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JEFFREY ALAN SELL

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ANGULAR DISTRIBUTIONS IN PHOTOELECTRON SPECTROSCOPY

Thesis by

Jeffrey Alan Sell

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To my wife, Laura

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ABSTRACT

This thesis describes the measurements of the angular distributions in the photoelectron spectroscopy of diatomic and polyatomic molecules. The apparatus used was constructed previously, and basically consists of a HeI radiation source, a scattering chamber, a set of electrostatic lenses, a 180° hemispherical electrostatic kinetic energy analyzer, and detector. The lenses, analyzer and detector are mounted on a gear and rotate about the center of the scattering chamber allowing the measurements of the photoelectron angular distributions.

The theoretical section outlines the quantum mechanics of the photoionization process and briefly describes recent attempts to calculate the photoelectron asymmetry parameter β for atoms and molecules. The results for the hydrogen molecule are compared to the experimental values measured by the present author and previous ones, with fairly good agreement.

Measurements of β were carefully performed for 24 vibrational transitions of carbon monoxide using both 537 Å and 584 Å radiation as excitation sources. Its variation with final state vibrational quantum number was found to be quite pronounced and non-monotonic. By consideration of this and other experimental and theoretical data, it was concluded that an autoionizing state of CO should exist at 584 Å, and that β is very sensitive to the presence of such a state.

The photoelectron angular distributions were measured for benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. Trends in the asymmetry parameter β as well as in the

spectral band positions and shapes across this series of molecules led to the assignments of all of the π orbitals and some of the σ orbitals associated with the features in the spectra.

Angular distributions of the photoelectrons ejected from SF_6 were measured using HeI radiation. By considering the trends in the β parameter across the spectral bands, as well as other data, the assignments of the corresponding orbitals to these bands were made.

Measurements of the photoelectron angular distributions in the heterocyclic molecules furan, thiophene, and pyrrole were performed. The trends in β and in the shapes and positions of the bands in the spectra were used to assign the peaks that correspond to ionization from the π orbitals in these molecules.

The photoelectron angular distributions of the lowest IP carbon-carbon π electrons in ethylene and all of its fluorinated derivatives, and benzene and some of its fluorinated derivatives were measured. It was noticed that the value of β for the maximum intensity of the lowest IP π band decreased monotonically in the fluoroethylene series from a value of 1.25 for ethylene to 0.05 for perfluoroethylene. On the other hand it decreased non-monotonically in the fluorobenzene series from a value of 1.23 in benzene to 0.65 for perfluorobenzene. This difference in the behavior of β upon fluorine substitution in the two series of molecules was attributed to the difference in the interaction of the fluorine π lone pair electrons with the carbon-carbon π electrons (the resonance effect).

The photoelectron angular distributions were measured for both σ and π electrons in all of the fluorine derivatives of ethylene. High resolution (20 meV) spectra were reported for the bands which have vibrational structure. Trends in the ionization potentials, the variation of β across bands, and the vibrational frequencies were used to assign several orbitals to the corresponding photoelectron bands.

Finally, all of the above results are briefly summarized in terms of the relationship of β to various characteristics of the molecular orbitals. In addition, future work in this field is suggested.

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CHAPTER 1

INTRODUCTION

Photoelectron spectroscopy is the study of the kinetic energy, intensity, and angular distributions of electrons which are ejected from atoms or molecules when light interacts with them.

According to the Einstein¹ relation, when a photon of energy $\hbar\omega$ strikes an atom or molecule, part of the energy of the photon is used to overcome the binding energy or ionization potential (IP) of an electron and the rest is converted into the kinetic energy (KE) of the electron:

$$\hbar\omega = \text{IP} + \text{KE} . \quad (1)$$

Most often, the quantity of interest is the IP of the electrons in an atom or molecule. According to an approximation sometimes called Koopmans' Theorem,² the IP of an electron is just the negative of the energy E of the orbital from which the electron was ejected:

$$\text{IP} = -E . \quad (2)$$

Thus the photoelectron spectrum approximately gives a direct representation of the orbital energy levels.

In a typical photoelectron spectrometer, an intense beam of light (often from a helium discharge) is directed toward a group of atoms or molecules in either a molecular beam or a sample chamber. The atoms or molecules (M) are then ionized by the process:



The electrons are separated according to their kinetic energy and then detected. The photoelectron spectrum is a plot of the intensity of electrons detected as a function of their kinetic energy or IP.

One of the major problems in photoelectron spectroscopy is to associate the photoelectron bands with the corresponding orbitals. In this light, it was felt that studies of the angular distributions of the ejected photoelectrons would be helpful. It has been known for a long time³ that the intensity of photoelectrons ejected from hydrogen atoms depends on the angle θ between the direction of the photoelectron and the propagation direction of the light beam in the manner

$$I(\theta) = a + b \cos^2 \theta . \quad (4)$$

This formula was later shown⁴⁻⁶ to be valid for photoionization of more complicated atoms and randomly oriented molecules. Another way of writing (4) is to say that the differential cross section $\frac{d\sigma_{if}}{d\Omega}$ for a photoionization transition from an initial state i to a final state f by unpolarized light has the form

$$\frac{d\sigma_{if}}{d\Omega} = \frac{\sigma_{if}}{4\pi} \left[1 - \frac{\beta_{if}}{2} P_2(\cos\theta) \right] \quad (5)$$

where σ_{if} is the integral photoionization cross section, P_2 is the second Legendre polynomial, and β is the asymmetry parameter which ranges from -1 to +2. Carlson and coworkers⁷⁻¹² were one of the first groups to accurately measure photoelectron angular distributions in randomly oriented molecules. Among other things, they found¹² that the value of β is about 0.3 to 1.0 units higher for photoionization of a

π orbital than a σ one in several methyl-substituted ethylenes. This empirical rule, if valid for other molecules, could then be used to determine the σ and π bands in the photoelectron spectra of those molecules.

Mintz and Kuppermann undertook similar studies of the angular distributions in argon, neon, N_2 , a series of linear alkenes, and a series of linear dienes, using the present variable angle photoelectron spectrometer. The results are summarized in the thesis by Mintz.¹³

In the present study, the photoelectron angular distributions are measured for several diatomic and polyatomic molecules. Trends in the variation of the asymmetry parameter as well as in the spectral band shapes and positions are used to assign the bands to the corresponding molecular orbitals. In addition the variation of β among vibrational levels and also among the electronic bands in the series of several fluorinated compounds leads to further understanding of the factors which affect β .

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CHAPTER 2

THEORY

2.1 Theory of Photoionization

In this section the quantum mechanics of the photoionization process is outlined. The semiclassical treatment of the interaction of radiation with a one-electron atom is used where the electromagnetic field is treated classically and the atom is treated quantum mechanically.

First the Schrödinger wave equation is written for the motion of the electron of mass m and charge e in the presence of a radiation field characterized by the vector potential $\underline{A}$ and scalar potential ϕ :

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + \frac{ie\hbar}{mc} \underline{A} \cdot \underline{\nabla} + \frac{ie\hbar}{2mc} \underline{\nabla} \cdot \underline{A} + \frac{e^2}{2mc^2} A^2 + e\phi + V \right] \psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (1)$$

The other symbols have their usual meaning. The electric and magnetic field vectors $\underline{E}$ and $\underline{H}$ can be related to $\underline{A}$ and ϕ by the expressions:¹

$$\underline{E} = -\frac{1}{c} \frac{\partial \underline{A}}{\partial t} - \underline{\nabla} \phi \quad (2)$$

$$\underline{H} = \underline{\nabla} \times \underline{A}. \quad (3)$$

If the gauge is chosen properly, it can be shown that

$$\underline{\nabla} \cdot \underline{A} = 0 \quad \phi = 0. \quad (4)$$

Also the ratio of the term in A^2 in (1) to the term in $\underline{\hat{A}} \cdot \underline{\hat{\nabla}}$ can be shown¹ to be approximately $\frac{eA}{pc}$ which for weak vector potentials and one-electron processes is about 10^{-5} . Thus the Schrödinger equation is reduced to

$$i\hbar \frac{\partial \psi}{\partial t} = (H_0 + H')\psi \quad (5)$$

where

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V \quad (6)$$

$$H' = \frac{ie\hbar}{mc} \underline{\hat{A}} \cdot \underline{\hat{\nabla}}. \quad (7)$$

In this case the wave equation for the vector potential is given by

$$\nabla^2 \underline{\hat{A}} - \frac{1}{c^2} \frac{\partial^2 \underline{\hat{A}}}{\partial t^2} = 0. \quad (8)$$

A solution to equation (8) can be written¹ as

$$\underline{\hat{A}} = |A_0| \underline{\hat{P}} e^{i(\underline{\hat{k}}' \cdot \underline{\hat{r}} - \omega t + \theta)} + |A_0| \underline{\hat{P}}^* e^{-i(\underline{\hat{k}}' \cdot \underline{\hat{r}} - \omega t + \theta)} \quad (9)$$

where $|A_0|$ is related to the intensity of radiation I in units ergs/cm² sec by

$$I = \frac{\omega^2 |A_0|^2}{2\pi c} \quad (10)$$

where ω is the frequency of the radiation, $\underline{\hat{P}}$ is the complex unit polarization vector, $\underline{\hat{k}}'$ is the propagation vector of the electromagnetic wave,

$\underline{r}$ is the position coordinate on which the vector potential depends, and θ is a real phase constant. The relations

$$\underline{P} \cdot \underline{k}' = 0 \quad (11)$$

$$\omega = |\underline{k}'| c \quad (12)$$

$$\underline{P} \cdot \underline{P} = e^{2i\theta} \quad (13)$$

are noted. In equation (9) the first term represents absorption of a photon and the second term represents emission. Thus for the photo-ionization experiment the solution to (8) is

$$\underline{A} = |\underline{A}_0| \underline{P} e^{i(\underline{k}' \cdot \underline{r} - \omega t + \theta)} \quad (14)$$

The time-dependent solution $\psi(\underline{r}, t)$ of the Schrödinger equation is expanded in terms of solutions ϕ_n of the stationary state Schrödinger equation:

$$\Psi(\underline{r}, t) = \sum_n c_n(t) \phi_n e^{-iE_n t/\hbar}, \quad (15)$$

E_n is the energy of the n^{th} stationary state and $c_n(t)$ is the time-dependent coefficient. If the system is in state n at $t = 0$, first-order time-dependent perturbation theory is applied to find the probability $|C_\ell^1(t)|^2$ of finding the system in state ℓ after the perturbation is removed:

$$|C_\ell^1(t)|^2 = \left| \frac{-\langle \ell | H' | n \rangle}{\hbar} \frac{e^{i(\omega_{\ell n} - \omega)t} - 1}{\omega_{\ell n} - \omega} \right|^2 \quad (16)$$

where

$$\langle \ell | H' | n \rangle = \frac{ie\hbar}{mc} |A_0| \int \phi_\ell^* e^{i\mathbf{k}' \cdot \mathbf{r}} \mathbf{p} \cdot \nabla \phi_n d^3r \quad (17)$$

and $\omega_{\ell n}$ is the frequency that corresponds to the energy difference between stationary states ℓ and n . The photoionization transition takes place to a continuous set of final states so that the transition probability has to be integrated over the energies of final states. Using the energy density of final states $\rho(k)$, where k is the wave vector of the ejected electron, the transition probability per unit time W is found to be

$$W = \frac{1}{t_0} \int |C_\ell^1(t)|^2 \rho(k) dE(k), \quad (18)$$

where t_0 is the length of time the perturbation (radiation) has been on. Assuming that $\rho(k)$ depends slowly on k , the Golden Rule Number 2 is found

$$W = \frac{2\pi}{\hbar} \rho(k) |\langle \ell | H' | n \rangle|^2 \quad (19)$$

where $\langle \ell | H' | n \rangle$ was defined above.

The density of final states can be found from the permitted values of k inside a cube of side length L . Since $E_k = \frac{\hbar^2 k^2}{2m}$ then

$$\rho(k) = \frac{mL^3}{8\pi^3 \hbar^2} k d\Omega \quad (20)$$

where $d\Omega = \sin\theta d\theta d\phi$.

Thus the photoionization transition probability per unit time W is

$$W = \frac{e^2 L^3}{4\pi^2 \hbar c} \frac{k |A_0|^2}{m} \left| \langle \phi_\ell | e^{i\mathbf{k}' \cdot \mathbf{r}} \mathbf{p} \cdot \nabla | \phi_n \rangle \right|^2 d\Omega . \quad (21)$$

This can be converted to a differential photoionization cross section $\frac{d\sigma}{d\Omega}$ by dividing W by the total incident current density $\frac{\omega^2 |A_0|^2}{2\pi c} \frac{1}{\hbar\omega}$

to obtain

$$\frac{d\sigma}{d\Omega} = \frac{e^2 k L^3}{2\pi m c \omega} \left| \langle \phi_\ell | e^{i\mathbf{k}' \cdot \mathbf{r}} \mathbf{p} \cdot \nabla | \phi_n \rangle \right|^2 . \quad (22)$$

In the dipole approximation the exponential $e^{i\mathbf{k}' \cdot \mathbf{r}}$ is expanded in a Taylor's series and only the first term is retained

$$e^{i\mathbf{k}' \cdot \mathbf{r}} \approx 1 . \quad (23)$$

In the photoionization experiment using radiation produced by HeI emission, $\mathbf{k}' \cdot \mathbf{r}$ is about $1/300$ so that the approximation is fairly good.

Next the matrix element in (22) can be simplified by noting the the commutation relation:

$$[\mathbf{r}, H] = \frac{i\hbar}{m} \mathbf{p} . \quad (24)$$

If ϕ_ℓ and ϕ_n are stationary states of H then

$$\int \phi_\ell^* [\mathbf{r}, H] \phi_n d^3 r = (E_\ell - E_n) \int \phi_\ell^* \mathbf{r} \phi_n d^3 r \quad (25)$$

and

$$\langle \phi_\ell | \hat{\mathbf{p}} \cdot \hat{\nabla} | \phi_n \rangle = \langle \phi_\ell | \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} | \phi_n \rangle \frac{m\omega}{\hbar} . \quad (26)$$

This is used to transform from the dipole velocity form (22) to the dipole length form (27). The equation for the differential photoionization $\frac{d\sigma}{d\Omega}$ cross section becomes

$$\frac{d\sigma}{d\Omega} = \frac{e^2 L^3 k m \omega}{2\pi c \hbar^2} |\langle \phi_\ell | \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} | \phi_n \rangle|^2 . \quad (27)$$

In equation (27) the final state wave function has a continuous character to it and is normalized to a box. Thus ϕ_ℓ is proportional to $L^{-\frac{3}{2}}$ so that ultimately $\frac{d\sigma}{d\Omega}$ is independent of L .

Equation (27) is equivalent to the expression for the differential cross section given by Bethe and Salpeter:²

$$\frac{d\sigma}{d\Omega} = \frac{2\pi e^2 \hbar^2}{m^2 c \nu} |D_{\Omega b}^{k_\nu j}|^2 \quad (28)$$

where ν is the frequency of the incident radiation, the other constants have their usual meaning, and

$$D_{\Omega b}^{k_\nu j} = \int u_\Omega e^{i\mathbf{k} \cdot \mathbf{r}} \frac{\partial u_b}{\partial \mathbf{x}} d\tau . \quad (29)$$

The continuum wavefunction of the electron u_Ω is

$$u_\Omega(\mathbf{r}) = \sqrt{\frac{k}{(2\pi)^3}} [e^{i\mathbf{k} \cdot \mathbf{r}} + V(\mathbf{r})], \quad (30)$$

where $V(\mathbf{r})$ is the scattered part of this eigenstate of the atomic Hamiltonian, and u_b is the initial atomic wavefunction.

Bethe and Saltpeter³ have also given a simple argument that the form of the photoionization differential cross section of a hydrogen-like atom is $\frac{d\sigma}{d\Omega} = a + b \cos^2 \theta$ where θ is the angle between the polarization vector of the light $\underline{\hat{P}}$ and the propagation direction of the electron $\underline{\hat{k}}$. Using the definition of the symbols appropriate through Eq. (27), the matrix element $\langle \phi_\ell | \underline{\hat{P}} \cdot \underline{\hat{r}} | \phi_n \rangle$ depends on the angle θ . Since ϕ_n is a discrete state depending on the quantum numbers n , ℓ , and m , then $\frac{d\sigma}{d\Omega}$ also depends on m and the quantization direction of ϕ_n . However, experimentally an average $(d\bar{\sigma}/d\Omega)$ is measured which is $\frac{d\sigma}{d\Omega}$, averaged over all possible m values from $-\ell$ to ℓ for the initial state. Thus the angular distribution for the averaged DCS $d\bar{\sigma}/d\Omega$, depends only on the angle θ between $\underline{\hat{k}}$ and $\underline{\hat{P}}$.

If the polarization vector is taken to be along the x axis then $\underline{\hat{P}} \cdot \underline{\hat{r}} = x$ and the matrix element in (27) becomes

$$\langle \phi_n | x | \phi_\ell \rangle = \int \phi_n^* x \phi_\ell d^3 r . \quad (31)$$

For the H-like atom the final wavefunction has the form of a sum of a plane wave and an incoming spherical wave as in Eq. (30). Thus changing $\underline{\hat{k}}$ to $-\underline{\hat{k}}$ in (31) is equivalent to changing $\underline{\hat{r}}$ to $-\underline{\hat{r}}$ and reversing the direction of quantization of ϕ_n^* . We note that $x \rightarrow -x$ and the volume element $d^3 \underline{\hat{r}}$ stays the same so that $\langle \phi_n | x | \phi_\ell \rangle$ changes sign upon a change of sign of $\underline{\hat{k}}$. Now we know that $k \cos \theta = k_x$ so that changing the sign of $\underline{\hat{k}}$ changes the sign of $\cos \theta$. The differential cross section is proportional to the square of the matrix element and therefore is an even function of $\cos \theta$.

Next it is shown that the form of $d\bar{\sigma}/d\Omega$ is $a + b \cos^2\theta$. For the coordinates of vector $\underline{r}$ in equation (31) we take $\underline{k}$ to be the polar axis and use a spherical polar coordinate system r, θ', ϕ' (see Figure 1). Using the spherical harmonics addition theorem x in equation (31) can be written as

$$x = \underline{P} \cdot \underline{r} = r \cos\theta'' = r(\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos\phi') . \quad (32)$$

Thus the matrix elements in equation (31) depend on θ only through the terms $\cos\theta$ and $\sin\theta$ in (32). The cross section $d\bar{\sigma}/d\Omega$ is obtained by summing the absolute squares of the matrix elements over the m values. It was shown above that the coefficient of the term $\cos\theta \sin\theta$ must vanish so that

$$\frac{d\bar{\sigma}}{d\Omega} \propto A \cos^2\theta + B \sin^2\theta = a + b \cos^2\theta . \quad (33)$$

Tseng et al.,⁴ have given a similar argument to that presented above. In their notation, the atomic photoeffect matrix element M_{fi} is

$$M_{fi} = \left(\frac{2\pi\alpha}{k} \right)^{\frac{1}{2}} \int \psi_f^* \underline{p} \cdot \underline{\epsilon} \psi_i d^3r \quad (34)$$

where $\underline{p}$ is the momentum vector of the ejected electron, $\underline{\epsilon}$ is the polarization vector of the light and $\underline{k}$ (magnitude k) is the momentum of the incident photon, and α is the fine structure constant. Now $|M_{fi}|^2$ must be quadratic in $\underline{\epsilon}$ and since one sums over the magnetic substates of the initial orbital, the only other vector in $\sum |M_{fi}|^2$ is $\underline{p}$. Since $|\underline{\epsilon}|^2 = 1$, the only dependence of the scalar quantity $\sum |M_{fi}|^2$ on

the direction of $\underline{p}$ is of the form $A + B|\underline{p} \cdot \underline{\epsilon}|^2$. After averaging over photon polarization

$$|\underline{p} \cdot \underline{\epsilon}|^2 = \frac{1}{2} |\underline{k} \times \underline{p}|^2 \quad (35)$$

the differential cross section $\frac{d\sigma}{d\Omega}$ has the form $A + \frac{1}{2}B\sin^2\theta$ or

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 - \frac{1}{2}\beta P_2(\cos\theta)] , \quad (36)$$

where σ is the integral photoionization cross section, P_2 is the second order Legendre polynomial, and $\beta = 2B/(3A+B)$ is the asymmetry parameter which ranges from -1 to +2.

Cooper and Zare⁵ showed that for photoionization of atoms or molecules by linearly polarized light the angular distribution has the form

$$\frac{d\bar{\sigma}}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta)] , \quad (37)$$

where β is an asymmetry parameter and $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$.

For hydrogen-like atoms they derived the form of β to be

$$\beta = \frac{\ell(\ell-1)\sigma_{\ell-1}^2 + (\ell+1)(\ell+2)\sigma_{\ell+1}^2 - 6\ell(\ell+1)\sigma_{\ell+1}\sigma_{\ell-1}\cos(\delta_{\ell+1} - \delta_{\ell-1})}{(2\ell+1)[\ell\sigma_{\ell-1}^2 + (\ell+1)\sigma_{\ell+1}^2]} \quad (38)$$

where ℓ is the orbital angular momentum of the initial state, $\delta_{\ell+1}$ and $\delta_{\ell-1}$ are phase shifts, and $\sigma_{\ell-1}$ and $\sigma_{\ell+1}$ are radial dipole integrals for the $\ell - 1$ and $\ell + 1$ outgoing waves:

$$\sigma_{\ell\pm 1} = \int_0^{\infty} r R_{n\ell}(r) G_{k\ell\pm 1}(r) dr . \quad (39)$$

Here $R_{n\ell}(r)$ is the radial wavefunction of the initial state and $G_{k\ell\pm 1}(r)$ is the radial wavefunction divided by kr of the continuum state. In (38) it can be seen that a value of $\beta = 0$ gives an isotropic angular distribution, a value of $\beta = 2$ gives a $\cos^2\theta$ distribution peaked about the polarization vector of the light and a value of $\beta = -1$ gives a $\sin^2\theta$ distribution peaked in a plane at right angles to the polarization vector of the light. Ionization of an s electron leads to a cosine squared distribution ($\beta = 2$) while ionization of a non-s type of electron leads to two competing outgoing channels. Thus the value of β will depend on the interference between the $\ell-1$ and $\ell+1$ partial waves.

Tully, Berry, and Dalton⁶ have started with an expression similar to (27) for the photoelectron differential cross section $\frac{d\sigma}{d\Omega}$ and have shown that even for molecular systems it has the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta)] \quad (40)$$

for the ionization by polarized light, where θ is the angle between the momentum vector of the electron and the polarization vector of the light. This derivation assumes only that: 1) the molecules are randomly oriented in space; 2) the dipole approximation holds; 3) photoejection occurs on a time scale fast compared to molecular rotation. They have applied their formulae to calculation of β for H_2 ; this will be discussed in section 2.3.

Similarly, Buckingham, Orr, and Sichel⁷ have derived the above formula for photoionization of diatomic molecules. However, they also treated molecular rotation explicitly and found that angular distributions for rotationally resolved transitions are different than rotationally unresolved ones. They did not apply their formulae to specific molecular examples.

2.2 Description of Theoretical Calculations of β for Atoms and Molecules

This section briefly describes some of the recent techniques for calculation of the asymmetry parameter β for atoms and molecules. The results of the earlier pioneering work by Cooper and Zare,⁸ Kennedy and Manson,⁹ and Manson¹⁰ will not be described here.

Atoms

Kabachnik and Sazhina¹¹ have derived equations for β that apply in the case of autoionization resonances. They have considered the existence of either one or two autoionization channels. They have applied their equations to the calculation of β for neon and argon and shown that β varies very rapidly as a function of electron energy at excitation wavelengths corresponding to the energies of autoionization states.

Taylor¹² has used an R-matrix program package to calculate β for neon and argon for both direct and autoionization. He used both the dipole length and dipole velocity forms of the transition matrix

element and also performed the calculations using simple single configuration as well as multiconfiguration wavefunctions for the initial orbitals. Taylor has applied the formalism of Kabachnik and Sazhina¹¹ for the calculation in the region of autoionization resonances and found very rapid variation of β (with a slope of up to 400 eV^{-1}) in such a region. Experimental verification of this would be difficult due to the necessity of using a synchrotron radiation source.

Ong and Manson¹³ calculated β for photoionization of the 5s orbital of xenon using jj coupling with Dirac-Fock wavefunctions over the electron energy from threshold to 100 eV. Only one experimental β point is available for comparison, but agreement between it and the calculation is good.

