This is accomplished in a standard fashion,⁷ by optimizing parameters of an assumed mathematical form chosen to represent the interaction potential. The appropriateness and uniqueness, and hence the accuracy, of this

procedure, has been examined in detail earlier in this thesis (Chapter 1).

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