Süzer et al.¹⁴ have calculated β for zinc, cadmium, and mercury atoms at several different photoelectron kinetic energies. The initial orbital was taken to be a one-electron, Hartree-Fock orbital. To determine the form of the one-electron continuum wave function, they assumed that the potential experienced by the photoelectron is the same before and after interaction with the photon. This is expected to be accurate only in a region near the nucleus; to insure that the potential has the proper long-range Coulombic form, a pure Coulomb potential is welded onto the potential described by the above method. The only experimental β values available for comparison are for mercury and the agreement is moderately good. This conceptually simple method should be applied to other atoms where β has been measured to determine the validity of the model.

Molecules

Huang and Ellison¹⁵ have employed the use of a plane wave orbital, orthogonalized to both occupied and unoccupied molecular orbitals, as the wavefunction of the photoelectron in their calculation of β for H_2 , N_2 , and CH_4 . The agreement with experiment is fair for H_2 as discussed later, and not at all good for N_2 and CH_4 . One serious problem with the plane wave formalism is that it does not account for the Coulombic attraction between the residual ion and the photoelectron.

Using a hydrogen-like continuum wavefunction for the ejected electron, Iwata and Nagakura¹⁶ have calculated β for neon, methane, water, argon, and hydrogen sulphide for kinetic energies up to 35 au. There are few experimental results for comparison, but agreement between Taylor's¹² calculation and theirs for neon and argon is not good. The behavior of the hydrogen-like continuum function approaches that of the plane wave for high photoelectron kinetic energies, giving a value of $\beta = 2$, which is unrealistic. The reliability of the calculation near threshold needs to be investigated further.

The angular distributions of photoelectrons for H_2 , N_2 , CO and O_2 have been calculated by Hirota¹⁷ using one-center Coulomb waves obtained by a pseudo-potential method. He used the length form of the transition dipole matrix element. The agreement with experimental values is best for H_2 , but is still not very good, as will be discussed later. The disagreement with experimental β 's for CO, N_2 , and O_2 may be due to inaccurate phase shifts or could be due to the occurrence of autoionization, which is not accounted for in the calculations.

The vibrational state dependence of the asymmetry parameter for H_2 , N_2 , and CO at $584 \text{ \AA}$ has been calculated by Kalman.¹⁸ The dependence of β on v' was incorporated into the theory by consideration of the dependence of the electronic transition matrix element on the internuclear distance R . Kalman found a moderate variation of β with vibrational state for $^1\Sigma \rightarrow ^2\Sigma$ transitions in CO and N_2 where the displacement of internuclear distance from the neutral to the ion is small. The agreement of the calculated β 's with the experimental ones for N_2 is not very good, possibly due to the presence of autoionization at this wavelength. The calculations could not be completed for CO due to lack of the required wavefunctions. The results for H_2 will be discussed in the next section.

Duzy and Berry¹⁹ have performed a similar calculation to that of Kalman¹⁸ for N_2 . They have used a Hartree-Fock wavefunction for the initial N_2 orbital, and have calculated a one-electron continuum wavefunction for the ejected photoelectron using a Coulombic monopole potential and an effective exchange monopole potential. The electronic transition matrix element was evaluated at different internuclear distances in an attempt to account for the vibrational state dependence of β . They did find a variation of β with v' for the $\text{N}_2^{+2}\Sigma_g^+$ state, but not the extent observed by Carlson and Jonas²⁰ and Mintz and Kuppermann.²¹ The reason may be the presence of autoionization.

Druger²² has considered the role of molecular symmetry in determining what angular distribution contributions with what symmetry-implied properties are allowed in various ionization models for molecules. He has applied the angular momentum transfer theory

of ionization to molecules and derived a series of tables that give the values of angular momentum transfer j_t which are forbidden by symmetry in ionization of various orbitals of the symmetry of different irreducible representations. Unfortunately, he does not apply his theory to specific examples of molecular photoelectron angular distributions and it is therefore difficult to see how this work enhances the understanding of the factors that affect β .

Finally, Chang²³ has recently discussed the influence of parity favoredness on the asymmetry parameter for photoionization of diatomic molecules. On this basis he can explain why the asymmetry parameter β is larger for $\Sigma^\pm \rightarrow \Sigma^\pm$ transitions than for $\Sigma \rightarrow \Pi$ transitions. In addition, he predicts that for $\Sigma^\pm \rightarrow \Sigma^\mp$ transitions, a value of $\beta = -1$ should be observed, independent of the photoelectrons kinetic energy. Experimental values of β have not been reported for any such transition.

2.3 Comparison of Theoretically and Experimentally Determined β Values for H_2

This section describes the results of experimental measurements of the asymmetry parameter β for H_2 and compares them to the theoretical results obtained previously. Experimental values are also given for D_2 .

The ground state of the hydrogen molecule has a very simple electronic configuration $1\sigma_g^2$, which of course corresponds to a bonding orbital. The photoelectron spectrum (Fig. 2) is therefore a long vibrational progression in a single electronic band corresponding

to the $^2\Sigma_g^+$ state of H_2^+ . This spectrum is similar to those reported previously.²⁴⁻²⁸ The asymmetry parameter has been measured for the vibrational levels $v' = 0$ through 6, by obtaining the spectra at nine different detector angles (from 45° to 120°) and fitting the intensities to the expression

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 - \frac{\beta}{2} P_2(\cos\theta) \right]. \quad (41)$$

The IP's and values of β are listed in Table 1, where they are compared to the β values obtained previously by Carlson and Jonas.²⁰ The agreement between values in Table 1 seem to be reasonably good for each vibrational level. The average of β for the seven vibrational levels is 1.76 which is in very good agreement with the average obtained from Carlson and Jonas,²⁰ values (1.72).

The high values of β obtained for this molecule can be attributed to the fact that the $1\sigma_g$ orbital is mostly composed of atomic 1s orbitals. Photoionization of a pure hydrogen 1s orbital leads to a value of $\beta = 2$, independent of the ejected photoelectron's energy.^{5, 8} The deviation of the β values for molecular hydrogen from 2 is due to admixture of some atomic p orbital character in the σ_g orbital since photoionization of an atomic p orbital has a value of β less than 2. The energy dependence of β will be discussed later.

The photoelectron spectrum of D_2 is shown in Figure 3. The ionization potentials and values of β for $v' = 0$ through 13 of the $^2\Sigma_g^+$ state of D_2^+ are listed in Table 2. No values of β for this molecule have been published previously. The vibrational frequency for the

ground state of D_2^+ is about 1450 cm^{-1} which is roughly $\frac{1}{\sqrt{2}}$ times that for H_2^+ , as expected. The value of β averaged over all 14 vibrational levels of D_2^+ is 1.75 which is essentially the same as that for H_2^+ (1.76). In the work of several theoretical^{6, 8, 18} calculations, β does not explicitly depend on the isotopic mass. Therefore, in the absence of any electron energy dependence of β the value of β should be the same for D_2 as H_2 . Figure 4 shows the values of β for H_2 and D_2 as a function of IP. The scatter of the data makes it difficult to ascertain if there is any energy dependence of β for these molecules; one is tempted to draw a straight horizontal line through the data at a value of $\beta = 1.75$.

The simple electronic structure of H_2 would seem to allow an accurate calculation of β for it. Indeed this is the case, as can be seen from Table 3 where the experimental H_2 β 's are compared to the ones calculated by several theoreticians. The next few paragraphs briefly describe the techniques used to calculate β for this molecule and some possible reasons that some of the results differ from the experimental values.

Dill²⁹ has used the angular momentum transfer theory of angular correlations to calculate β for H_2 at threshold with the restriction that the neutral and ion are both vibrationally unexcited ($v'' = v' = 0$) and ejection of the electron occurs only into p waves ($\ell = 1$). His value of $\beta = 1.71 \pm 0.05$ is in very good agreement with the experimental values, indicated that the contribution of f waves to β is negligible.

Shaw and Berry³⁰ have reported calculations of β for H_2 using the correlated pseudopotential method. The value obtained (1.65) is slightly lower than the experimental ones for unknown reasons.

Tully, Berry, and Dalton⁶ have calculated β using the dipole velocity form of the photoejection transition matrix element with a Weinbaum function as the initial orbital of H_2 . They have taken the final state to be an electron moving in the field of 2 point charges of half elementary charge each. They have neglected the contribution of f electron waves, and calculated a value of $\beta = 1.76$, in excellent agreement with experiment.

Huang and Ellison¹⁵ have used the dipole velocity form of the transition element along with a minimal basis ($1s_A, 1s_B$) initial H_2 orbital and a plane wave which is orthogonalized to both occupied and unoccupied molecular orbitals. The resulting β is 1.87 which is higher than the experimental value. This could be due to an inadequate initial orbital or to the plane wave representation of the final state, which is not sufficiently flexible in the region near the ion.

Hirota¹⁷ has employed an initial H_2 orbital which is a linear combination of Slater-type orbitals. The photoelectron orbital $\psi_{q\ell m}$ $\psi_{q\ell m} = F_\ell(kr) \cos \mu_{\ell m} + G_\ell(kr) \sin \mu_{\ell m}$ is obtained by the pseudopotential method where F_ℓ and G_ℓ are the regular and irregular Coulomb functions and $\mu_{\ell m}$ is the phase shift of the ℓm partial wave due to the deformation of the Coulomb field. Estimating the values of β from Fig. 1 of his paper gives a value of $\beta = 1.94$ for the calculation using a simple initial orbital and $\beta = 1.88$ using an initial orbital in

which some configuration interaction is included. The deviation of these values from the experimental ones may be due to inaccurate estimate of the phase shift $\mu_{\ell m}$.

Kalman¹⁸ has calculated the asymmetry parameter β for vibrational levels $v' = 0$ to 3 of H_2 . The slight dependence of β on v' is due to the variation of the electronic transition matrix element with internuclear distance. He used the matrix elements from Itikawa's³¹ computation in which the initial H_2 orbital is the Weinbaum function and the photoelectron wavefunction is expanded in terms of a prolate spheroidal angular function. The agreement with experiment is good although the error bars in the experimental data are not small enough to be able to reproduce the slight variation of β with v' .

Finally, Itikawa³² has taken into account the effect of vibrational and rotational motion on the β parameter for H_2 . He used a Weinbaum function for the initial orbital, and has expanded the photoelectron orbital in terms of a two-center prolate spheroidal angular function. He also restricted the calculation to considering only one partial wave ($\ell = 1$). The values of β show a noticeable dependence on the final vibrational level, which cannot be accounted for by the Franck-Condon factor approximation. (It should be mentioned that experimental relative vibrational band intensities in the photoelectron spectrum do not agree with those calculated using the Franck-Condon factor approximation).²⁷ The variation of β from 1.675 for $v' = 0$ to 1.863 for $v' \leq 6$ is about the same as the variation in the experimental values (1.69 to 1.86) but the experimental values do not show the same monotonic increase with v' . The variation in experimental values is more

likely due to data scatter. Measurements repeated several times would probably clarify this point. It is unlikely that accurate values of β could be measured for vibrational levels beyond $v' = 10$ due to the extremely low intensity of the bands which correspond to these levels.

In summary, the agreement between the experimental values of β is seen to be good. The agreement between theory and experiment is also fairly good, the largest discrepancy occurring for the results of Hirota,¹⁷ Huang and Ellison,¹⁵ and Shaw and Berry.³⁰ Hirota's¹⁷ calculation may be in error due to inaccurate phase shifts, the calculation by Huang and Ellison¹⁵ is in error due to inaccurate initial and final orbitals. The results of Shaw and Berry³⁰ are slightly lower than experiments for unknown reasons. In general it appears that it is not necessary to include f waves in the calculations in order to get reasonable agreement with experiment for H_2 . It also seems that when the Franck-Condon factor approximation is not used and the dependence of the transition moment on internuclear distance is taken into account, β increases slowly and monotonically with vibrational level of the ion, but to an extent that cannot presently be detected experimentally.

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Table 1. β values and ionization potentials for H_2 at 584 Å

$^2\Sigma_g^+$	IP(eV)	β	
		Present Work	Carlson & Jonas [20] ^a
$v = 0$	15.42	1.69 ± 0.05	1.80 ± 0.07
1	15.69	1.77 ± 0.04	1.70 ± 0.09
2	15.95	1.75 ± 0.04	1.75 ± 0.05
3	16.18	1.80 ± 0.04	1.68 ± 0.09
4	16.41	1.69 ± 0.06	1.73 ± 0.08
5	16.62	1.87 ± 0.03	1.75 ± 0.09
6	16.81	1.76 ± 0.04	1.65 ± 0.13

^aThe only value of β explicitly given in Ref. [20] is that for $v' = 2$. However, the authors also give values of the ratio of relative intensities at 20° and 90° ($I(20)/I(90)$) for vibrational levels $v' = 0$ through 6 to that of level $v' = 2$. The values given in this column have been computed from this data.

Table 2. β values and ionization potentials for D_2 at 584 Å

$^2\Sigma_g^+$	IP(eV)	β
$v' = 0$	15.45	1.74 ± 0.04
1	15.65	1.73 ± 0.03
2	15.84	1.71 ± 0.03
3	16.02	1.76 ± 0.05
4	16.19	1.82 ± 0.04
5	16.36	1.75 ± 0.04
6	16.53	1.79 ± 0.05
7	16.68	1.71 ± 0.03
8	16.82	1.64 ± 0.06
9	16.96	1.82 ± 0.05
10	17.10	1.70 ± 0.03
11	17.22	1.75 ± 0.07
12	17.34	1.74 ± 0.05
13	17.45	1.87 ± 0.08

Table 3. Comparison of theoretically and experimentally determined β values for H_2 at 584 Å

$2\Sigma^+_g$	v'	β									
		Theoretical						Experimental			
		Ref. 32	Ref. 18	Ref. 30	Ref. 6	Ref. 15	Ref. 18 ^a	Ref. 29	Present Work	Ref. 20 ^b	
	0	1.675	1.70	1.65	1.76	1.87	1.94, 1.88	1.71 ± 0.05	1.69 ± 0.05	1.80 ± 0.07	
	1	1.726	1.71						1.77 ± 0.04	1.70 ± 0.09	
	2	1.766	1.73						1.75 ± 0.04	1.75 ± 0.05	
	3	1.798	1.74						1.80 ± 0.04	1.68 ± 0.09	
	4	1.824							1.69 ± 0.06	1.73 ± 0.08	
	5	1.847							1.87 ± 0.03	1.75 ± 0.09	
	6	1.863							1.76 ± 0.04	1.65 ± 0.13	
	7	1.878									
	8	1.891									
	9	1.902									
	10	1.911									
	11	1.919									
	12	1.925									
	13	1.931									
	14	1.935									
	15	1.938									
	16	1.942									
	17	1.943									
	18	1.944									

^aValues estimated from Fig. 1 of Ref. [17], see text.^bDetermined in the same way as in Table 1.

FIGURE CAPTIONS

Fig. 1. Coordinate system pertaining to Eq. (32), section 2.1.

$\underline{\hat{P}}$ is the polarization vector of the light, $\underline{\hat{r}}$ is the position vector of the electron, and $\underline{\hat{k}}$ is the direction of the ejected electron.

Fig. 2. Photoelectron spectrum of H_2 obtained at a detector angle of 54.7° using 511 adjacent 8 meV wide channels and 50 scans. Total dwell time was 50 s.

Fig. 3. Photoelectron spectrum of D_2 obtained at a detector angle of 54.7° using 511 adjacent 8 meV wide channels and 50 scans. Total dwell time was 50 s.

Fig. 4. Plot of β versus IP for H_2 (solid dots $\bullet$) and D_2 (open diamonds $\diamond$).

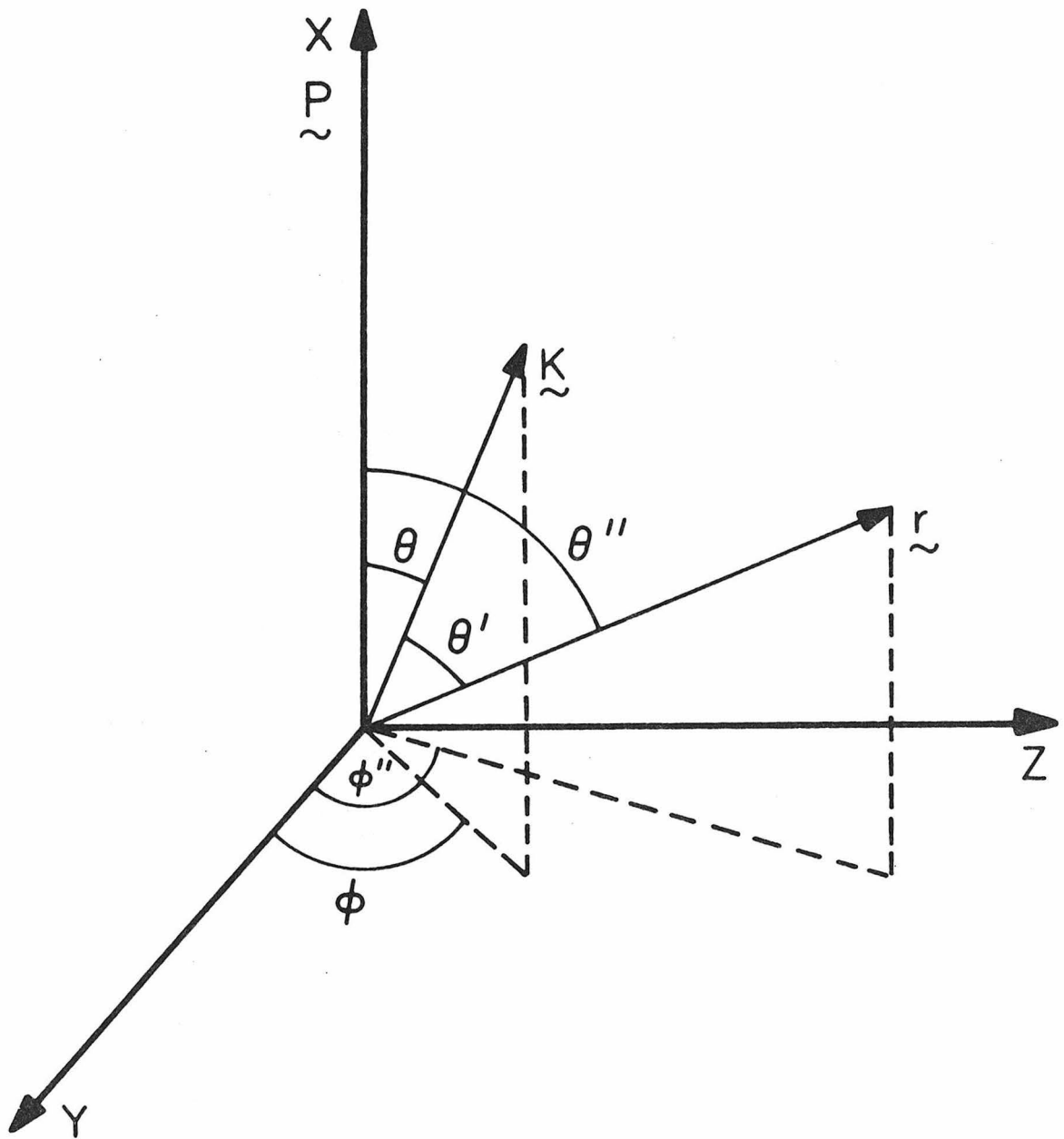


Figure 1

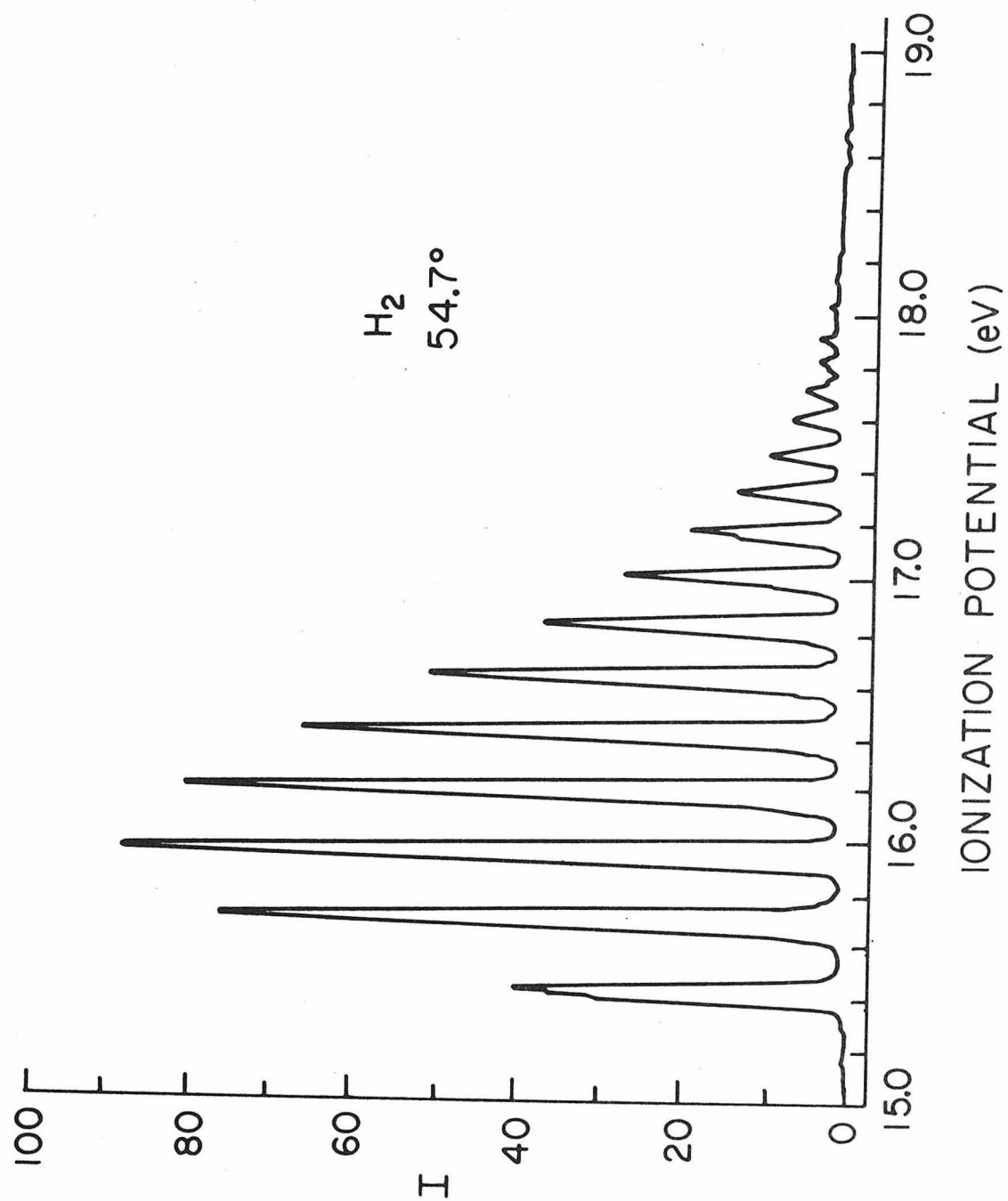


Figure 2.

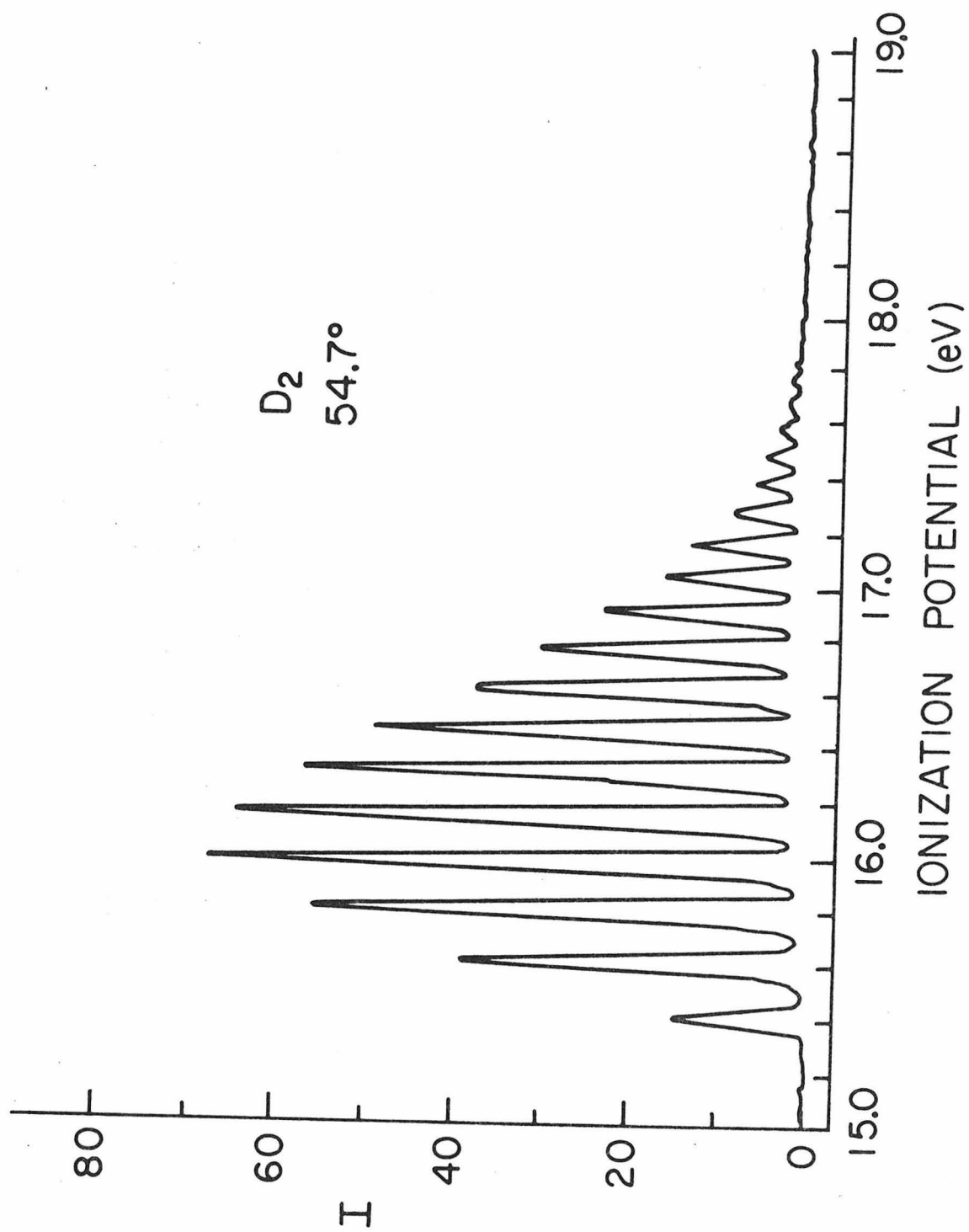


Figure 3.

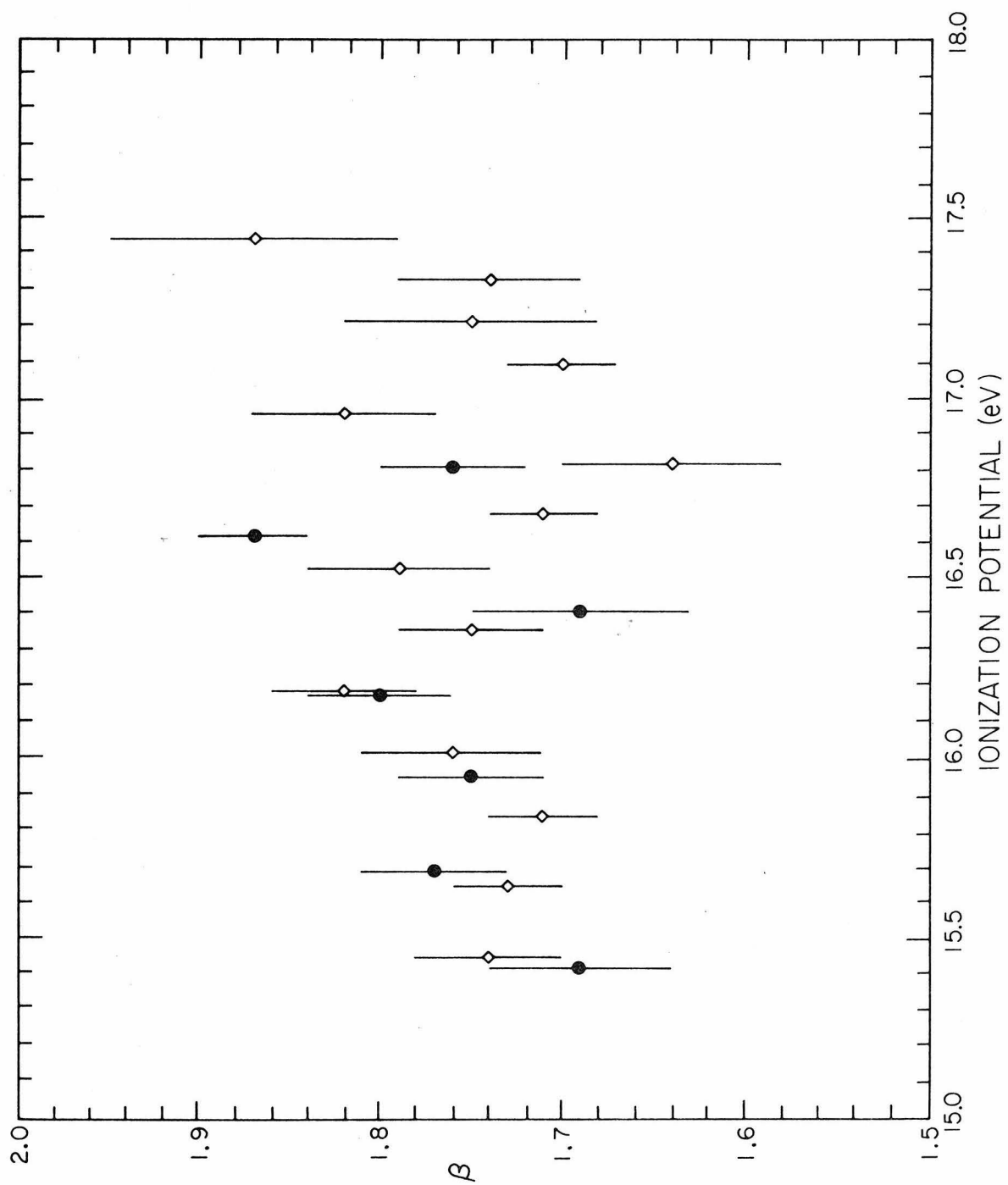


Figure 4.

CHAPTER 3

EXPERIMENTAL

In this section the operating principles and capabilities of the multiple angle photoelectron spectrometer (MAPS) are discussed. The apparatus was mostly designed and built by D. Mason and D. Mintz, and their theses^{1, 2} as well as Ref. 3 contain more detail than the present discussion. Any modifications that have been made by the present author have been incorporated into the following discussion.

A block diagram of the spectrometer is shown in Figure (1). Ultra-high purity helium (UHP) flows into discharge lamp which is located on the inside of the main vacuum chamber. The beam of light (mostly 584 Å) is collimated and passes into the scattering chamber which contains sample gas at a pressure of 1 to 3 mTorr. The photoelectrons produced exit through a slot in the scattering chamber and are collimated and decelerated by electrostatic lenses before entering the electron energy analyzer. The electrons are energy selected in the 180° hemispherical electrostatic energy analyzer. Photoelectrons are then recollimated and accelerated into the cone of an electron multiplier (Spiraltron). The Spiraltron sends out a low voltage pulse for each electron detected, and this signal is shaped and amplified by a preamp (not shown) on the outside of the instrument. The pulses are directed to a PDP 8/e computer which acts as a sophisticated multichannel scaler. The photoelectron spectrum is normally displayed on an oscilloscope or plotted by an X-Y recorder. The electrostatic lenses, energy analyzer, and electron multiplier can be rotated about the

center of the scattering chamber through an angle $\theta = 45$ to 120° with respect to the photon beam. In addition, the main vacuum chamber is lined with μ metal and located at the center of three pairs of Helmholtz coils which reduce the ambient magnetic field to about 0.3 m Gauss. Each major component of the instrument will be described in some detail in the next section.

3.1 Vacuum System

The internal parts of the spectrometer are attached to an 18 inch flange which can be mounted on a cart and rolled away from the main chamber. The flange and internal parts are shown in Figure (2). The main diffusion pump is a Varian-NRC 6 inch oil diffusion pump which is hung from the bottom of the vacuum chamber. The liquid nitrogen trap is a Granville-Phillips Model 278 which has a holding time of about 12 hours. Another oil diffusion pump acts as a booster pump on the outlet side of the main diffusion pump. Finally a 6.1 ℓ /sec mechanical pump backs the booster pump. After a day of pumping, a pressure of 2×10^{-7} torr in the main chamber can be achieved with no sample gas in the chamber or helium flowing through the discharge lamp. With the instrument actually taking spectra, the pressure in the main chamber is typically 5×10^{-6} torr. Pressure in the main chamber is monitored with a General Electric ionization gauge and a Varian RG-830 controller.

3.2 Lamp

Helium (99.999% pure) flows through a zeolite trap at 77°K before entering the discharge lamp through the main flange. A scaled section

view of the lamp is given in Figure (3). The discharge occurs through a quartz capillary tube between the anode which is maintained at about +555 volts and the cathode (at ground potential). The region between the discharge and the main vacuum chamber is pumped differentially by two mechanical pumps. The purpose of this is to reduce helium flow into the main chamber and cut down the self absorption of HeI radiation ($584 \text{ \AA}$) by helium atoms in their ground state. Lamp power is supplied by a DC power supply through a current limiting 150 W ballast resistor. A typical operating current is 150 ma at a helium pressure of about 15 torr. Photon flux (estimated to be 1.8×10^{11} photons/sec) is monitored at the rear of the scattering chamber by a tungsten photocathode.

It is difficult to keep the helium discharge continuously running for long periods of time. When the lamp is operating properly, the discharge should stay on for about 3 weeks. It seems that the discharge is very sensitive to surface conditions of the tungsten cathode. Sputtering of the cathode causes these undesirable surface conditions, which can best be removed by disassembling the lamp and sandblasting the cathode. It is possible that the cathode would be less susceptible to sputtering if it were made of some other material. However, both tungsten carbide and molybdenum have been tried in addition to the tungsten; of these three tungsten is the best material.

3.3 Scattering Chamber and Inlet System

The scattering chamber consists of three coaxial shells which are made of goldplated copper. The inner and outer shells are

connected to the energy analyzer and rotate along with it while the middle shell is fixed. Sample gas enters the chamber through a $\frac{1}{2}$ inch hole in the base. Sample pressure can be measured by both a Schulz Phelps ionization gauge⁴ and a Baratron capacitance manometer.⁵ It was found that organic halides damaged the ionization gauge filament so the Baratron was acquired since its stainless steel diaphragm is unharmed by these compounds. Also, it measures true pressure, independent of the nature of the gas.

Due to the design of the sample chamber, the sample pressure in the chamber is a function of the angle at which the detector is located. Since counting rates depend on the pressure of the gas as well as detector angle, it is necessary to divide counting rates by the sample pressure. This means that the sample pressure has to be measured frequently and angular distributions have to be obtained in a pressure region where intensity is a linear function of sample pressure. Usually this is in the range of 1 to 3 mTorr, as verified for each sample by studying intensity as a function of sample pressure.

The MAPS inlet system consists of a glass manifold line on the outside of the instrument. For gas samples, the inlet system is normally evacuated to 10 mTorr before loading gases in to a pressure of about an atmosphere. Gases are stored in a ballast flask whose capacity is 5 liters and leaked into the instrument through a Granville Phillips variable leak valve. When samples are liquids, the vapor from the bulb containing the liquid is admitted to MAPS and the leak valve is heated to reduce condensation inside the valve.

The inlet system is thoroughly cleaned and baked in a glass blower's annealing oven between each sample to avoid cross contamination of the samples.

3.4 Energy Analyzer and Detector

The electron energy analyzer and detector system consists of two lens assemblies, a hemispherical analyzer, and a Spiraltron electron multiplier. The whole detection system is mounted on a 20 cm diameter gear and is rotated in a vertical plane about the center of the scattering chamber. Due to mechanical constraints the analyzer can only be rotated through the angles 38° to 128° with respect to the photon beam. The lens elements and energy analyzer are made of OFHC copper and are goldplated and coated with Aero-Dag, a graphite coating applied by a spray can.

Photoelectrons emerging from the scattering chamber with an energy T are decelerated by the first lens system to a kinetic energy V , which is usually 1.5 eV. The voltage $T-V$ is called the sphere center voltage and it is this voltage to which most of the lens voltages are referenced. The analyzer is operated in a mode such that photoelectrons with voltage 1.5 eV are passed through and all others are not. By operating the analyzer with a constant transmission energy the resolution of the analyzer (typically 40 meV) is constant throughout the energy spectrum. Photoelectrons are then reaccelerated to 6.5 eV by the second lens system and pass into the front cone of the Spiraltron which is kept at +75 volts potential. The electron multiplier provides an electron gain of about 10^8 . Charge pulses at the copper plate at the end of the Spiraltron are converted into voltage pulses by an RC

differentiating network. The pulses are then amplified and discriminated by a preamp located outside the main vacuum chamber. Counting rates for the $\text{Ar } ^2\text{P}_{\frac{3}{2}}$ peak at about 1 mTorr pressure are about 700 counts/second.

3.5 Computer and Other Hardware

The heart of the whole experiment is a 12 bit digital PDP 8/e computer with 12K of memory. The peripheral devices that are used are a 300 character/sec high speed paper tape reader and a high speed paper tape punch. Other features are a 120 Hz real time clock and three channels of a digital to analog conversion (DAC). One DAC channel operates the energy scanning of the instrument and the other two channels are used for oscilloscope display and XY plotting of spectra.

There are three interfaces from the experiment to the computer. One interface consists of a 12 bit counter and six digit digital display. This counter is operated in a mode where a number of counts are accumulated in a fixed time interval. The second interface consists of a 4 bit sense register and a 12 bit drive register. The sense register monitors status logic levels of four lines connected to critical devices in the experiment. For example, if the vacuum system fails, then the change in the status switch causes a computer interrupt and initiates a computer interrupt service program. The drive registers allow the computer to apply a voltage to various drive lines that perform the following tasks: turn the teletype motor on, apply voltage to the motor that changes detector angle, turn on the audio alarm, and others. The third interface consists of an analog to digital converter (ADC). The

computer controls a multiplexer which (through the ADC) is able to read many analog voltages in the experiment such as the voltages that are proportional to the sample pressure, lens and sphere voltages, and lamp flux. These voltages are read often during an angular distribution and are printed out by the teletype.

Other experimental hardware includes three pairs of square Helmholtz coils about 10 feet on each side. These coils are powered by three DC power supplies which draw their power from an uninterruptible power supply (UPS). Also, the inside of the vacuum chamber is lined with a single layer of mu metal shielding. Together, these two devices reduce the magnetic field to about 0.3 mGauss inside the instrument. This is a very critical part of the experiment since the detector moves with respect to the magnetic field of the earth.

3.6 Software and Methods of Data Acquisition

The PDP 8/e computer memory is divided into three 4 K segments. The first 4 K contains a monitor program which provides access to the real time clock, floating point arithmetic, and input output devices. The second 4 K contains the actual data acquisition program, and the third 4 K contains the data reduction program. The computer is operated in a time sharing mode; pseudoinstructions in the second and third 4 K interrupt the computer and cause it to be trapped in the first 4 K where the instructions are processed.

When a photoelectron spectrum is being taken, a counter interface accumulates counts for a fixed time with the lens and sphere voltages at a fixed value. The total count at the end of this time is

loaded into a memory location. The computer then increments a counter and outputs it to the DAC which drives the voltages of the lenses and sphere. The counts accumulated with the analyzer set at this voltage are loaded into the next sequential memory location. In this manner each location in the data buffer corresponds to a voltage interval and contains the counts accumulated while the analyzer was set to that voltage. It is possible to use from 1 to 511 channels in memory; each channel can contain over 8 million counts. The computer scans through a user determined voltage interval and then stops data taking to read the sample pressure. It then returns to the start and begins the process again. The operator determines how many times the spectrum is scanned over. After the last scan, the computer calculates an average pressure during the run and records it on the teletype. This approximately corrects for pressure variation during the data accumulation.

The data are partially reduced while the computer is on-line. A smoothing routine by Savitzky and Golay⁶ is used to smooth spectra and a derivative algorithm to locate the peak maxima. The counting rates and ionization potentials of peaks are printed on the teletype along with other spectrum parameters.

Full photoelectron spectra are usually obtained with the detector set at 54.7° with respect to the photon beam. At this angle $P_2(\cos\theta) = 0$ and the measurement of the ratio of two peak intensities should be equal to the ratio of their integral photoionization cross sections, in the absence of discrimination by the kinetic energy analyzer. Stated another way, the ratio of the differential cross sections for two

transitions is equal to the ratio of their integral photoionization cross sections, independent of their respective β 's.

In taking angular distribution measurements, spectra are obtained at 9 detector angles in the range 45° to 120° . The procedure is automated by commanding the computer to read its instruction off of a paper tape. This automation is necessary since an angular distribution can last up to 12 hours.

For molecules that have well resolved vibrational structure, angular distributions are taken for each vibrational peak in the spectrum. This is done by scanning the energy analyzer over a narrow energy range (typically 0.060 eV) at each of the nine angles. Beta values are then calculated only at the peak maxima. For molecules with a more continuous spectrum, β values are determined every few meV.

There is a background signal of 0 to 3 counts/second which rises at low kinetic energy but is approximately independent of sample pressure. Since some organic molecules often have counting rates this low, it is necessary to subtract the background from the measured photoelectron intensities before calculating β . To parameterize this background the sample gas is pumped from the instrument and spectra of background alone are obtained at 9 angles from 45° to 120° . Each spectrum is plotted on graph paper and three line segments are drawn through each spectrum in order to parameterize it. The slopes and intercepts of the three lines of each spectrum are then computed and this data is input to the β calculating program. Background is found

to be fairly constant over a period of time; it is usually necessary to parameterize only about once a week.

It is also necessary to correct intensity for the volume of intersection of the photon beam and the detector acceptance cone. At small detector angles the detector samples a larger volume where molecules are being ionized than at large angles. Due to the geometry involved, this effect can be accurately accounted for by multiplying the intensity at angle θ by $\sin \theta$.

The data taking program does not actually calculate β values. After the angular distribution is taken another program is used to calculate β for a band. The data input to this program is by either the teletype or by paper tapes is:

1. the angles at which the distribution was taken,
2. the intensity of the peak at each angle,
3. the average sample pressure at each angle, and
4. the parameters of lines drawn through background spectra at each angle.

The program then subtracts the background counts from the intensity of the peak, and corrects for the volume of the view cone and the sample pressure at each angle. Then it does a linear weighted least squares fit to the expression $I(\theta) = A + B \sin^2 \theta$. Values of A and B are found by linear regression analysis along with the variances σ_A^2 and σ_B^2 . The value of β in equation (41) can be related to A and B by the expression

$$\beta = \frac{4B}{2A + 3B} .$$

Finally the variance, σ_{β}^2 , of β is found by propagating the variances σ_A^2 and σ_B^2 . The data are input to this program by the teletype for spectra with sharp peaks and by the high speed paper tape reader for spectra with more continuous bands. Another program is used to plot spectra and β versus IP on an XY recorder.

3.7 Magnetic Fields

As mentioned earlier, it is essential to keep the stray magnetic fields below about 0.3 mGauss in the central region of the main vacuum chamber in order to accurately determine β values. One method of checking this without opening the apparatus is to plot the pressure and ionization volume corrected intensities for a transition as a function of θ . The intensities should be symmetric about the 90° point. Also if β is measured for the transition corresponding to the formation of the argon ion $^2P_{\frac{3}{2}}$ state, it should be close to 0.88 ± 0.02 , which is the value reported previously.³

It has been found that there are many sources of stray magnetic fields besides the field of the earth. For example, it was discovered that some of the pressurized 160 l liquid nitrogen Dewars are magnetized to an extent that they produce fluctuations of several tenths of a mGauss inside the apparatus when the Dewars are brought within about 8 feet of it. This is an intolerably high field; the simplest remedy is to keep the Dewars spatially well separated from the apparatus. Also it was found that the NMR magnets located in the basement of the building can produce a change of about 0.6 mGauss inside MAPS when they are turned off. Apparently, the voltages

applied to the Helmholtz coils were originally set to null out the stray magnetic fields which included fields produced by these magnets. Thus when the magnet is turned off, the Helmholtz coil overcorrects for the stray field and this produces a resultant field of about 0.6 mGauss. This can be removed by adjusting the voltages applied to the Helmholtz coils. Finally, it was found that internal parts in the photoelectron spectrometer could become magnetized and give unreliable values of β . For example, it was found that the stainless steel worm gear and differential pumping lines became magnetized to the extent that they affected the β values by about 0.1 unit. The solution of this problem was to replace them by materials that cannot become magnetized.

It should be noted that as long as the apparatus has a movable detector, the problem of stray magnetic fields will probably occasionally reappear. However, if proper diagnostic techniques are used, the source of the perturbation should be apparent. At this point, the question becomes one of removal of the perturbation or of shielding the apparatus from it.

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FIGURE CAPTIONS

Fig. 1. Block diagram of the variable angle photoelectron spectrometer. He, cylinder of UHP helium. ZT, liquid nitrogen immersed zeolite trap for lamp helium supply. RB, lamp ballast resistor, $1320\ \Omega$. LPS, lamp power supply, 555 V, 300 mA maximum. SC, sample chamber. PC, photocathode for light flux measurement. CL, electron lens elements before hemispherical analyzer. ANALYZER, 180° hemispherical electrostatic electron energy analyzer. ML, electron lens elements between hemisphere and detector. S, Spiraltron electron multiplier. CPS, power supply to Spiraltron cathode. APS, power supply to Spiraltron anode. R, C, differentiating network for Spiraltron pulses: $R = 1\text{M}\Omega$, $C = 500\ \text{pF}$. PDP 8/e, Digital Equipment Corporation PDP 8/e minicomputer. INTER, counting system interface to experiment. OUTPUT, computer output devices to user.

Fig. 2. Side view of apparatus when main flange is separated from vacuum chamber (not drawn to scale).

Fig. 3. Section view of lamp. Hatched and stipled parts, except for the stainless steel lamp anode, A, are of aluminum and constitute the lamp body. K, tungsten cathode. C, quartz discharge capillary, HV, high voltage power lead. S, starter electrode. He, helium inlet. OA, lamp flux outlet capillary. DP, differential pumping connections. WAT, water cooling inlet (outlet not shown). M, Mica spacer. CE, water cooling envelope inside lamp body. Flows of helium and kerosene are indicated by horizontal arrows.

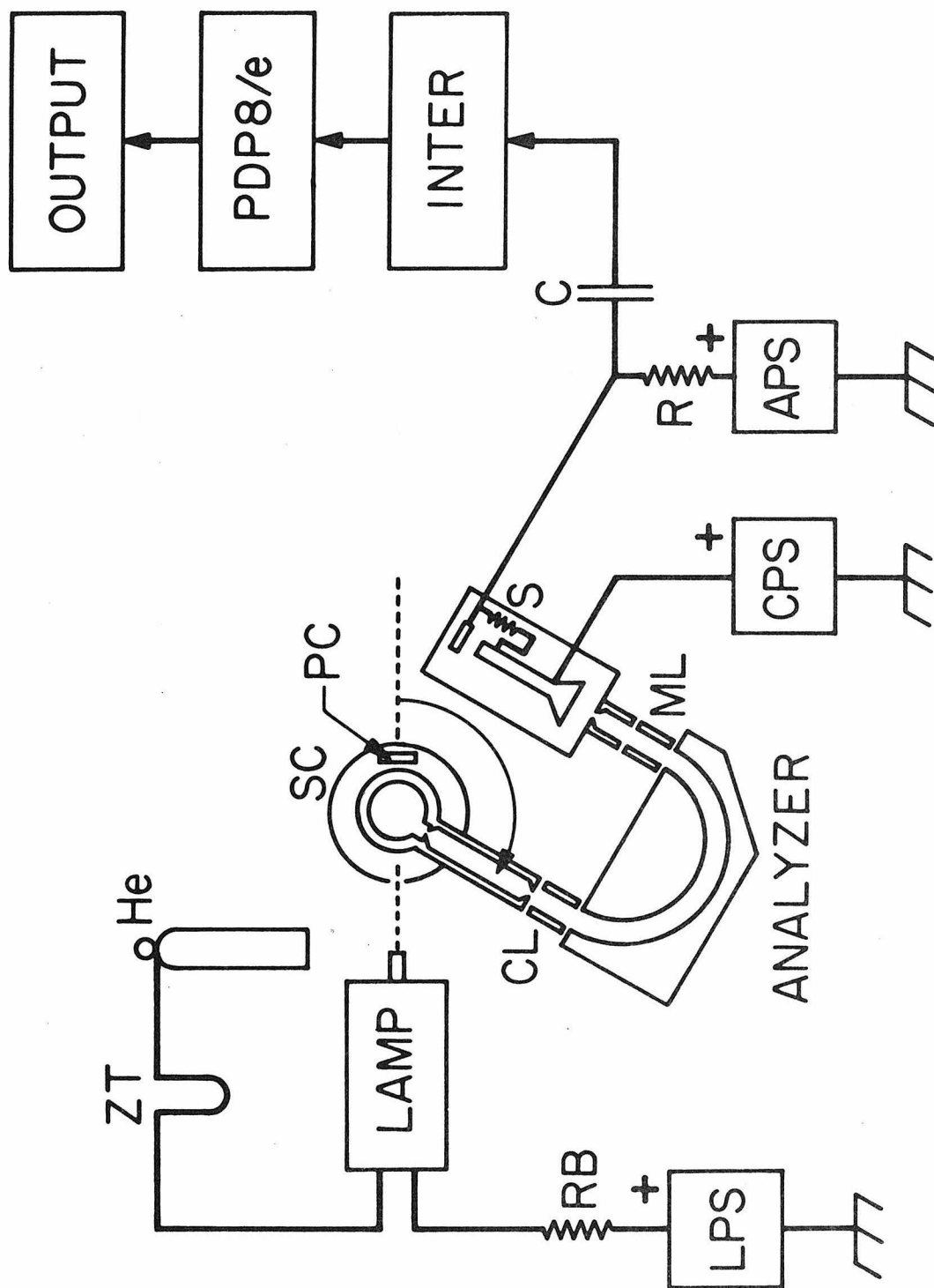


Figure 1.

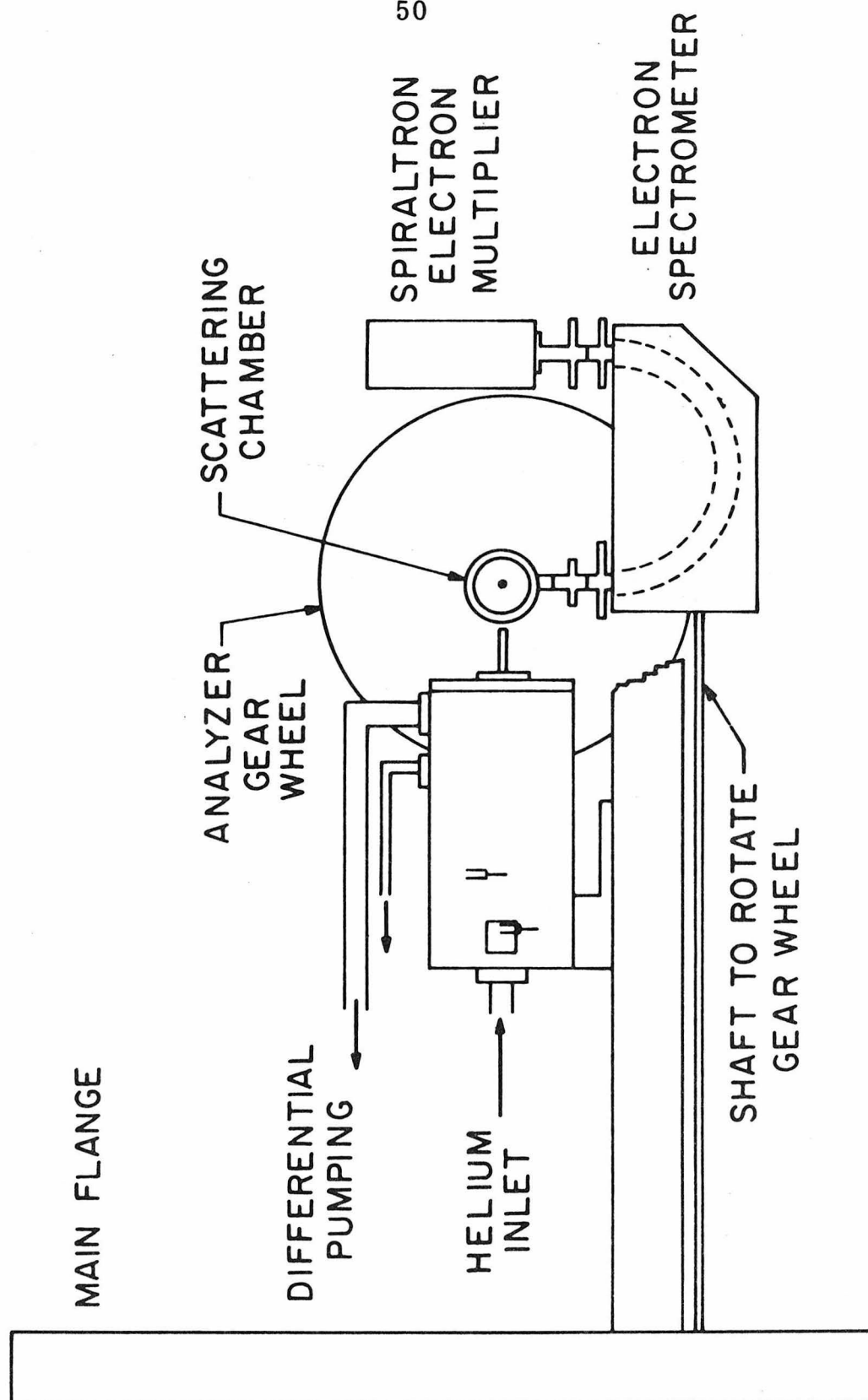


Figure 2.

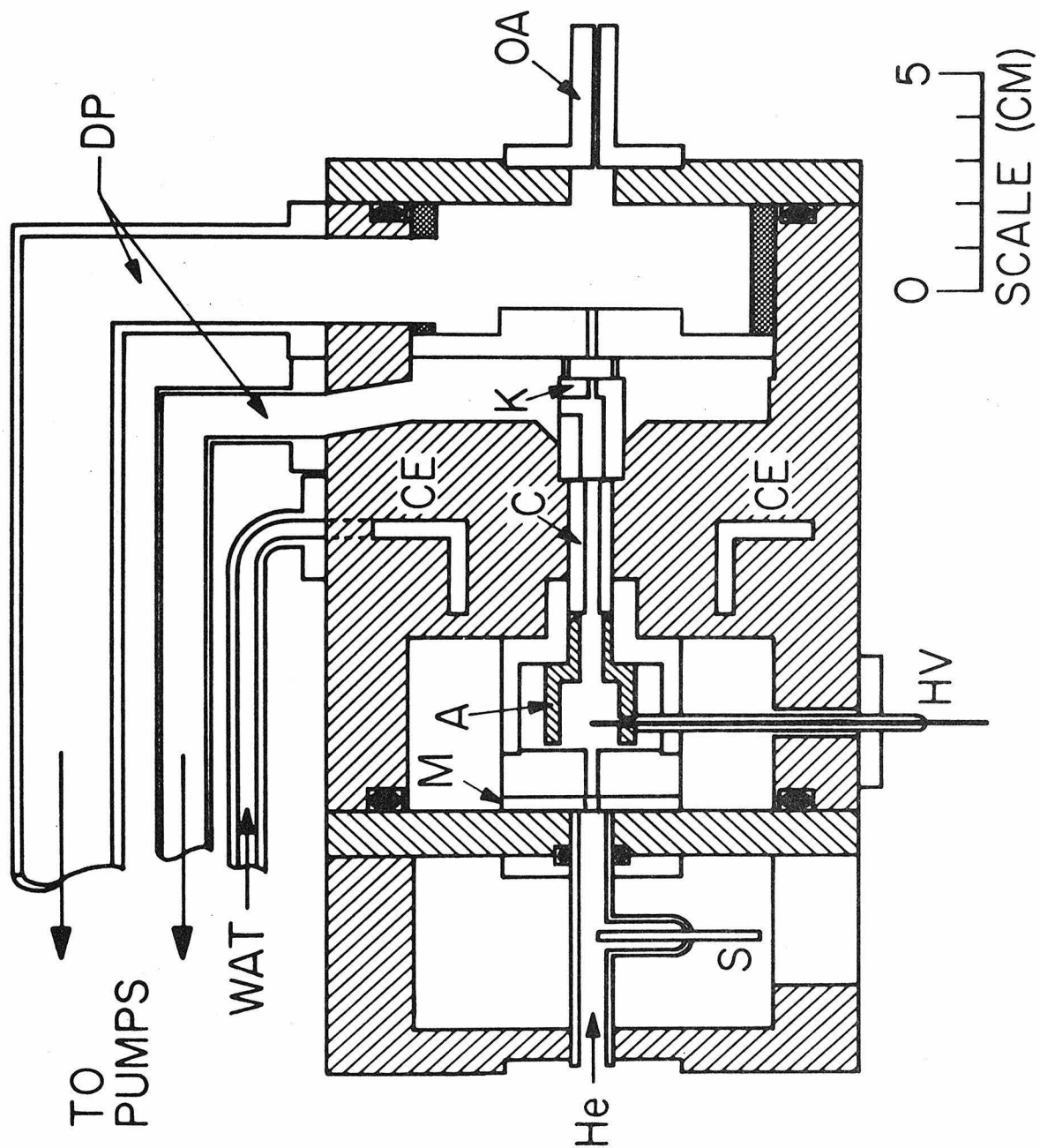


Figure 3.

CHAPTER 4: RESULTS AND DISCUSSION

Paper 1: Angular Distributions in the Photoelectron Spectroscopy of Carbon Monoxide

ANGULAR DISTRIBUTIONS IN THE PHOTOELECTRON
SPECTROSCOPY OF CARBON MONOXIDE*

JEFFREY A. SELL,[†] ARON KUPPERMANN, and DONALD M. MINTZ[‡]

Arthur Amos Noyes Laboratory of Chemical Physics,[§]
California Institute of Technology, Pasadena, California 91125

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ABSTRACT

The angular distributions of the photoelectron intensity for CO have been investigated using a photoelectron spectrometer that has a rotatable detector and a HeI light source. The asymmetry parameter β was carefully measured for 24 vibrational transitions spanning three ionization bands. Its variation with final state vibrational quantum number was found to have an unusual behavior. It is concluded that an autoionizing state of CO should exist at 584 Å in order to account for this behavior, and that the value of β is very sensitive to the presence of such a state.

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[†]Work performed in partial fulfillment of the requirements for the Ph.D. in Chemistry at the California Institute of Technology.

[‡]Present address: TRW Defense and Space Systems Group, Redondo Beach, CA 90278.

[§] Contribution No. 5747.

I. INTRODUCTION

Angular distributions of photoelectron intensity of small molecules are important for the understanding of the interaction of ultraviolet radiation with molecules. They are very helpful in probing the physics of the ionization process itself if there are different ionization pathways available.¹ Angular distributions of photoelectrons are especially important for chemistry because they can help distinguish between ionization from σ or π types of molecular orbitals.²⁻⁸ Finally, angular distributions are needed to correct relative peak intensities in fixed-angle photoelectron spectra (taken at scattering angles other than 54.7°) before making the approximation that peak intensity is proportional to the degeneracy of the molecular orbital from which an electron was removed.

We have recently been involved in the measurement of the angular distribution of photoelectron intensity of small molecules in this laboratory. This study was prompted by the theoretical work of Cooper and Zare⁹ and the experimental angular distributions of photodetached electrons from atoms of Hall and Siegel.¹⁰ Briefly, the differential cross section (DCS) $d\sigma/d\Omega$, for a given transition and given incident wavelength using unpolarized light has the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left\{ 1 - \frac{\beta}{2} [P_2(\cos \theta)] \right\}, \quad (1)$$

where θ is the direction between the incident light beam and the photoelectron, $P_2(\cos \theta)$ is the second Legendre polynomial, σ is the integral ionization cross section, $d\Omega$ is an element of solid angle around the photoelectron direction, and β is an asymmetry parameter that ranges

from -1 to +2.⁹ In the case of atoms, it was found^{9,10} that the asymmetry parameter depended on the photoelectron energy and also on the angular momentum of the orbital from which the electron was ejected. For molecules it was hoped that there would be a corresponding difference in the asymmetry parameter for ionization out of π orbitals compared with σ orbitals. Carlson and co-workers³⁻⁸ have studied many molecules and found that for unsaturated^{7,8} ones the asymmetry parameter β for ionization out of π orbitals is generally higher by + 0.2 to 1.0 units higher than for σ orbitals. Early results^{2,11} from this laboratory confirm this analysis and agreement between the two laboratories is generally good, especially for strong transitions and photoelectron energies in excess of 1 eV.

There have been several investigations of the angular distributions of photoelectron intensity in carbon monoxide.^{3,12,13} Carbon monoxide is an important molecule because of its fundamental role in the chemistry and physics of planetary atmospheres and comet tails.¹⁴ Carbon monoxide is also very important in chemistry; the carbonyl group is an active site for the absorption and emission of radiation in many molecules. The results of the angular distributions of CO have not significantly clarified the physics and chemistry of CO so far due to the disagreement among the various investigators.^{3,12,13} In addition there seems to be no accurate measurement of the variation of the angular distribution asymmetry parameter β with vibrational peak. We have reinvestigated angular distributions in CO using HeI radiation and have paid particularly close attention to that variation. Only a gradual variation of β with electron energy for ionization of electrons

from a single orbital in low atomic weight systems is expected and therefore the variation of β across the vibrational envelope of an electronic band should be slow and monotonic.^{15,16} This conclusion assumes that the main effect on β of varying the vibrational quantum number in a given electronic band is due to the corresponding variation in the photoelectron energy and that a similar effect could be achieved by varying the incident photon wavelength for a fixed vibronic transition. For direct photoionization, the only important effect of the final vibrational quantum number is to change the relative intensities of the vibrational peaks of a given band according to the Franck-Condon factors and in a manner independent of the direction of electron ejection. This is the case, for example, for ionization of H_2 by 584 Å radiation where the β values for the $v' = 0$ through $v' = 6$ components of the $^2\Sigma_g^+$ state are essentially the same within experimental error.³ If large and/or nonmonotonic variations of β do occur across an electronic band, this may indicate the presence of other ionization channels such as autoionization or the breakdown of assumptions leading to the Franck-Condon intensity factors. In this paper we present our results and discuss them in terms of several different physical processes that could be occurring during ionization or shortly thereafter.

II. EXPERIMENTAL

The variable angle photoelectron spectrometer used in this work was described in detail elsewhere¹⁷ and will be summarized here only briefly. A block diagram of the photoelectron spectrometer is shown in Fig. 1. Ultrahigh purity (99.999%) helium flows into the discharge lamp

which is located on the inside of the main vacuum chamber. The beam of light (mostly HeI 584Å) is collimated and passes into the scattering chamber which contains sample gas at a pressure of 1 to 10 mTorr as measured by an uncalibrated Schultz-Phelps ionization gauge. The photoelectrons produced exit through a slot in the scattering chamber and are collimated and decelerated by electrostatic lenses before entering the electron energy analyzer. They are then energy-selected in the hemispherical electrostatic analyzer which has a mean radius of 6.80 cm and are recollimated and accelerated by additional lenses into the cone of a Spiraltron electron multiplier. The Spiraltron sends out a low voltage pulse for each electron detected, which is shaped and amplified by a preamplifier on the outside of the instrument. The pulses are directed to a PDP 8/e computer which acts as a multichannel scaler. The photoelectron spectrum is normally displayed on an oscilloscope or plotted by an XY recorder. The electrostatic lenses, energy analyzer, and detector are rotated about the center of the scattering chamber through a variable angle θ with respect to the photon beam. In addition, the main vacuum chamber is lined with mu metal and located at the center of three pairs of Helmholtz coils to reduce the earth's magnetic field to about 0.3 mG. This is necessary since the photoelectrons have low kinetic energy and are easily deflected by stray magnetic fields.

The data are partially reduced while the computer is on-line. The spectra are smoothed and a derivative algorithm is used to locate the peak maxima.¹⁸ Spectral intensities measured as peak heights at each of nine detector angles in the range 45 to 120° are fitted by a weighted least squares program to Eq. (1), with $d\sigma/d\Omega$ a linear function of $\cos^2\theta$.

Correction for background photoelectron counts is critical for accurate measurements of β , especially when the signal-to-background ratio becomes as low as 1:2. At each of those nine angles we accumulate a spectrum with no sample gas in the scattering chamber. As the electron energy decreases from 13 eV to 1 eV, this background increases at a rate of about $1/6 \text{ count eV}^{-1} \text{ sec}^{-1}$. These background data are later used to correct the peak intensities at each of the nine angles before β is calculated.

The performance of the instrument is checked by its ability to reproduce the β values of 0.88 for the $^2P_{3/2}$ and 0.86 for the $^2P_{1/2}$ peaks of argon which are very close to the values reported previously.^{3,13,19} The resolution of the instrument is typically 0.040 eV as measured by the full width at half maximum of the argon $^2P_{3/2}$ peak. The energy scale is calibrated by mixing the samples gas with a small amount of argon.

III. RESULTS

A. Fixed angle spectrum

The photoelectron spectrum of CO was obtained at the "magic" detector angle of 54.7° at which $P_2(\cos \theta)$ vanishes and the intensity is independent of β . As a result, the ratio of the DCS of two transitions at this angle is the same as that of the corresponding integral cross sections, a very useful property. The 584 Å spectrum (Fig. 2) shows three distinct bands labeled $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$. In addition, features due to the HeI β (537 Å) and HeI γ (522 Å) lines (which account for 2% and 0.5% of the total light intensity respectively) are also displayed²⁰. The most significant result of this fixed-angle spectrum is that it shows resolved

structure in the abscissa region between 14.2 eV and 16.3 eV. This structure has not previously been reported, probably due to the low intensity of the peaks. A more detailed spectrum covering this region is shown in Fig. 3. This structure does not seem to be due to chemical impurities in the sample gas, since the same spectrum is obtained using 99.9% or 99.99% purity CO. Also, it is unlikely that the structure is due to chemical impurities in the helium lamp gas, since we use 99.999% purity helium. Furthermore, this structure is not present in the background spectrum. We assign this structure to high vibrational levels of the $X^2\Sigma^+$ band as well as 537 Å ionization of the $A^2\Pi$ band.

B. Angular distributions

We have studied the angular distributions of the intensities of 24 vibronic transitions in the photoelectron spectrum of CO, which is twice the number of transitions reported on previously.³ These distributions were measured at least three times for all of the peaks. Each angular distribution is obtained from repeated scans to improve the signal-to-noise ratio, with some runs lasting up to 12 hours. In spite of the low intensity of some of the peaks, the corresponding anisotropy parameters were usually reproducible to ± 0.1 or better. The β values for the most intense peaks were reproducible within ± 0.02 . The average values of the asymmetry parameters β are shown in Table I together with the results of Carlson and Jonas³ and Hancock and Samson.¹³ We have not measured the angular distribution of the 584 Å, $v' = 3$ and $v' = 4$ levels of the $X^2\Sigma^+$ state since they are overlapped by the $v' = 1$ and $v' = 2$ levels of the $A^2\Pi$ band formed by 537 Å radiation.

C. $X^2\Sigma^+$ band

A plot of β versus electron energy for the $X^2\Sigma^+$ band is shown in Fig. 4. It indicates an unusually rapid variation of β as the electron energy increases from 5.9 eV to 7.2 eV as well as a noticeable dip at 6.94 eV. This behavior is discussed in Sec. IV.

D. $A^2\Pi$ band

A plot of β versus electron energy for the $A^2\Pi$ band is shown in Fig. 5. Again, we see an unusually rapid and non-monotonic variation of β over the relatively narrow energy range of 2.9 to 4.1 eV. A straight line can be drawn through nine of the 14 points, as indicated in the figure. The 584 Å points corresponding to $v' = 0, 4, 8, 9$, and 10 lie significantly off that line. The error bars for these peaks are fairly small and our value of β for $v' = 0$ agrees well with that of Carlson and Jonas³ as can be seen from Table I, but not our value for $v' = 4$. Those authors have not reported angular distributions for $v' = 8, 9$, and 10. It is interesting to note that when β values of the $A^2\Pi$ band of CO are plotted on the same graph as β values of the $A^2\Pi_u$ band of N_2 ,¹ the CO values fall along the general trend line of the N_2 results, except for $v' = 0, 4, 8, 9$, and 10 of CO. This may merely be a coincidence, since plots of β versus electron energy for the $X^2\Sigma^+$ and $B^2\Sigma^+$ bands of CO do not coincide at all with plots for the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ bands of N_2 .

E. $B^2\Sigma^+$ band

A plot of β versus electron energy for the $B^2\Sigma^+$ band is shown in Fig. 6. Our value of β for $v' = 0$ is outside the error bars of the Carlson and Jonas³ value, but it agrees fairly well with that of Hancock and Samson,¹³ as can be seen from Table I. The plot once again shows an

an unusually rapid and non-monotonic dependence of β on electron energy. A straight line can be drawn through the points except for the $v' = 3$ one. However, this line would have a slope of 1 eV^{-1} , which is much larger than most other slopes reported^{1, 15, 16} for this type of plot.

IV. DISCUSSION

In attempting to explain the anomalous behavior of β as a function of electron energy (Figs. 4, 5, and 6) it is important to first establish whether or not the peaks in the corresponding spectra are due to single vibronic transitions. Overlapping contributions are possible because of the nature of the light emitted by our discharge lamp, which includes atomic emission lines at $584 \text{ \AA}$ ($\text{HeI}\alpha$), $537 \text{ \AA}$ ($\text{HeI}\beta$), and $522 \text{ \AA}$ ($\text{HeI}\gamma$) at relative intensities of 100, 2 and 0.5, respectively. We have systematically looked for coincidental electron energy matchups (within 50 meV) due to ionization of different vibronic levels by these three different wavelengths. The near-coincidences obtained for which we measure β are given in Table II. The experimental intensity at a given electron energy for these near-coincident transitions should be the simple sum of the intensities of the corresponding transitions, instrumental resolution effects included. For the case in which the difference between the electron energies corresponding to the center of the contributing peaks is smaller than or comparable to the instrumental resolution (which is the case for all the near-coincidences of Table II), the observed β will be a weighted average of the asymmetry parameters for the individual peaks,

$$\beta_{\text{obs}} = \frac{I_1 \sigma_1 \beta_1 + I_2 \sigma_2 \beta_2}{I_1 \sigma_1 + I_2 \sigma_2} = \frac{\beta_1 + \frac{I_2 \sigma_2}{I_1 \sigma_1} \beta_2}{1 + \frac{I_2 \sigma_2}{I_1 \sigma_1}} \quad (2)$$

The coefficients σ_1 and σ_2 are the total cross sections of the contributing ionizations and I_1 and I_2 are the intensities of the corresponding incident photon lines. Using this equation we can approximately correct our observed β for perturbation by overlapping peaks.

For example, consider the pair of transitions given in the first line of Table II. The observed effective β is 0.52. We will assume that these two transitions are due to direct ionization. This assumption is consistent with the subsequent analysis in this section. The β value for the 522 Å, $v' = 8$ $A^2\Pi$ ionization can be estimated as 0.42 which is obtained from the β value of the solid trend line in Fig. 5 at an electron kinetic energy of 5.78 eV. This is the kinetic energy of a photoelectron ejected by a 522 Å photon leaving behind an ion in the $A^2\Pi$, $v' = 8$ state. The procedure assumes that this trend describes the variation of β with electron energy for direct ionization (see discussion toward the end of the present section). We estimate the ratio of the total ionization cross sections for the $v' = 8$ $A^2\Pi$ state by 522 Å photons and the $v' = 4$ $A^2\Pi$ state by 537 Å photons. Since these wave-lengths are fairly close to one another, we will assume that this ratio is approximately equal to the corresponding theoretical ratio of Franck-Condon factors given by Table III as 6.63/65.5. The 522 Å to 537 Å photon intensity ratio for our lamps is 0.5/2. From these numbers and Eq. 2 we obtain for the $v' = 4$ $A^2\Pi$ ionization by 537 Å photons the β value of 0.52 which is equal to the value measured for the composite transition being considered. The main reason that the transition to the $A^2\Pi$ $v' = 8$ CO^+ state produced by the 522 Å line does not significantly perturb the β value of the $A^2\Pi$ $v' = 4$ state resulting from the 537 Å line is the smallness of the corresponding

Franck-Condon factor ratio just mentioned.

By using the same kind of procedure we have examined the rest of the transitions in Table II and found that the β values for the transitions indicated in the left half of Table II are not significantly perturbed due to overlap by the transitions indicated in the right half. The reason for this is primarily that the 522 Å and 537 Å lines are so much weaker in intensity than the 584 Å line. Also, for the last two lines in Table II, transitions to the $D^2\Pi$ state of CO are believed²¹⁻²³ to be due to two-electron processes where one electron is removed and another is excited $[(\pi 2\rho)^4 \rightarrow (\pi 2\rho)^2(\pi^* 2\rho)^* + e^-]$ and the corresponding cross sections are weaker than those due to a one-electron process. We conclude that the anomalous energy dependence of β for the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ bands of CO^+ depicted in Figs. 4, 5 and 6, are not due to contributions from overlapping features resulting from the 537 Å and 522 Å lines present in low intensity in our predominantly 584 Å light source.

We consider next the effect that secondary scattering of the low-energy photoelectrons by neutral CO molecules would have on the observed angular distributions. In our scattering chamber there is a steady stream of photoelectrons and a fairly high concentration (~ 4 mTorr) of neutral CO molecules; collisions between the two might lead to temporary negative ion states for resonant energies. To determine the optimum sample pressure, the intensity of the most intense peak in the 584 Å spectrum ($X^2\Sigma^+ v' = 0$, photoelectron energy of 7.2 eV) as a function of pressure was determined. It was found that the curve representing this dependence was linear up to

4 mTorr, bending downwards thereafter. The operating pressure of 4 mTorr was therefore chosen; it maximizes the photoelectron signal intensity without apparently introducing secondary scattering. Nevertheless, for the 584 Å $B^2\Sigma^+$ band, the photoelectrons have an energy around 1.5 eV and are more susceptible to secondary scattering. In addition, in the electron energy range around 1.5 eV there are temporary negative ion resonances in CO.²⁴ The effect of resonances of that kind on the peak intensities of fixed angle photoelectron spectra of CO, N₂, and CO₂ at sample pressures between 50 mTorr and 200 mTorr has been previously observed by Streets, Potts, and Price.²⁵ Such processes could conceivably be affecting our spectra, although our pressures are significantly lower.

To check out this possibility, we determined the variation of the intensity of the $v' = 1$ relative to the $v' = 0$ $B^2\Sigma^+$ 584 Å peak with pressure and found an increase in this ratio of about 10% in going from zero pressure (by extrapolation) to 4 mTorr. This small variation should not however have any appreciable effect on the value of β . The reason is that the small change in the intensity of the photoelectron beam due to such secondary processes, with the detector at an angular position θ , should be independent of θ . This conclusion has been found to be correct since we have measured β for the $v' = 0$ and $v' = 1$ levels of the $B^2\Sigma^+$ state at pressures of 4 mTorr and 9 mTorr and found them to be equal within experimental error bars. Therefore, we conclude that the anomalous trends in the plots of β versus electron energy shown in Figs. 4, 5, and 6 are not due to secondary electron scattering.

A possible explanation of these anomalous results might be a breakdown of the Born-Oppenheimer approximation. This has been suggested previously to explain the unusual dependence of β on the vibrational quantum number for some transitions in N_2 and CO.^{3,26} Kalman²⁷ has argued against such an explanation. The most significant cause of such a breakdown is the strong interaction between two potential energy curves occurring in the vicinity of a crossing or near-crossing. For CO^+ , the potential energy curves of the $X^2\Sigma^+$ state and $A^2\Pi$ state have been found to cross. Singh and Rai²⁸ have used experimental spectroscopic data to construct the potential energy diagrams of the X, A, and B states of CO^+ . Their results show that the $X^2\Sigma^+$ state at the $v' = 13$ level intersects the $A^2\Pi$ state at the $v' = 5$ level. In this region the relative intensities for the vibrational levels might be expected to disagree with calculated Franck-Condon factors. It would also be possible for the corresponding asymmetry parameters to be anomalous. This, however, would only be the case if the ionic state curve crossing region fell inside the vertical Franck-Condon band determined by the initial neutral species vibrational wavefunction. This is not the case for CO, where this Franck-Condon band extends from 1.06 Å to 1.20 Å²⁹ whereas the crossing between the $X^2\Sigma^+$ and $A^2\Pi$ curves occurs at 1.48 Å.²⁸ Since this is the only known instance of curve crossing in the X, A, and B states of CO^+ it is unlikely that a breakdown in the Born Oppenheimer approximation is causing the unusual dependence of β on electron energy.

Another possible explanation of the unusual dependence of β on vibrational quantum number is the variation of the electronic transition

dipole matrix element on the internuclear distance. For the case of N_2 , Kalman³⁰ has shown that there is some variation of β with vibrational quantum number for the $X^2\Sigma_g^+$ band, but not the large variation observed in the experiments.^{1,3} Additional data are needed before similar conclusions can be made for CO, but it is unlikely that such arguments would account for the large variation in β for the three bands

The most probable cause of the anomalous energy dependence of β is, in our view, either an electronic autoionization or a shape resonance. In the nomenclature of the present paper, we use the term "electronic autoionization" to denote an internal electronic Feshbach resonance. This implies a two-electron, two-step process in which a deeply buried electron is first promoted to an excited bound atomic or molecular orbital, which, however, places the atom or molecule as a whole at an energy above its lowest ionization potential. After some time, this excitation energy is transferred to the other electron which is in a lower energy orbital, causing its ionization.³¹ [Another form of autoionization is vibrational autoionization in which ionization of a bound excited electron is assisted by transfer of vibrational energy to it; this usually involves highly excited Rydberg orbitals and results in the ejection of an electron with very low kinetic energy.³¹ It is not relevant for the present case, and from here on we will use the word autoionization to denote the electronic variety.] In a shape resonance, on the other hand, ionization takes place from the orbital originally excited, but the nature of the interactions of the excited electron with the remaining electrons (see below) also results in a delay in the ionization.^{32,33}

Autoionization has been observed experimentally^{34, 35} and investigated theoretically³⁶ in many atoms and some molecules such as H_2 , O_2 , N_2 , and CO. Experimentally, autoionization is observed in photoelectron spectroscopy and in photoionization experiments, where the ionization cross section is measured as a function of photon wavelength. In these experiments³⁷ autoionization is observed as sharp peaks or dips superimposed on the continuum spectra due to direct photoionization. In photoelectron spectroscopy, autoionization is usually suspected when relative vibrational intensities in a band deviate from calculated Franck-Condon factors. Bahr *et al.*³⁵ have observed relative vibrational intensities in the photoelectron spectra of O_2 , N_2 , and CO which they attribute to autoionization at wavelengths 600 to 800 Å. They show how high vibrational levels of the ion state, which are not populated by direct ionization through the Franck-Condon principle, can be populated by autoionization. These authors dramatically illustrate how the photoelectron spectra can change appearance when the photon source is changed from an off-resonance to a resonance wavelength. The anomalous variation of β values with vibrational state for the ionization of the $X^2\Sigma_g^+$ state of N_2^+ by 584 Å has also been interpreted to be due to an autoionization process.¹

We now examine the possibility of autoionization in CO at the wavelengths used in this study. Codling and Potts²¹ have obtained the absorption spectrum of this molecule in the region 530 to 610 Å. Asbrink *et al.*²² made the assignments in their spectrum and found that there is a state at 21.24 eV that corresponds to a 3p member of a Rydberg series converging to the $C^2\Sigma^+$ state of CO^+ . They argue that this state is derived from a two-electron transition from the

ground state. They represent the ground state configuration of CO as

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^2 \quad {}^1\Sigma^+, \quad (3)$$

so that the two-electron transition could be written as

$$X \ {}^1\Sigma^+ \rightarrow \dots (\pi 2p)^3(\sigma 2p)^1(\pi^* 2p)^1(3p\sigma \text{ or } 3p\pi)^1 \quad (4)$$

or

$$X \ {}^1\Sigma^+ \rightarrow \dots (\pi 2p)^2(\pi^* 2p)^1(3p\sigma \text{ or } 3p\pi)^1. \quad (5)$$

In addition, Lee *et al.*³⁸ have seen the same spectral features as Codling and Potts²¹ in the photoabsorption cross sections of CO from 520 to 730 Å. Their absorption cross section spectrum shows sharp structure in the range 550 to 730 Å, and there appears to be a peak at about 584 Å. They agree with the assignments given by Codling and Potts.²¹

Samson and Gardner³⁹ have measured partial photoionization cross sections and branching ratios of CO from 750 to 304 Å using a duoplasmatron and a dc glow discharge in He, Ne, Ar, and N₂ as excitation sources coupled to a vacuum ultraviolet monochromator. In their plot of partial photoionization cross sections as a function of wavelength for the production of the CO⁺ X ²Σ⁺ state, a large dip in the cross section is seen near 584 Å. There is a corresponding increase in the partial cross section for the production of the CO⁺ A ²Π state at about 584 Å. They tentatively assign the structure in the partial cross section plots to autoionization resonances and attribute to such an autoionization state the difference in the β

parameters of the $v' = 0$ and $v' = 1$ levels in the $X^2\Sigma^+$ band observed by Carlson and Jonas.³

Plummer *et al.*⁴⁰ have measured the partial photoionization cross sections and branching ratios of CO using synchrotron radiation over the photon energy range of 14 to 50 eV. They observe structure (both dips and peaks) in the partial photoionization cross sections between 19 and 22 eV in the $A^2\Pi$ and $X^2\Sigma^+$ ionic states. They state that some of this structure is due to autoionization and some of it may be due to shape resonances. In a photoionization shape resonance, the escaping photoelectron has to overcome a potential energy barrier as it moves away from the remaining ion. The barrier is due to scattering by the ionic field,^{32, 33} which can be the result of direct coulomb interaction or exchange interactions of the outgoing electron with the other ionic electrons.³² As a result of this barrier, a quasibound state can exist which tends to affect the photoelectron cross section at the excitation energy equal to the energy of that state. For the case of molecular systems, this potential can be anisotropic and can affect the angular distributions of the photoelectrons. Dehmer and Dill³³ have shown, however, that for N_2 the variation of β due to this effect occurs over several eV, which is the typical width of these shape resonances.^{32, 33, 41} Therefore it seems unlikely that a shape resonance at 584 Å would cause the anomalous variation in β that we observe since this variation occurs over the energy range of vibrational spacings, which are roughly 0.2 eV. In addition, the $X\alpha$ scattering calculation by Davenport,⁴¹ which seems to be the best theoretical description of shape resonances so far, does not indicate the presence of any such resonance in the

A $^2\Pi$ state of CO. Therefore, if the calculation is correct, the anomalous variation in β shown in Fig. 5 could not be accounted for by a shape resonance. Autoionization resonances are much narrower (typically < 0.1 eV)³⁷ than the former because of the relatively weak coupling between the electrons involved. As a result, they are expected to cause a variation in β over an equivalently narrow energy range.^{42, 43} It seems likely therefore that an autoionization resonance, rather than a shape resonance, is responsible for the anomalous variation in β .

The effect of autoionization on vibrational intensity distributions has been investigated by Smith.⁴⁴ Using the Fano configuration interaction theory,⁴⁵ he showed that the vibrational intensities I of the resulting positive ions can be written as the sum of two terms involving Franck-Condon factors (FCF),

$$I \propto F_{if}^2 + q F_{i\nu}^2 F_{\nu f}^2, \quad (6)$$

where q is a parameter related to the oscillator strengths to the quasi-excited neutral and to the ion state, and the line width of the neutral state. F_{if}^2 is the FCF for the initial neutral vibrational state to the positive ion state (associated with direct photoionization), $F_{i\nu}^2$ is the FCF to the excited quasi-bound neutral state, and $F_{\nu f}^2$ is the FCF from the latter to the final positive ion state. Expression (6) indicates that we can observe vibrational intensities in photoelectron spectroscopy that do not agree with the direct Franck-Condon factors F_{if}^2 . In our spectra of CO we observe gross deviations from calculated Franck-Condon factors for $v' \geq 2$ of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states. As mentioned above, the structure for $v' \geq 2$ of the $X^2\Sigma^+$ state has not been reported

previously using 584 Å radiation. However, the peaks for $v' = 2$ to 6 of the $B^2\Sigma^+$ state can be seen even in the low pressure spectra of Streets *et al.*²⁵ These authors attribute these peaks to autoionization, although they do not discuss this point in detail. We feel that the intensity of the $v' \geq 2$ peaks of the $X^2\Sigma^+$ and $B^2\Sigma^+$ bands must be at least in part due to autoionization.

One may attempt to determine the contribution from autoionization to a given peak intensity from an analysis of the corresponding β value, since autoionization peaks in the photoelectron spectrum should in general show a different angular distribution from peaks due to direct ionization. For the case where the lifetime of the autoionizing state is long compared with the rotational period of the molecule we would expect $\beta_{\text{auto}} = 0$, which corresponds to an isotropic distribution. For peaks which are due to both direct and autoionization the observed β can, to a first approximation, be described as a non-interfering superposition of the two processes, and therefore

$$\beta_{\text{obs}} = \frac{\sigma_{\text{dir}}\beta_{\text{dir}} + \sigma_{\text{auto}}\beta_{\text{auto}}}{\sigma_{\text{dir}} + \sigma_{\text{auto}}} \quad (7)$$

where σ_{dir} and σ_{auto} are the total cross sections for the direct and autoionization processes.

Since as stated above the $v' = 2$ and $v' = 5$ peaks of the $X^2\Sigma^+$ band are due at least in part to autoionization, let us assume in one extreme case that they are totally due to such a process. This permits us to establish a rough energy dependence of β_{auto} by merely drawing a straight line through these two points. Similarly, we can estimate the

energy dependence of β_{dir} for the $X^2\Sigma^+$ band if we assume that the $v' = 0$ peaks of the 537 Å and 584 Å spectra are populated by direct ionization only and take β_{dir} to be a linear function of the photoelectron energy. From these assumptions, Equation (7) and the observed β value for the $v' = 1$ peak in the 584 Å spectrum, we can calculate the $\sigma_{\text{dir}}/\sigma_{\text{auto}}$ ratio for this transition. The result is -0.67, which is not physically meaningful. Therefore at least one of these assumptions is incorrect. The assumption of noninterference between the auto-ionized and directly ionized electrons is probably not correct.⁴² By studying β as a function of electron energy for xenon through a region where autoionization exists, Dill⁴⁶ and Samson and Gardner⁴⁷ have shown that there is interference between these two processes and this leads to complex oscillations in β as a function of electron energy. This has also been shown to occur in neon and argon.^{42, 43} To our knowledge this has not been studied directly for molecules but β would be expected to exhibit similar behavior for the molecular case. Not enough information is therefore available to determine the relative extents of the autoionization and direct ionization contributions to the anomalous peaks of the $X^2\Sigma^+$ band. A similar conclusion is valid for the $A^2\Pi$ and $B^2\Sigma^+$ bands.

V. SUMMARY AND CONCLUSIONS

It was found that the relative intensities of high ($v' \geq 2$) vibrational levels of the $X^2\Sigma^+$ and $B^2\Sigma^+$ bands resulting from the ionization of CO by 584 Å light do not agree with calculated Franck-Condon factors. The asymmetry parameter β was measured for many photoelectron transitions and was found to have an anomalous dependence on photoelectron energy, varying non-monotonically and/or very steeply with this energy. We attribute this behavior to the contribution of autoionization processes to some of the vibrational components of those bands, but not enough information is presently available to quantitatively determine the extent of such contribution. From this work it is apparent that the asymmetry parameter β is very sensitive to the presence of autoionization channels. It may turn out that the photon energy dependence of β is a more sensitive indicator of the presence of autoionization than the corresponding energy dependence of total or partial ionization cross sections.

Photoelectron angular distribution experiments with a continuously variable wavelength light source (such as a synchrotron source) would provide very useful additional information for the interpretation of the present results. It would also be interesting to study the photoelectron angular distributions of $C^{13}O$ at 584 Å since the vibrational frequency of $C^{13}O$ is 2.3 % lower than that of $C^{12}O$. As a result the photoelectrons from high vibrational levels of $C^{13}O$ would have sufficiently different kinetic energy from those of $C^{12}O$ to provide additional information on β at photoelectron energies around 3 eV, where this anisotropy parameter is changing very rapidly.

The crossing known to exist²⁸ between the $X^2\Sigma^+$ and $A^2\Pi$ potential energy curves of CO^+ occurs at excessively large distances to account for our observations. However, in other systems such crossings could occur within the vertical Franck-Condon envelope. Under these conditions, a breakdown of the Born-Oppenheimer approximation resulting from such crossings could affect the corresponding β values, and it would be interesting to use theoretical methods to assess the magnitude of such an effect.

TABLE I. Values of β for CO.

			Present Work ^a	Carlson and Jonas ^b	Hancock and Samson ^c
537 Å	X ² Σ ⁺	v' = 0	1.03 ± 0.12		
584 Å	X ² Σ ⁺	v' = 0	0.95 ± 0.02	0.8 ± 0.1	0.95 ± 0.05
		v' = 1	0.60 ± 0.03	0.37 ± 0.17	0.56 ± 0.07
		v' = 2	0.73 ± 0.08		
		v' = 3			
		v' = 4			
		v' = 5	0.45 ± 0.15		
537 Å	A ² Π	v' = 0	0.45 ± 0.15		
		v' = 1			
		v' = 2			
		v' = 3	0.38 ± 0.16		
		v' = 4	0.52 ± 0.10		
584 Å	A ² Π	v' = 0	0.47 ± 0.05	0.39 ± 0.14	0.31 ± 0.05
		v' = 1	0.32 ± 0.02	0.27 ± 0.14	0.31 ± 0.05
		v' = 2	0.29 ± 0.02	0.3 ± 0.1	
		v' = 3	0.25 ± 0.05	0.3 ± 0.15	
		v' = 4	0.10 ± 0.04	0.23 ± 0.16	
		v' = 5	0.27 ± 0.05	0.27 ± 0.16	
		v' = 6	0.24 ± 0.03	0.24 ± 0.16	
		v' = 7	0.22 ± 0.09	0.29 ± 0.16	
		v' = 8	-0.07 ± 0.07		
		v' = 9	-0.02 ± 0.06		
		v' = 10	0.32 ± 0.08		
584 Å	B ² Σ ⁺	v' = 0	0.41 ± 0.05	1.0 ± 0.02	0.28 ± 0.05
		v' = 1	0.54 ± 0.08	1.11 ± 0.3	
		v' = 2	1.03 ± 0.10		
		v' = 3	0.63 ± 0.08		
		v' = 4	1.22 ± 0.10		

a. The values reported are averages of at least three determinations.

The errors indicated are standard deviations obtained by the least square fit described in Sec. II.

b. Ref. 3.

c. Ref. 13.

TABLE II. Electron Energy near coincidences in CO for 584 Å, 537 Å, and 522 Å photons.^a

Line number	Wavelength (Å)	State	IP (eV)	Electron Energy (eV)	Wavelength (Å)	State	IP (eV)	Electron Energy (eV)
1.	537	$v' = 4$ $A^2\Pi$	17.278	5.808	522	$v' = 8$ $A^2\Pi$	17.962	5.779
2.	584	$v' = 7$ $A^2\Pi$	17.800	3.417	537	$v' = 0$ $B^2\Sigma^+$	19.654	3.432
3.	584	$v' = 3$ $A^2\Pi$	17.098	4.119	522	$v' = 0$ $B^2\Sigma^+$	19.654	4.087
4.	584	$v' = 8$ $A^2\Pi$	17.962	3.255	537	$v' = 1$ $B^2\Sigma^+$	19.862	3.224
5.	584	$v' = 7$ $A^2\Pi$	17.800	3.417	522	$v' = 3$ $B^2\Sigma^+$	20.334	3.407
6.	584	$v' = 8$ $A^2\Pi$	17.962	3.255	522	$v' = 4$ $B^2\Sigma^+$	20.450	3.291
7.	584	$v' = 3$ $B^2\Sigma^+$	20.334	0.883	537	$(v' = 0$ $D^2\Pi)^b$	22.218	0.868
8.	584	$v' = 1$ $B^2\Sigma^+$	19.862	1.355	522	$(v' = 1$ $D^2\Pi)^b$	22.392	1.349

a. The energies of these photons are 21.217 eV, 23.086 eV, and 23.741 eV, respectively.

b. References 21-23.

TABLE III. Comparison of experimental Franck-Condon factors with two sets of theoretical ones for CO.

		Experimental FCF ^a	Present Results ^b	Theoretical FCF ^c	Theoretical FCF ^d
$X^2\Sigma^+$	$v' = 0$	100.0	100.0	100.0	100.0
	$v' = 1$	3.46	4.49	3.72	3.77
	$v' \geq 2$	--	$\sim 0.8^e$	$< 10^{-3}$	$< 10^{-3}$
$A^2\Pi$	$v' = 0$	39.4	42.7	36.8	36.9
	$v' = 1$	83.4	75.5	81.8	81.9
	$v' = 2$	100.0	100.0	100.0	100.0
	$v' = 3$	86.7	85.3	89.4	89.3
	$v' = 4$	67.8	67.1	65.5	65.4
	$v' = 5$	50.3	48.6	41.9	41.7
	$v' = 6$	24.2	23.0	24.2	24.1
	$v' = 7$	14.8	17.1	13.0	12.9
	$v' = 8$	8.31	10.2	6.63	6.58
	$v' = 9$	5.08	5.74	3.24	3.21
	$v' = 10$	2.53	4.27	1.53	1.51
$B^2\Sigma^+$	$v' = 0$	100.0	100.0	100.0	100.0
	$v' = 1$	35.0	43.4	36.2	36.1
	$v' = 2$	7.75	17.2	7.68	7.62
	$v' = 3$		9.93	1.44	1.30
	$v' = 4$		10.0	0.22	0.21
	$v' = 5$		8.81	0.04	0.04
	$v' = 6$		8.66	0.00	0.00

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b. Obtained with electron energy analyzer which is uncorrected for detection efficiency.

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e. See Fig. 3.

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FIGURE CAPTIONS

FIG. 1. Block diagram of the variable-angle photoelectron spectrometer. He, cylinder of ultra-high purity helium; ZT, liquid nitrogen-immersed zeolite trap for lamp helium supply; RB, lamp ballast resistor; LPS, lamp dc power supply; SC, sample chamber; PC, photocathode for light flux measurement; CL, electron lens elements; ANALYZER, hemispherical electrostatic electron energy analyzer; ML, electron lens element; S, Spiraltron electron multiplier; CPS, Spiraltron cathode power supply; APS, spiraltron anode power supply; R, C, resistance and capacitance of differentiating network for spiraltron pulses.

FIG. 2. Photoelectron spectrum of CO at a detector angle of 54.7° over the ionization potential range of 11.26 to 20.46 eV. The spectrum was obtained using 511 adjacent 18 meV-wide channels and 50 scans. Total dwell time per channel was 50 sec. Average CO pressure was about 4 mTorr. The features labeled 537 Å and 522 Å are due to the HeI β and HeI γ impurity lines of the predominantly HeI α lamp. The abscissa scale refers to ionization by 584 Å light.

FIG. 3. Spectrum of the region between the $v' = 1$ level of the $X^2\Sigma^+$ 584 Å band and $v' = 7$ $A^2\Pi$ 537 Å band. The spectrum was taken over 376 adjacent 5 meV wide channels at a total dwell time of 35 sec per channel. Other parameters are the same

as for Fig. 2. The abscissa scale refers to ionization by 584 Å light.

FIG. 4. Anisotropy parameter β as a function of electron energy for the $X^2\Sigma^+$ band. Closed circles (●) indicate ionization by 537 Å radiation and open diamonds (◇) by 584 Å radiation. The upper abscissa is common to all points. The lower abscissa refers to ionization by 584 Å light.

FIG. 5. Anisotropy parameter β as a function of electron energy for the $A^2\Pi$ band. Symbols and abscissa scales have the same meanings as in Fig. 4.

FIG. 6. Anisotropy parameter β as a function of electron energy for the $B^2\Sigma^+$ band formed by 584 Å radiation.

Figure 1.

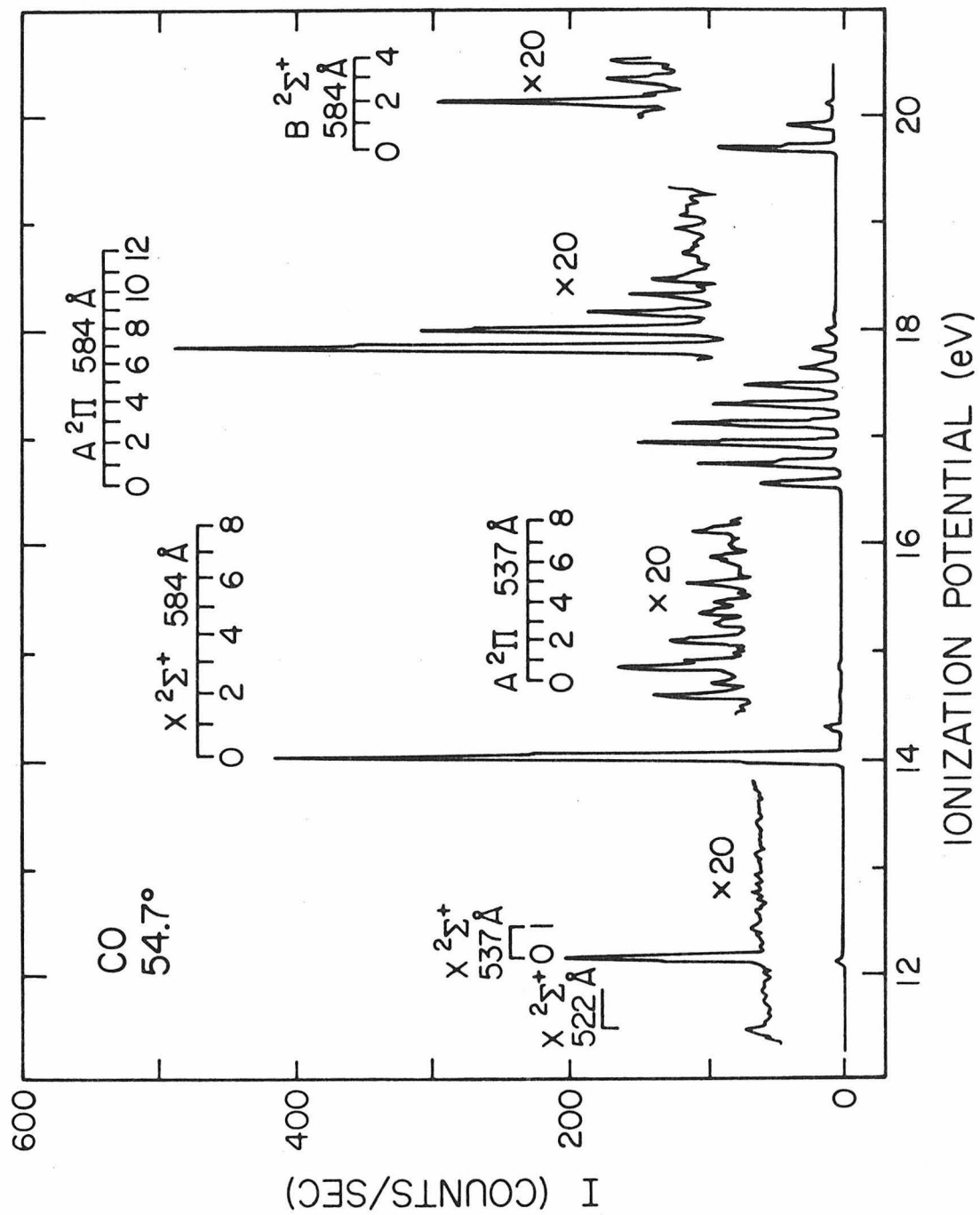


Figure 2.

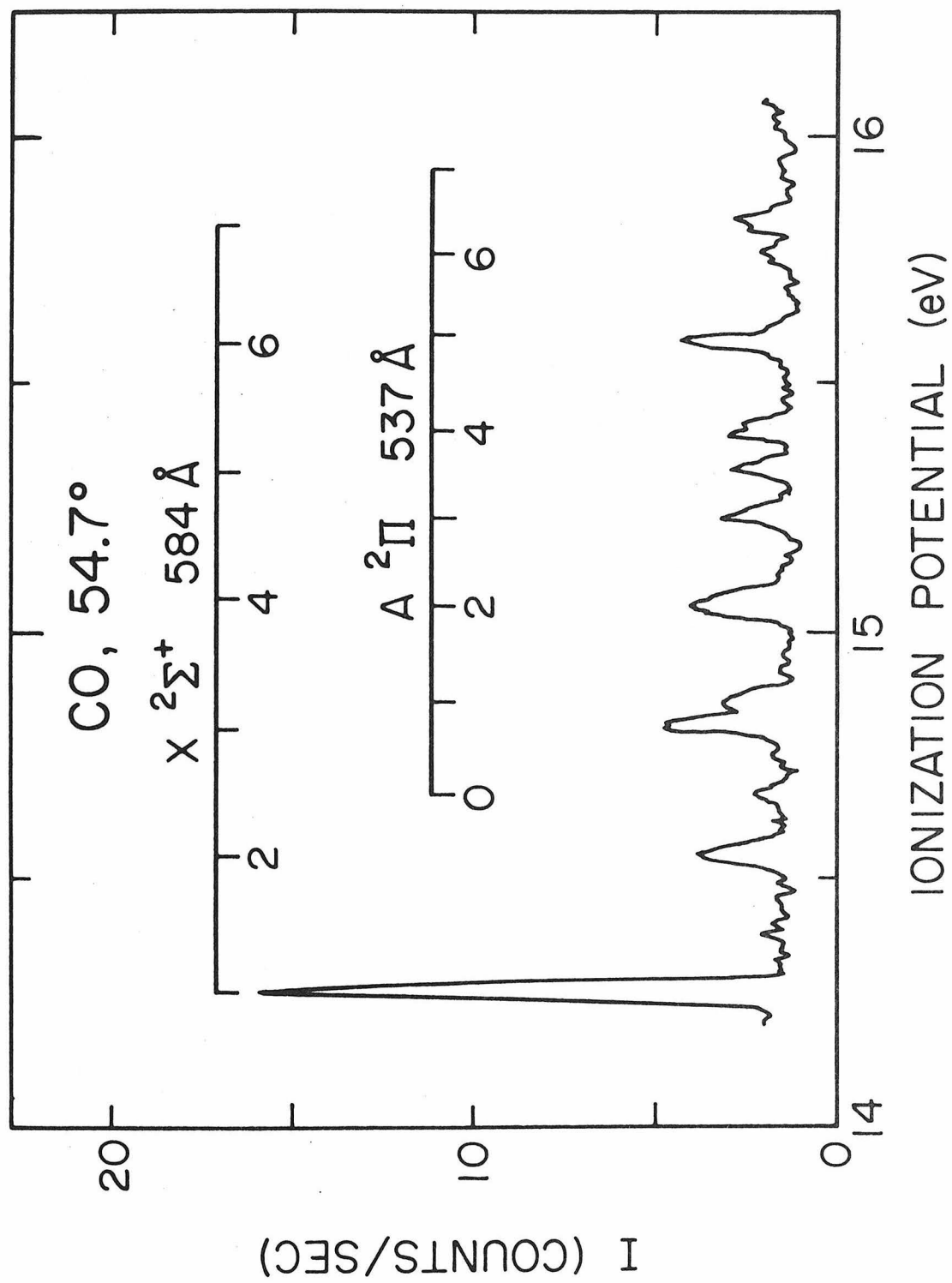


Figure 3.

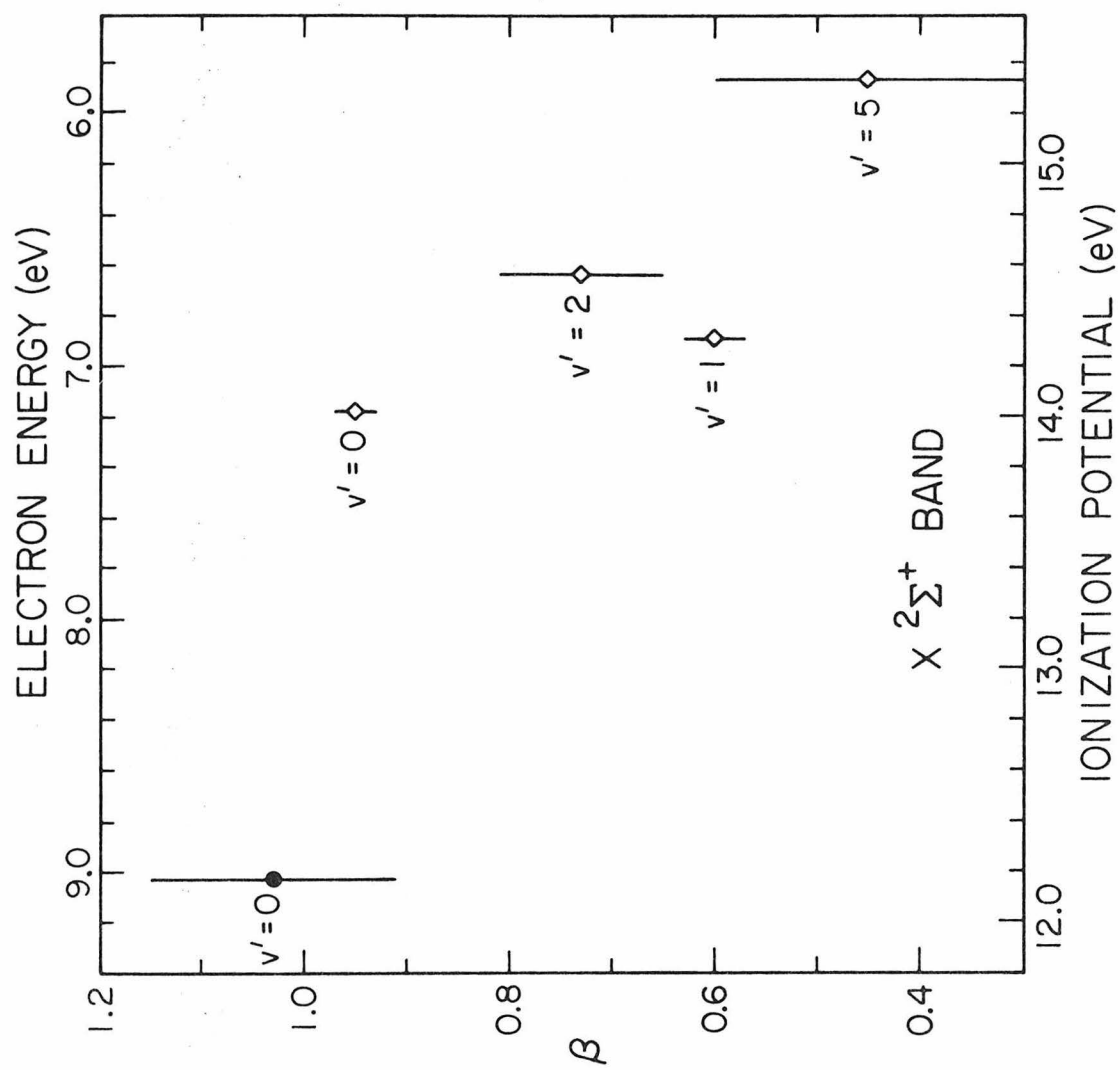


Figure 4.

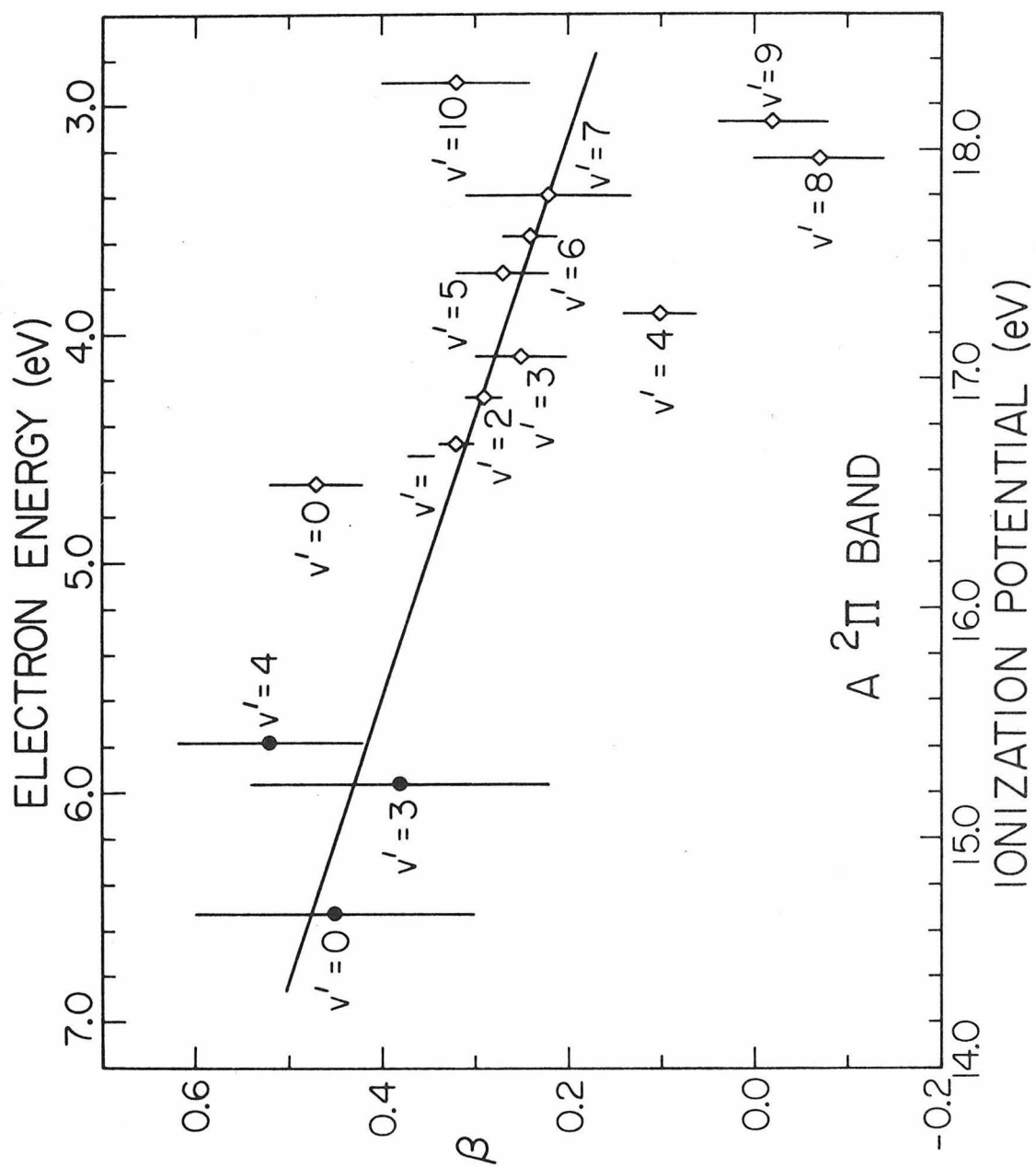


Figure 5.

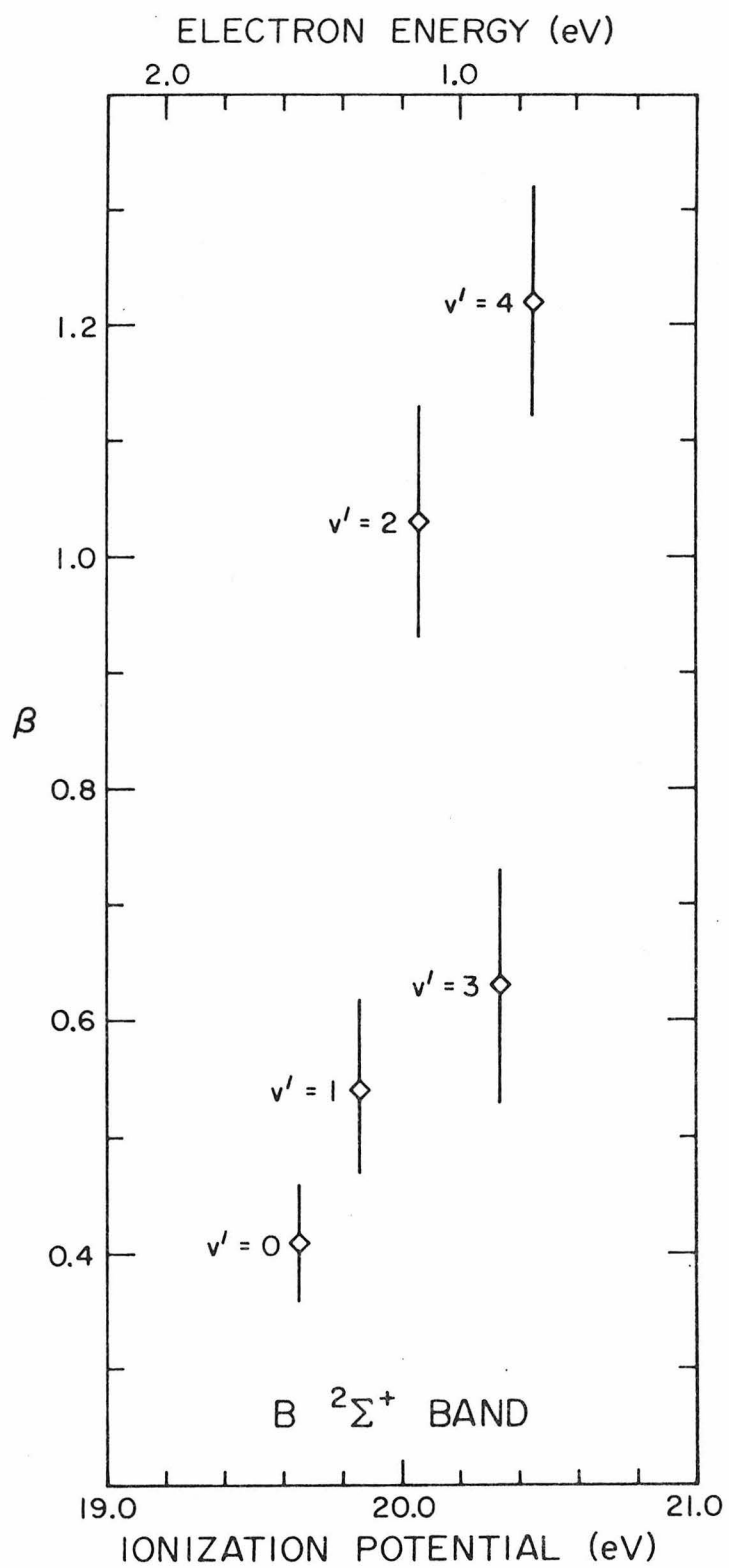


Figure 6.

CHAPTER 5: RESULTS AND DISCUSSION

Paper 2: Angular Distributions in the Photoelectron Spectra of Benzene and its Monohalogenated Derivatives

ANGULAR DISTRIBUTIONS IN THE PHOTOELECTRON SPECTRA
OF BENZENE AND ITS MONOHALOGENATED DERIVATIVES*

Jeffrey A. SELL[†] and Aron KUPPERMANN

Arthur Amos Noyes Laboratory of Chemical Physics[‡],

California Institute of Technology, Pasadena, California 91125, USA

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The results of measurements of the photoelectron angular distributions of benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene are presented. Trends in the asymmetry parameters β as well as in the band positions and shapes across this series of molecules lead to assignments of all of the π orbitals and some of the σ orbitals associated with the features in the spectra.

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[†]Work performed in partial fulfillment of the requirements for the Ph.D degree in Chemistry at the California Institute of Technology.

[‡]Contribution No. 5738.

1. Introduction

This paper is one of several from this laboratory [1-4] which reports the results of our measurements of angular distributions in the photoelectron spectroscopy of small molecules. This work and that of Carlson and coworkers [5-10] and of Hancock and Samson [11] have shown that these measurements can yield important data on the physical and chemical properties of molecules. Briefly, it has been shown theoretically [12] and experimentally [1-11, 13] that the differential cross section $\frac{d\sigma}{d\Omega}$ for photoionization of an atom or molecule by unpolarized light has the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 - \frac{\beta}{2} P_2(\cos\theta) \right] , \quad (1)$$

where σ is the integral photoionization cross section, P_2 is the second Legendre polynomial, θ is the scattering angle between the momentum vector of the ejected electron and the direction of propagation of the incident light beam, and β is the asymmetry parameter which ranges from -1 to +2. Typically, the β parameter is measured over each band in the photoelectron spectra of a series of related molecules. By examining the trends in the value of β over the series of molecules it is possible in some cases to make assignments of the orbitals from which the electrons are photo-ejected [5-10]. These studies are usually carried out using only one photon wavelength. Ideally, the measurements of the β parameter should be done as a function of the photon wavelength so that the energy dependence of β could be

accounted for in making assignments of the orbitals from which the electrons are photo-ejected. This is difficult due to the lack of a convenient vacuum ultraviolet photon source that is tunable over a wide range of wavelengths. Synchrotron radiation sources could be used for this purpose but are not readily available. On the other hand if certain empirical rules relating β to chemical concepts are developed by measuring β for analogous direct photoionization transitions in series of related molecules using only one photon wavelength, the relatively small change in photoelectron energy from molecule to molecule is not expected, in general, to significantly affect the conclusions derived by studying trends in which the effect of the variation of β with electron energy is neglected.

In this paper we report the results of measurements of β for benzene and fluoro, chloro, bromo, and iodobenzene using 584 Å photons. Using this information, we assign the peaks in the photoelectron spectra that are due to removal of electrons from the π orbitals, the halogen lone pair orbitals, and some of the σ orbitals. In some cases our assignments differ from those made previously.

2. Experimental

The apparatus used is essentially the same as the one previously described in detail [4] and will be summarized here only briefly. A helium discharge lamp produces mostly 584 Å light which interacts with the sample vapor in a scattering chamber at a pressure of about 1 to 2 mTorr as measured by a factory-calibrated capacitance manometer [14]. The photoelectrons produced are energy-selected by a hemispherical electrostatic analyzer and detected by a Spiraltron electron multiplier. The analyzer and detector are mounted on a gear wheel which rotates about the center of the scattering chamber scanning scattering angles from 45° to 120°. The instrument is surrounded by a μ metal shield and is located at the central region of three pairs of Helmholtz coils in which the residual magnetic field is only about 0.3 mGauss. Background is subtracted before β is calculated and the angular distributions of argon are used to check the performance of the instrument. The resolution of the apparatus as measured by the full width at half maximum of the peaks in the argon spectrum is 40 meV.

The samples used in this study were obtained commercially with the following stated purities: benzene 99.9%, iodobenzene 98%, and chlorobenzene 99%. The fluorobenzene boiling point range was stated as being 1° and that of bromobenzene as 2°. All samples were dried with calcium hydride and subjected to three liquid nitrogen freeze-pump-thaw cycles before use. The energy scale was calibrated with the help of a mixture of the sample vapor with a small fractional amount of argon.

3. Results

The photoelectron spectra and plots of β as a function of ionization potential (IP) for benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene are shown in figs. 1 through 5, respectively. All five photoelectron spectra were obtained at the "magic" detector angle of $\cos^{-1}(\sqrt{3}/3) = 54.7^\circ$ for which $P_2(\cos\theta) = 0$ and the relative intensities in the spectrum are equal to the relative integral photoionization cross sections, regardless of the value of β . We will first discuss the salient trends in the five spectra and then the trends in the plots of β as a function of IP.

Unless otherwise stated, all ionization potentials mentioned will be those of the most intense feature of the corresponding electronic band.

The benzene spectrum (fig. 1) is well known [10,15-19] and the assignments of the peaks to the corresponding orbitals have been discussed repeatedly [18,20,21]. The bands whose most intense features occur at 9.2 eV, 11.5 eV, and 16.9 eV (bands I, II and VII, respectively) show resolved vibrational structure. There are four more broad bands whose IP's are at 12.3, 13.9, 14.8, and 15.5 eV (bands III through VI, respectively).

The fluorobenzene spectrum shown in fig. 2 is essentially the same as that reported earlier [16,20]. Three bands having vibrational structure appear with IP's of 9.2, 12.2, and 17.8 eV (bands I, II and VIII, respectively) and correspond to the benzene features mentioned above which also have resolved vibrations.

The first fluorobenzene band is somewhat broader than the corresponding benzene one, but the 17.8 eV band has a shape similar to the band in benzene at 16.9 eV. There are several other bands in the energy range of 12 to 16 eV (bands III through VI). In addition, there is an intense band at 16.3 (band VII) which will later be associated with the 14.8 eV benzene band. Finally, a new sharp band, which is not present in benzene, appears at 13.9 eV (band IV)

In the chlorobenzene spectrum shown in fig. 3, which is similar to those reported previously [16,20] the first band clearly shows two maxima at 9.1 and 9.7 eV (I and Ia). As part of a variety of bands there are two sharp peaks at 11.3 and 11.7 eV (II and III) and additional ones whose IP's are 12.2, 13.2, 14.5, 14.7, 15.4, 15.9, and 17.0 (bands IV through X). The band at 17.0 eV resembles the bands in benzene at 16.9 eV (VII of fig. 1) and fluorobenzene at 17.8 eV (VIII of fig. 2).

In the bromobenzene spectrum shown in in fig. 4 (which is similar to those reported previously [16,20]) the first band has two maxima at 9.1 and 9.7 eV (I and Ia) but the vibrational structure is no longer resolved. There is a sharp intense band at 10.7 eV (II). In addition, peaks appear at 11.3, 12.0, 12.7, 14.1, 14.5, 15.2, 15.7 and 16.9 eV (III through X). The last one is similar in shape to the corresponding bands in the other molecules.

Finally, the spectrum of iodobenzene shown in fig. 5 (which is similar to those reported earlier [16,20]) has 11 peaks whose IP's are 8.7, 9.4, 9.6, 10.5, 11.5, 12.2, 13.5, 14.3, 14.9, 15.4, and 16.6 (I through XI). The sharp peaks at 9.4 and 9.6 (II and III) are

probably associated with two different electronic bands as will be discussed later. The band at 14.9 eV is particularly intense and the band at 16.6 eV is similar in shape to the corresponding bands for the other molecules.

Plots of β as a function of IP for the five molecules are shown directly above the photoelectron spectra in figs. 1 through 5. The values of β for benzene at 584 Å are listed in table 1 where they are compared with the results of Carlson and Anderson [10], Kobayashi and Nagakura [22], Milyaev and Vilesov [23] and Siegbahn [24]. It can be seen that bands I and I_a have relatively high values of β ranging from 1.23 to 0.86, typical of π orbitals, and there is good agreement among the four measurements for band I. The value of β then drops for bands II and III and again there is good agreement between different laboratories. Band III has been established [19, 20, 25] to be due to removal of an electron from the $a_{2u} \pi$ orbital. It is not clear why the β value is so low for this band; values of β for π orbitals are typically [9] 0.3 to 1.0 units higher than those for σ orbitals. The agreement in the values of β for bands IV through VII, between different laboratories, is not very good as can be seen from table 1. The electron kinetic energy for these transitions are lower than for bands I through III, making them more susceptible to deflection by magnetic fields. In our apparatus, however, we have checked for such effects down to less than 1 eV and found them to be negligible. This is due to the fact that our residual magnetic fields are very low, of the order of 0.3 mGauss [4]. In any event, we have no reason to suspect the reliability of our β values. For bands V through VII our values of β agree more closely with those of Milyaev and

Vilesov [23] than of Carlson and Anderson [10] and of Siegbahn [24]. The peaks in this region are due [21] to ionization from σ orbitals and values of β from -0.34 to 0.44 are more typical [1-11] of σ bands than are 0.70 or 0.79. However, the shapes of our β versus IP curves are very similar to all those published previously [23,10,24].

The fluorobenzene β values are shown in fig. 2 and listed in table 2. As far as we know, angular distributions for fluorobenzene, as well as for chloro and iodobenzene, have not been reported previously. It can be seen from that figure and table that β for band I has dropped slightly to 0.86 from the benzene value of 1.23. This effect has been seen in the π band of fluoroethylene ($\beta = 0.82$) compared with ethylene ($\beta = 1.25$) [3,26]. The ranges of β for the bands II and III in fluorobenzene are 0.03 to 0.26 and -0.33 to 0.18, respectively. This is the reverse of the order of the β ranges for the corresponding bands in benzene which for band II is -0.18 to -0.03 and for band III is -0.01 to 0.26. This reversal will be used in section 4 to assign the corresponding fluorobenzene orbitals. The value of β drops down to about -0.52 for the sharp peak at 13.9 eV (band IV) and then rises to about 0.41 and 0.42 for bands V and VI, respectively. It then drops to a minimum value of about -0.11 for the peak of band VII and ranges from 0.10 to 0.37 for band VIII.

The values of β for chlorobenzene are shown in fig. 3 and listed in table 3. For bands I and I_a they again range from 0.87 to 1.17. In band II, β has dropped to the range 0.44 to 0.68 and rises sharply to 1.25 at the beginning of band III from where it drops very rapidly to 0.51 at the end of that band. This strong energy dependence of β over

the 0.27 eV range of band III is unusual but is reproducible and will be discussed in section 4. β rises again in band V and is fairly low (-0.38) for the maximum of band VIII.

The values of β for bromobenzene are shown in fig. 4 and listed in table 4 along with the measurements of Milyaev and Vilesov [23]. The agreement of the two different measurements is only fair; the largest discrepancy is for band IV. There is probably a systematic error in either of the measurements, but a careful search for sources of systematic errors in our apparatus yielded negative results and we believe our values to be free of such errors.

The results for bromobenzene are similar to that for chlorobenzene in that β is relatively high for the first four peaks (bands I to III). Of particular interest is band III where β ranges from 0.76 to 1.19 over a narrow energy range of about 0.27 eV. In band IV, β has dropped to about -0.09 and then rises to a maximum of 0.4 for band V. Finally, it drops to -0.29 for the band at 15.2 eV (band VIII), which is similar to the bands at 15.4 eV in chlorobenzene (band VIII), 16.4 eV in fluorobenzene (band VII), and 14.8 eV in benzene (band V).

The results of the measurements for iodobenzene are shown in fig. 5 and listed in table 5. Once again the values of β range from 0.84 to 1.39 for bands I through IV, and for band IV have a strong, sharply decreasing dependence on the IP. The interesting features of the variation of β with IP for the rest of the spectrum are the high value (0.50) for band VI and the low value (-0.09) for the intense band IX, which is similar to the corresponding bands in the other four molecules examined. In addition, for band XI, β ranges from 0.27 to 0.45, which

are close to the corresponding ranges for the bands near 17 eV in the other molecules.

4. Discussion

4.1 General considerations

We now indicate how trends presented in section 3 can be used to make assignments in the photoelectron spectra.

Upon monohalogenation of benzene the symmetry of the point group of the molecule drops from D_{6h} to C_{2v} . (In the C_{2v} standard [27] coordinate system the z and y axes lie in the molecular plane, the first one being the C_2 axis and the x axis is perpendicular to the molecular plane.) Thus the π orbital of symmetry e_{1g} is expected to be split into orbitals of a_2 and b_1 symmetry in the C_{2v} point group.

In benzene, the band at 9.2 eV is well established [18,21] to be due to ionization from the e_{1g} orbital and this band is slightly split due to the Jahn-Teller effect [28] (peaks I and I_a in fig. 1). Halogenation eliminates this effect but introduces a splitting due to the inductive and resonance interactions of the halogens [29,30] as can be seen in figs. 2 through 5 (peaks I and I_a in figs. 2 through 4 and peaks I and II in fig. 5). The splitting is 0.6 to 0.7 eV for the four halobenzenes.

As mentioned in section 3 the vertical IP of the first band decreases from 9.2 eV in benzene to 8.7 eV in iodobenzene. In general, inductive effects are stabilizing and tend to increase the IP whereas the stabilizing influence of resonance interactions is on the ionic state and tends to decrease the IP [29]. Therefore, this decrease in the first IP is attributed to the resonance effect of the halogenation on the π orbital. The halogen atom should also shift the other π and σ orbitals of benzene (see section 4.3). It is expected that the resonance inter-

actions should be largest for iodine and the inductive effect should be largest for fluorine [31].

4.2 Bands associated to halogen lone pair orbitals

The very sharp peak in the spectrum of fluorobenzene at 13.9 eV (peak IV of Fig. 2) has been attributed [16] to ionization from the fluorine lone pair p_x and p_y orbitals. In chlorobenzene the two sharp peaks (bands II and III in fig. 3) are separated by 0.4 eV from one another. In bromobenzene the corresponding peaks (bands II and III in fig. 4) are separated by 0.6 eV and in iodobenzene (bands III and IV in fig. 5) by 0.8 eV. The main question is whether the splitting of these orbitals is due to a spin-orbit type of interaction or to a difference between the p_x and p_y halogen orbital interactions with the benzene π orbitals. The spin-orbit splittings for the two lowest states of atomic Cl^+ , Br^+ , and I^+ are, respectively, 0.07, 0.31, and 0.63 eV [32]. The fact that the halobenzene separations just described are larger than these atomic splittings seems to indicate that the interaction responsible for the former is not solely of spin-orbit character. Brogli and Heilbronner [33] have argued that there is a competition between spin-orbit coupling and resonance interaction in the alkyl halides. They have shown that increasing that interaction increases the splitting between halogen lone pairs and that the spin-orbit contribution to this splitting decreases. Baker *et al.* [20] have obtained the photoelectron spectra of the monohalobenzenes and in each case have assigned two bands to ionization of the in-plane p_y and out-of-plane p_x halogen orbitals. The p_x orbital has a higher IP and is slightly

broadened to its interaction with the π orbitals of benzene. Boschi and Salahub [34], Debies and Rabalais [35], and Clark et al. [36] have concurred with this assignment. Finally, Dunbar and Fu [37] have done a two-photon photodissociation study of bromobenzene cations trapped in an ion cyclotron resonance (ICR) cell and have shown by consideration of the appropriate selection rules that the peak at 11.25 eV in the bromobenzene photoelectron spectrum is due to ionization from the p_x orbital of Br.

The results of the measurements of β presented here lead to assignments of the halogen lone pair orbitals which agree with the above assignments. In all previous cases of bands split by spin-orbit coupling for which β has been measured, the β values of the two spin-orbit components do not differ by more than 0.1 units. This has been studied by Carlson and White [8] for the halomethanes and is true even for xenon [6] which has a spin-orbit splitting of 1.3 eV. As can be seen from tables 3, 4, and 5, the difference in β for the two lone pair peaks is as high as 0.8 units. On this basis we argue that the splitting of the lone pair halogen peaks is not primarily due to spin-orbit coupling. In view of Brogli and Heilbronner's analysis [33] this suggests that resonance effects may be primarily responsible for this splitting.

The value of β sharply decreases with increasing IP for the out-of-plane p_x orbital of the halogen atom for chlorobenzene (band III of fig. 3), bromobenzene (band III of fig. 4), and iodobenzene (band IV of fig. 5). The rate of this decrease is 2.7 eV^{-1} for chlorobenzene,

1.6 eV⁻¹ for bromobenzene, and 2.2 eV⁻¹ for iodobenzene as can be seen from the corresponding figures. These values are unusually high; for direct photoionization, the energy dependence of β is typically less than 0.4 eV⁻¹ [38, 39]. One possible cause of this sharp energy dependence could be autoionization, since this process has been shown to cause anomalous variation of β with electron energy for other molecules [2]. However, it is very unlikely that autoionization in a given band (whose IP decreases by about 1 eV in going from chlorobenzene to iodobenzene) would occur at the same photon energy in all three molecules. A less unlikely explanation is that this unusual energy dependence is a result of the strong mixing of the halogen p_x orbital with the benzene π orbitals. In a simplified analysis we consider the resulting orbital ψ to be a linear combination $\psi = c_1 \phi_1 + c_2 \phi_2$ where ϕ_1 is the halogen lone pair orbital and ϕ_2 is the benzene π orbital. The angular dependence of the photoelectron differential cross section comes from the square of the absolute value of the matrix element $\langle \psi_e | \hat{\epsilon} \cdot \underline{r} | c_1 \phi_1 + c_2 \phi_2 \rangle$ where $\hat{\epsilon}$ is the unit vector in the polarization direction of the light beam, $\underline{r}$ is the position vector of the electron, and ψ_e is the wavefunction of the ejected photoelectron. Multiplying the matrix element by its complex conjugate leads to four terms of which two have an angular dependence associated with the ϕ_1 orbital alone and the ϕ_2 orbital alone. These terms should lead to β values which have a gradual energy dependence of β for the E_{1g} band of benzene (see band I of fig. 1) and of the lone pair electrons in atomic halogens [8, 40] or in the halomethanes [8]. The other two terms

represent interference between electron waves photoejected from the two orbitals ϕ_1 and ϕ_2 and could be very energy-sensitive and lead to a strongly energy-dependent β . The lack of such a strong energy dependence for the corresponding orbital in fluorobenzene (band IV in fig. 2) is consistent with this simple model since the fluorine p_x orbital energy is about 4 eV lower than the benzene e_{1g} orbital and the corresponding mixing between these orbitals should be small. Of course these arguments are very qualitative and should be regarded as highly speculative in the absence of other experimental or theoretical data.

4.3 Bands associated to sigma orbitals

We now discuss the origin of the peaks in the spectra of benzene at 14.8 eV (band V in fig. 1), fluorobenzene at 16.3 eV (band VII in fig. 2), chlorobenzene at 15.4 eV (band VIII in fig. 3), bromobenzene at 15.2 eV (band VIII in fig. 4) and iodobenzene at 16.5 eV (band IX in fig. 5). The pattern in these ionization potentials and the similarity of their β values for the corresponding band maxima (all of which are in the range of -0.1 to -0.4) suggests that these peaks are associated with the removal of an electron from the same type of orbital in each of the five molecules. Since the relative intensity of these bands with respect to the neighboring bands is larger than unity for the halobenzenes, it could be argued that the corresponding orbital is doubly degenerate. If this argument were correct, the benzene orbital associated with this peak should be the doubly degenerate $2e_{1u}$ which would become a_1 and b_2 orbitals in the C_{2v} symmetry of the halo-

benzenes. However, this would necessitate reordering the assignments of the b_{2u} and e_{1u} orbitals of C_6H_6 made by Jonsson and Lindholm [25] and by Asbrink et al. [18]. Calculations of the energy levels of benzene by Hay and Shavitt [41] and by Ermler et al. [42] show that the e_{1u} orbital in C_6H_6 has an energy about 0.8 eV below the b_{2u} orbital. However, comparing these calculations with the experimental $C_6H_6^+$ band energies requires the use of Koopmans' approximation which in many cases is not accurate to within 0.8 eV [43]. Unfortunately, Hay and Shavitt [41] did not calculate the energies of these ionic states in their study of $C_6H_6^+$. Freiser and Beauchamp [44] and Orłowski et al. [45] studied the two-photon photodissociation of benzene ions trapped in an ICR cell but were unable to establish the nature of the 14 eV state of this ion. Potts et al. [46] give rather convincing arguments that the e_{1u} orbital does have a lower IP than the b_{2u} one. If the strong intensity of the bands in the halobenzenes are ignored and assignments of the e_{1u} and b_{2u} orbitals of benzene of Jonsson and Lindholm [25] are accepted, the peaks near 15 eV in the halobenzene spectra can be attributed to ionization from a b_2 σ orbital. This assignment is consistent with the fact that the halogen atoms are expected to shift the σ orbitals to a higher IP due to the inductive effect and the magnitude of the shift should be largest for fluorine [30].

Let us next consider the bands around 17 eV. Their positions and shapes in all five molecules are similar and the corresponding vertical β are in the range 0.3 to 0.4, except for chlorobenzene, which is slightly higher. This indicates that these bands are due to

ionization from an orbital that is similar in all five molecules.

In benzene it has been assigned by Asbrink et al. [18] and by Johnsson and Lindholm [25] as due to ejection of an electron from the $3a_{1g}$ orbital. Baker et al. [20] agree with this assignment since their vibrational analysis indicates that a σ_{CC} bonding orbital is involved. Our angular distribution measurements reinforce this assignment since β values of 0.3 to 0.4 are typical [4-10] of σ C-C orbitals. Thus we conclude that the state in $C_6H_6^+$ at 16.9 eV is $^2A_{1g}$ and in the halobenzene ions at corresponding energies it is the 2A_1 state.

4.4 Bands associated with the lowest π orbital

In benzene the lowest energy (highest IP) π orbital is $1a_{2u}$ which is associated [18, 21, 22, 25] with the band at 12.3 eV. The corresponding β value is in the range 0.0 to 0.26 which is higher than the range -0.18 to -0.03 for the σe_{2g} orbital associated with the 11.6 eV band. A similar variation in β values for the bands in fluorobenzene suggests that the transition at 12.2 eV is of π type (b_1 symmetry) and that at 13.0 eV is due to ejection of a σ electron. This assignment agrees with that given by Baker et al. [20], Momigny and Lorquet [47], Streets and Caesar [30], Dewar and Kelemen [48], and Narayan and Murrell [49]. This use of the β values to distinguish between σ and π orbitals in fluorobenzene is similar to that used by Kobayashi and Nagakura [22] to distinguish σ and π orbitals in benzene and hexafluorobenzene.

A similar analysis permits us to assign the band at 13.2 eV in chlorobenzene (band V, fig. 3) to the lowest π orbital, due to the sharp rise in β between the onset (at about 12.8 eV) and the peak of that band. This differs from the assignment of Baker et al. [20] of the band at 12.3 eV to this lowest π orbital. Those authors, however, do not justify their claim. Similarly, we assign the lowest π band in bromobenzene to the peak at 12.6 eV (band V, fig. 4) due to the increase of the value of β as one approaches this band from its low IP side. Again, Baker et al. [20] have favored the assignment of this π orbital to the adjacent peak at 12.0 eV (band IV, fig. 4) without substantiating this assignment. Finally, for analogous reasons, we attribute the peak at 12.3 in iodobenzene (band VI, fig. 5) to ionization of the lowest energy π orbital. This agrees with the assignment of Boschi and Salahub [34].

5. Summary and conclusion

It has been shown that by observing trends in the asymmetry parameter β and similarities in the photoelectron spectra of benzene and the monohalobenzenes it is possible to make assignments in the spectra and thereby learn more about the chemical nature of these molecules. In particular we have identified the peaks resulting from ionization of the lone pair halogen electrons and have argued that the corresponding orbitals are split by resonance rather than spin-orbit interactions. We have also assigned the peaks associated with ionization from two σ orbitals and the lowest π orbitals of the halobenzenes.

The discussion of section 4 indicates that the photoelectron angular distributions contain important information regarding the orbital structure of molecules. Initially it was expected that measurements of β in benzene and the halobenzenes would permit a differentiation between σ and π types of orbitals as has been found for ethylene [1, 3, 9] and in analogy with atoms where β depends on the orbital angular momentum ℓ of the electron to be ejected [12, 13]. In addition, however, it appears that β is sensitive to such diverse chemical effects as the resonance and inductive interactions [3], the interactions between lone pair and aromatic electrons, and auto-ionization [2]. A reliable theoretical calculation of the effect of these electron interactions on β is presently impractical. Therefore, a continuation of studies of the present kind, in which photoelectron angular distributions are measured for series of related molecules,

is very important as they may lead to the development of empirical rules relating β to interesting characteristics of the electronic structure of molecules.

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Table 1
 β values and ionization potentials for benzene at 584 Å

Band	Initial Orbital ^{a)}	Vertical IP (eV)	β				
			This Work		Carlson and Anderson ^{c)}	Kobayashi and Nagakura ^{d)}	Milyaev and Vilesov ^{e)}
			Range Across Band ^{b)}	Vertical			
I	$1e_{1g}\pi$	9.22	1.03 ± 0.11 to 1.23 ± 0.04	1.23 ± 0.04	1.15	1.29 ± 0.05	1.3
Ia	$1e_{1g}\pi$	9.50	0.86 ± 0.10	0.86 ± 0.10	1.00		0.95
II	$3e_{2g}\sigma$	11.48	-0.18 ± 0.07 to -0.03 ± 0.08	-0.18 ± 0.07	-0.13	-0.11 ± 0.05	-0.3
III	$1a_{2u}\pi$	12.29	-0.01 ± 0.10 to 0.26 ± 0.06	0.24 ± 0.03	0.16	0.22 ± 0.05	0.2
IV	$3e_{1u}\sigma$	13.94	-0.06 ± 0.06 to 0.22 ± 0.05	0.22 ± 0.05	0.48		0.6
V	$1b_{2u}\sigma$	14.80	-0.34 ± 0.05 to -0.07 ± 0.13	-0.26 ± 0.05	0.03	-0.25	-0.1
VI	$2b_{1u}\sigma$	15.46	0.22 ± 0.12	0.34 ± 0.09	0.79		0.2
VII	$3a_{1g}\sigma$	16.86	-0.03 ± 0.17 to 0.44 ± 0.06	0.44 ± 0.06	0.70		0.35

a) The orbital assignments for benzene are those made in ref. [21].

b) The first and second values quoted are respectively the lowest and highest values of β for the corresponding band. The uncertainties given are twice the standard deviation.

c) Ref. [10]. d) Ref. [22]. e) Ref. [23].

f) Values estimated from the figures in ref. [24]. The values given here correspond to the most intense features of the spectral bands.

Table 2

 β values and ionization potentials for fluorobenzene at 584 Å

Band	Initial Orbital	Vertical IP (eV)	β a)	
			Range Across Band	Vertical
I	$b_1\pi$	9.22	0.86 ± 0.06	0.91 ± 0.06
Ia	$a_2\pi$	9.80	0.91 ± 0.10 to 1.09 ± 0.04	1.09 ± 0.04
II	$b_1\pi$	12.20	0.03 ± 0.08 to 0.26 ± 0.08	0.26 ± 0.04
III	σ	13.01	-0.33 ± 0.16 to 0.18 ± 0.10	-0.10 ± 0.08
IV	F np_x, np_y	13.89	-0.52 ± 0.13 to -0.24 ± 0.12	-0.52 ± 0.13
V		14.61	0.09 ± 0.15 to 0.41 ± 0.04	0.40 ± 0.06
VI		15.14	0.17 ± 0.07 to 0.42 ± 0.06	0.42 ± 0.06
VII	$b_2\sigma$	16.27	-0.11 ± 0.08 to 0.32 ± 0.19	0.06 ± 0.04
VIII	$a_1\sigma$	17.79	0.10 ± 0.16 to 0.37 ± 0.13	0.37 ± 0.13

a) The range and uncertainties have the same meaning as in table 1.

Table 3
 β values and ionization potential for chlorobenzene at 584 Å

Band	Initial Orbital	Vertical IP (eV)	β a)	
			Range Across Band	Vertical
I	$b_1\pi$	9.08	1.11 ± 0.06 to 1.16 ± 0.06	1.11 ± 0.06
Ia	$a_2\pi$	9.69	0.87 ± 0.09 to 1.17 ± 0.09	1.17 ± 0.09
II	$Cl\,np_y$	11.31	0.44 ± 0.09 to 0.68 ± 0.02	0.68 ± 0.02
III	$Cl\,np_x$	11.70	0.51 ± 0.09 to 1.25 ± 0.12	1.25 ± 0.12
IV		12.21	-0.03 ± 0.07 to 0.16 ± 0.08	0.07 ± 0.06
V	$b_1\pi$	13.21	0.46 ± 0.06 to 0.83 ± 0.03	0.83 ± 0.03
VI		14.49	0.11 ± 0.07 to 0.40 ± 0.08	0.34 ± 0.06
VII		14.71	0.12 ± 0.12 to 0.25 ± 0.05	0.15 ± 0.07
VII	$b_2\sigma$	15.36	-0.38 ± 0.14 to 0.18 ± 0.08	-0.38 ± 0.14
IX		15.90	0.24 ± 0.08 to 0.47 ± 0.10	0.47 ± 0.10
X	$a_1\sigma$	16.95	-0.15 ± 0.14 to 0.66 ± 0.08	0.66 ± 0.08

a) The range and uncertainties have the same meaning as in table 1.

Table 4

 β values and ionization potentials for bromobenzene at 584 Å

Band	Initial Orbital	Vertical IP (eV)	β		Milyaev and Vilesov ^{b)}
			This Work ^{a)}		
			Range Across Band	Vertical	
I	$b_1\pi$	9.05	0.88 ± 0.12 to 1.04 ± 0.03	1.04 ± 0.03	1.3
Ia	$a_2\pi$	9.68	0.73 ± 0.08 to 1.07 ± 0.05	1.07 ± 0.05	1.16
II	Br np_y	10.65	0.88 ± 0.09	0.88 ± 0.09	1.17
III	Br np_x	11.25	0.76 ± 0.09 to 1.19 ± 0.05	1.19 ± 0.05	0.9
IV		12.01	-0.09 ± 0.06 to 0.15 ± 0.08	-0.07 ± 0.06	0.73
V	$b_1\pi$	12.66	0.15 ± 0.05 to 0.40 ± 0.05	0.40 ± 0.05	0.50
VI		14.07	0.16 ± 0.07 to 0.34 ± 0.07	0.16 ± 0.07	0.08
VII		14.53	-0.03 ± 0.07 to 0.32 ± 0.06	0.21 ± 0.06	0.08
VIII	$b_2\sigma$	15.20	-0.29 ± 0.06 to 0.20 ± 0.04	-0.29 ± 0.05	0.1
IX		15.70	0.12 ± 0.11 to 0.39 ± 0.15	0.12 ± 0.11	0.13
X	$a_1\sigma$	16.85	0.15 ± 0.12 to 0.51 ± 0.16	0.33 ± 0.03	

^{a)} The range and uncertainties have the same meaning as in table 1.^{b)} Ref. [23].

Table 5

 β values and ionization potentials for iodobenzene at 584 Å

Band	Initial Orbital	Vertical IP (eV)	β a)	
			Range Across Band	Vertical
I	$b_1\pi$	8.67	0.91 ± 0.13 to 1.38 ± 0.07	1.38 ± 0.07
II	$a_2\pi$	9.41	1.02 ± 0.05 to 1.26 ± 0.11	1.26 ± 0.11
III	I np_y	9.64	1.06 ± 0.07 to 1.29 ± 0.04	1.29 ± 0.04
IV	I np_x	10.47	0.84 ± 0.11 to 1.39 ± 0.09	1.11 ± 0.07
V		11.48	0.03 ± 0.04 to 0.20 ± 0.07	0.03 ± 0.04
VI	$b_1\pi$	12.23	-0.07 ± 0.12 to 0.50 ± 0.13	0.06 ± 0.06
VII		13.48	0.14 ± 0.09	0.14 ± 0.09
VIII		14.25	0.28 ± 0.05 to 0.46 ± 0.05	0.38 ± 0.07
IX	$b_2\sigma$	14.88	-0.09 ± 0.09 to 0.13 ± 0.09	-0.09 ± 0.09
X		15.42	0.22 ± 0.20 to 0.47 ± 0.12	0.22 ± 0.20
XI	$a_1\sigma$	16.55	0.27 ± 0.10 to 0.45 ± 0.08	0.38 ± 0.10

a) The range and uncertainties have the same meaning as in table 1.

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Figure Captions

- Fig. 1. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for benzene. The spectrum was obtained at a detector angle of 54.7° using 511 adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 seconds.
- Fig. 2. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for fluorobenzene. The spectrum was obtained at a detector angle of 54.7° using 511 adjacent 18 meV wide channels and 60 scans. Total dwell time per channel was 60 seconds.
- Fig. 3. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for chlorobenzene. The spectrum was obtained at a detector angle 54.7° using 511 adjacent 18 meV wide channels and 60 scans. Total dwell time per channel was 60 seconds.
- Fig. 4. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for bromobenzene. The spectrum was obtained at a detector angle 54.7° using 511 adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 seconds.

Fig. 5. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for iodobenzene. The spectrum was obtained at a detector angle 54.7° using 511 adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 seconds.

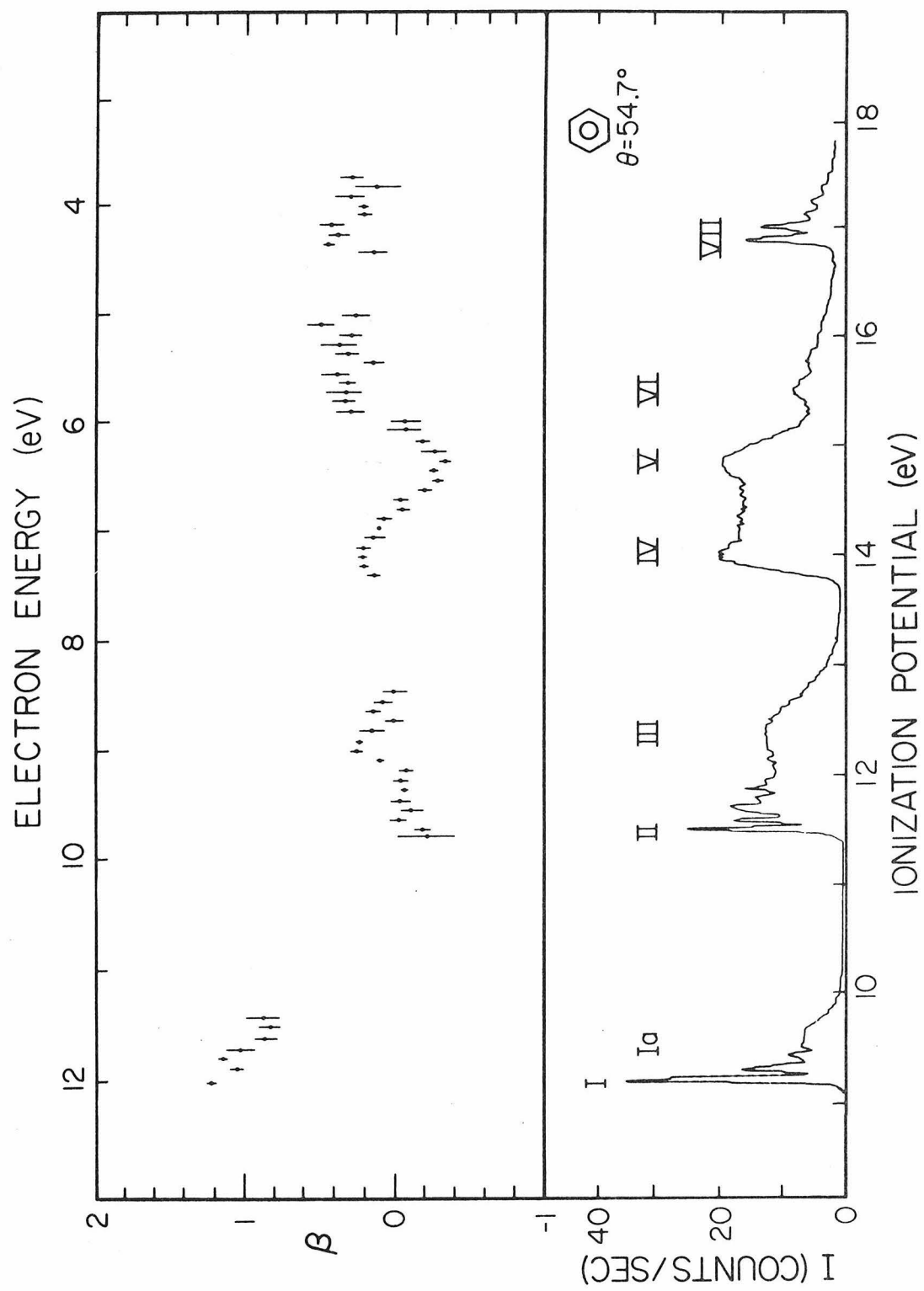


Figure 1.

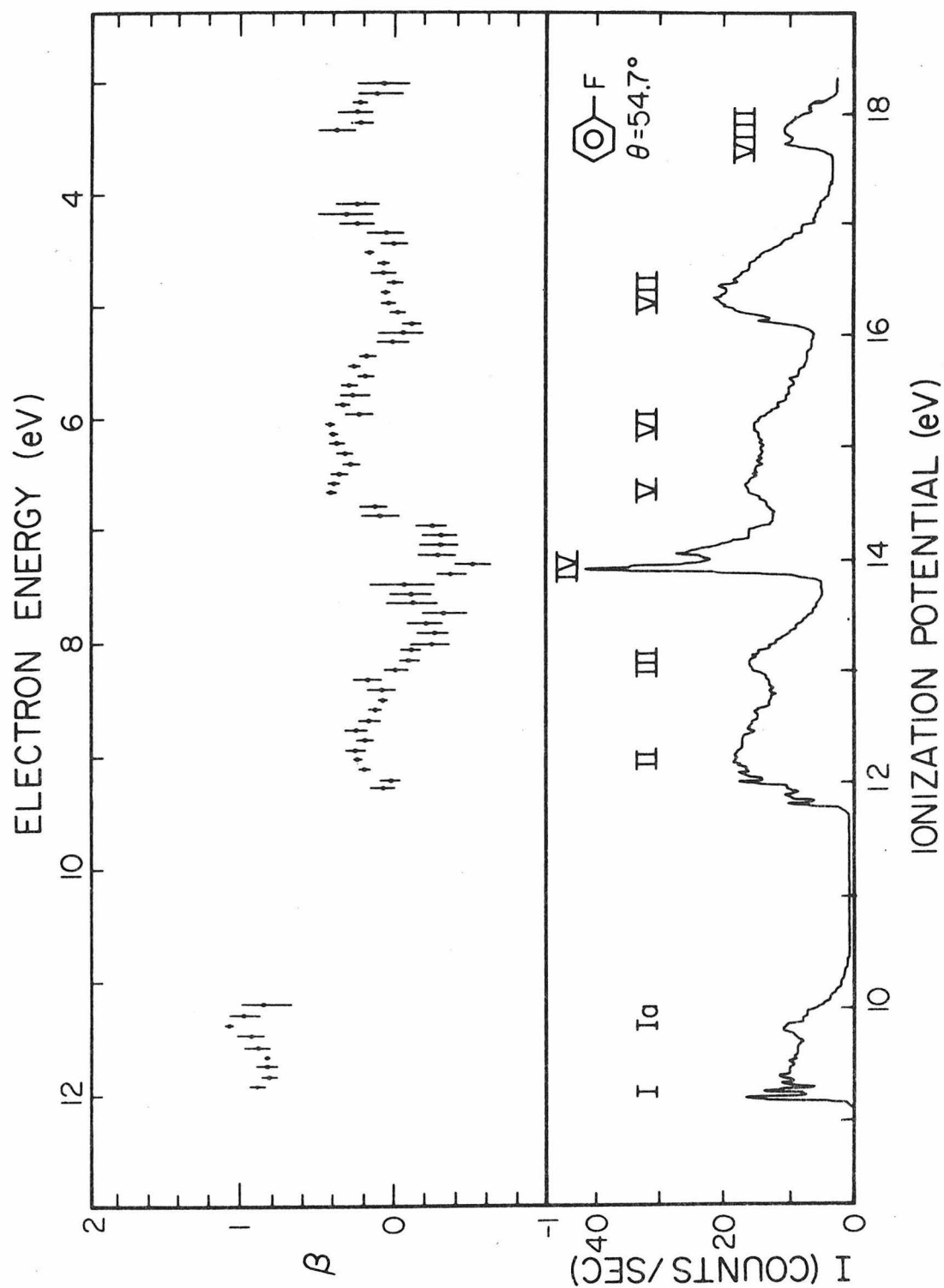


Figure 2.

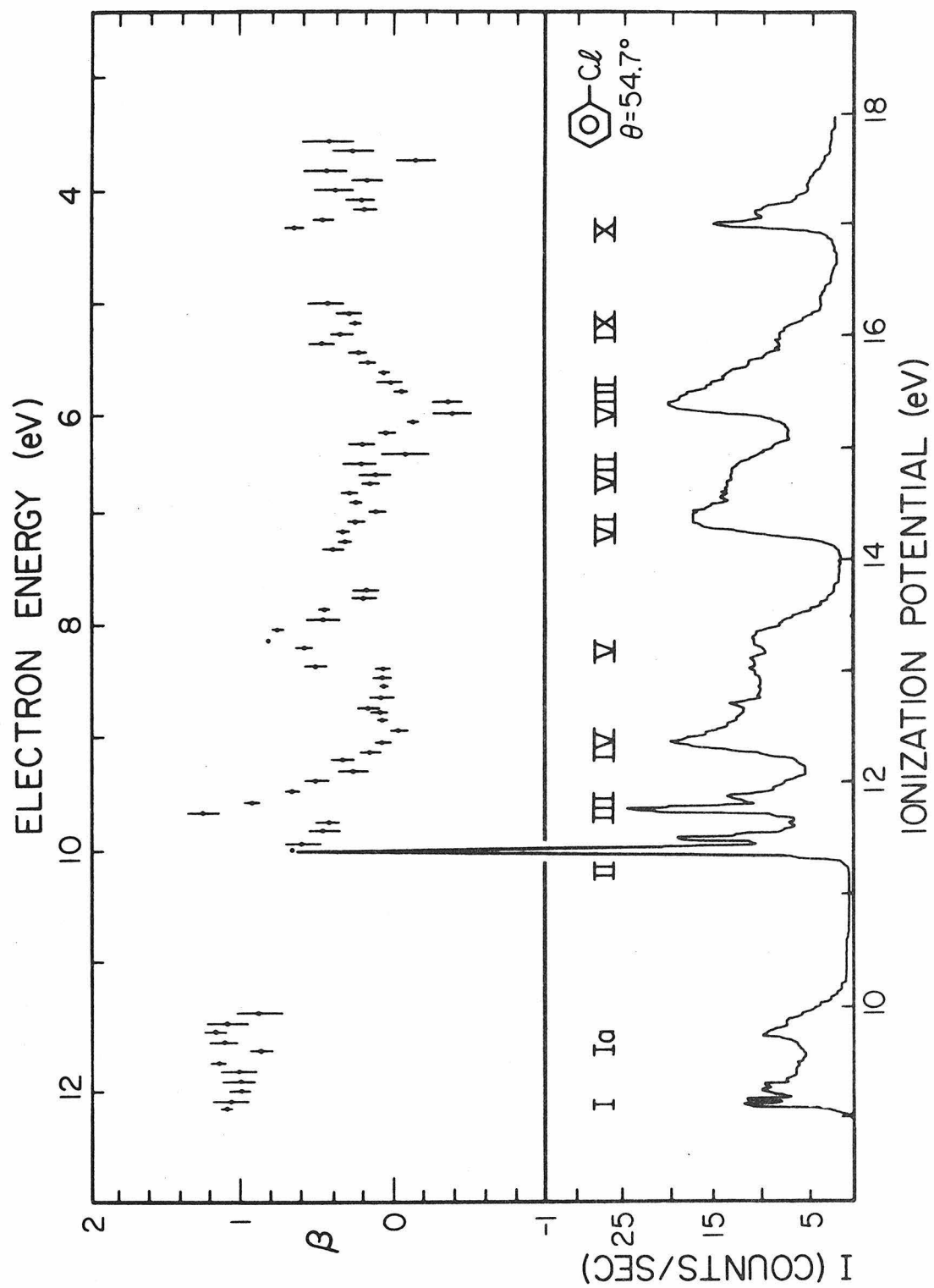


Figure 3.

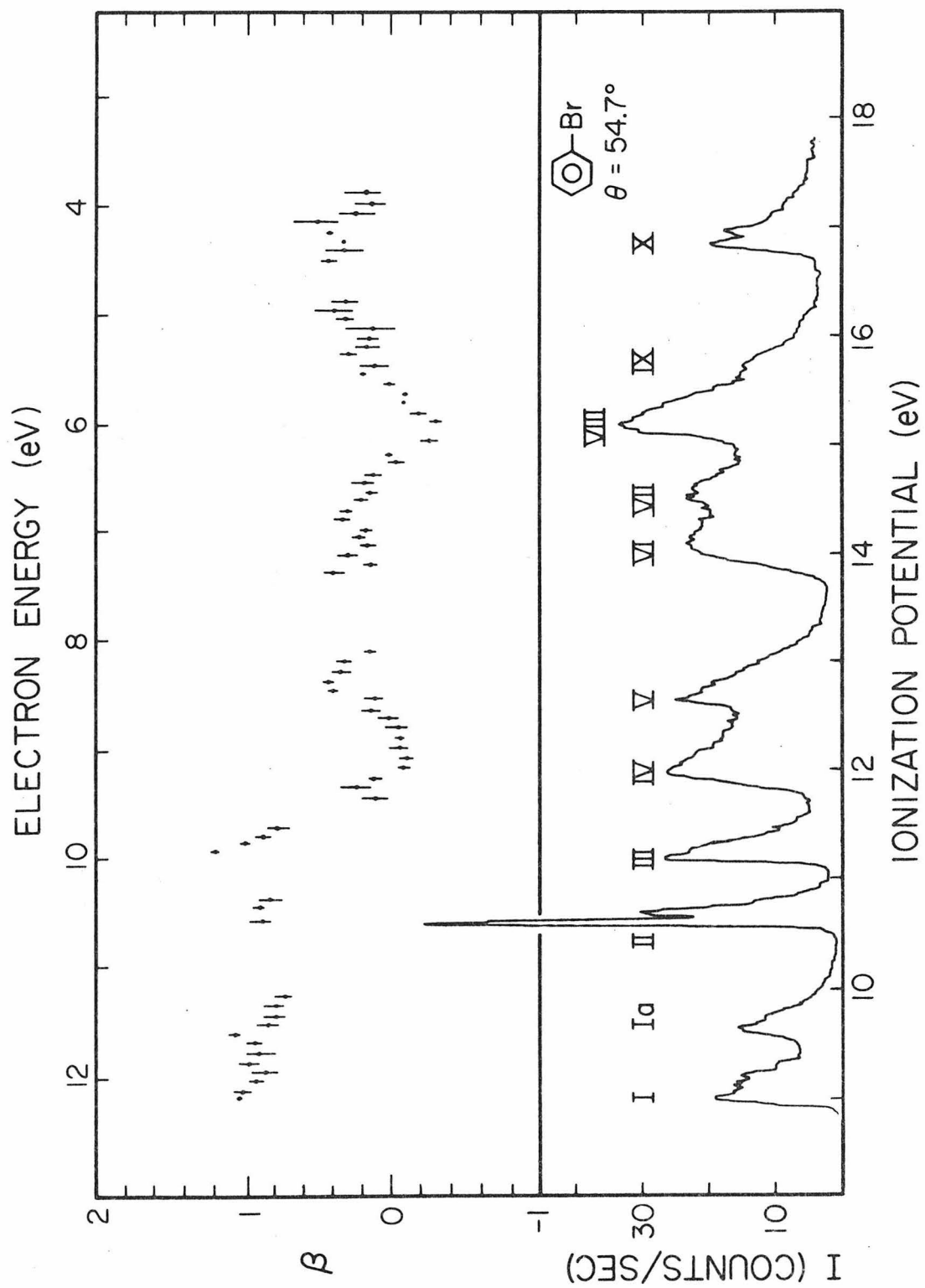


Figure 4.

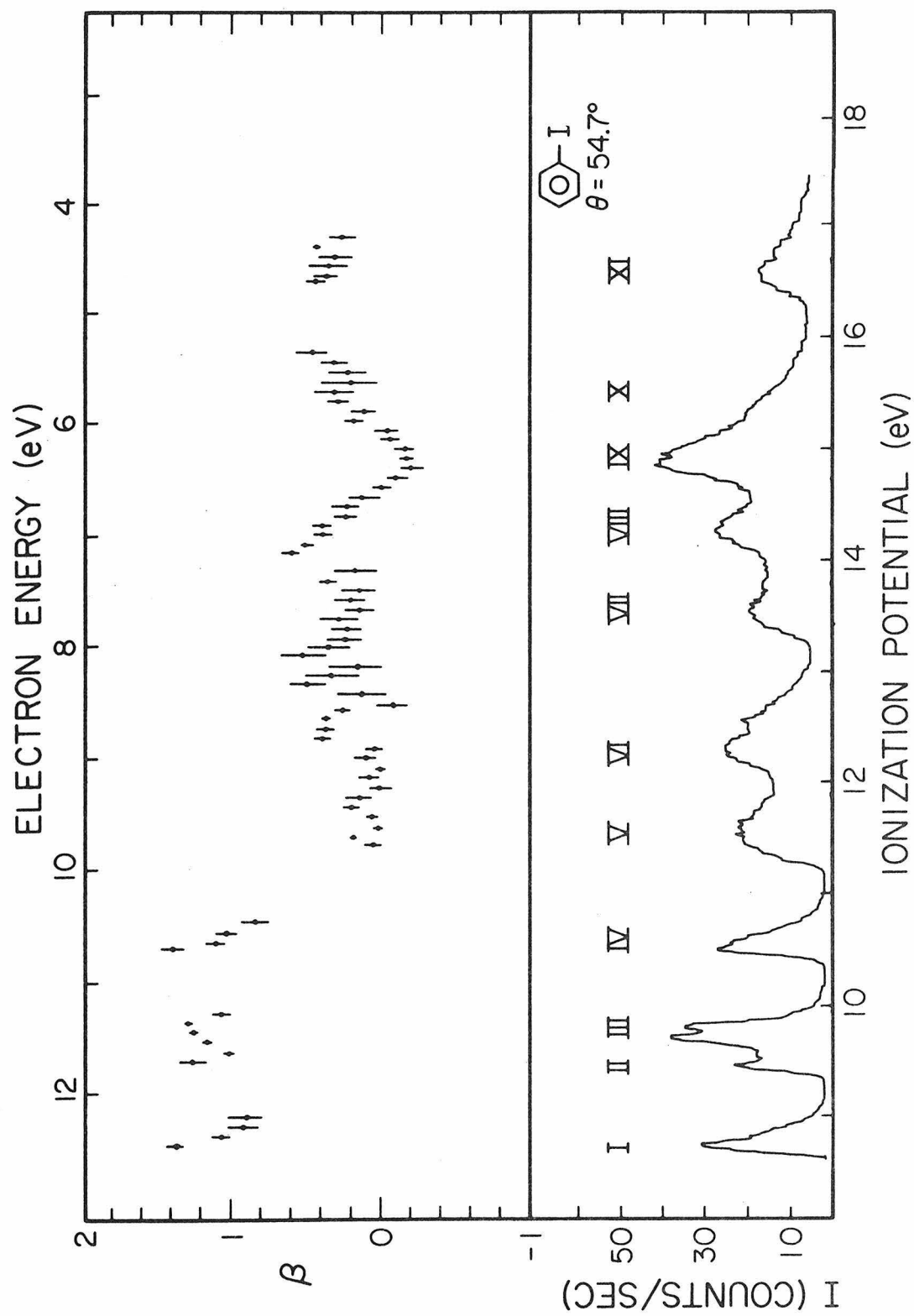


Figure 5.

CHAPTER 6: RESULTS AND DISCUSSION

Paper 3: Angular Distributions in the Photoelectron Spectroscopy of SF₆

ANGULAR DISTRIBUTIONS IN THE PHOTOELECTRON
SPECTROSCOPY OF SF₆*

Jeffrey A. SELL[†] and Aron KUPPERMANN

Arthur Amos Noyes Laboratory of Chemical Physics,[‡]
California Institute of Technology, Pasadena, California 91125, USA

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The photoelectron angular distributions of SF₆ have been obtained using 584 Å light. The assignments of the photoelectron bands to the corresponding orbitals are based on the trends in the asymmetry parameter β and other theoretical and experimental data.

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[‡] Contribution No. 5749.

I. INTRODUCTION

The results of measurements of the angular distributions in the photoelectron spectrum of SF_6 obtained with 584 Å radiation are reported. This paper is one of several from this laboratory which describe the results of measurements of the photoelectron angular distributions in small molecules such as CO [1], N_2 [2], the series of fluoroethylenes [3], and the series of monohalobenzenes [4]. These results indicate that the angular distribution measurements are very important since one can extract from them information on the details of the ionization process and also on the orbital structure of molecules which fixed-angle spectra alone cannot furnish. There has recently been much interest in SF_6 [5, 6] and measurements of its photoelectron angular distributions serves to contribute to the body of knowledge on this molecule.

It has previously been shown [7-9] that the differential cross section $d\sigma/d\Omega$ for photoionization of an atom or molecule using unpolarized light has the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 - \frac{\beta}{2} P_2(\cos \theta) \right] \quad (1)$$

where σ is the integral photoionization cross section for the transition being considered, $P_2(\cos \theta)$ is the second Legendre polynomial, θ is the angle between the momentum vector of the ejected electron and the direction of propagation of the light beam, and β is the asymmetry parameter which ranges from -1 to +2. For photoionization of atoms,

β depends on the angular momentum of the orbital from which the electron was ejected and on the kinetic energy of the photoelectron[7, 8]. In the molecular case, β similarly depends on the kinetic energy of the photoelectron, and on the nature of the orbitals from which the electron is ejected. For example, in fluorine substituted ethylenes[3] it seems to be sensitive to the resonant interactions that occur between the lone pair fluorine orbitals and the carbon-carbon π bond. It has also been found [10] that in hydrocarbons such as methyl-substituted ethylenes and linear dienes, the value of β is about 0.3 to 1.0 units higher for ionization from a π orbital than from a σ orbital. This effect has also been observed by White, Carlson, and Spears [11]. Finally, Carlson and White [12] have shown that for a given molecular orbital β increases with the atomic number of the atoms involved. They have also shown that β is essentially the same for the two components of a single electronic band which are split by spin orbit interactions or by Jahn-Teller interactions. These findings are useful for the analysis of our SF_6 results.

II. EXPERIMENTAL

The apparatus used in the present study has been described in detail previously [13] and will be summarized here only briefly. The radiation produced by a helium discharge lamp (predominantly 584 Å) interacts with the sample vapor at a pressure of about 5 mTorr contained in a sample chamber. The photoelectrons produced are energy-analyzed in a hemispherical electrostatic analyzer and detected with a Spiraltron electron multiplier. The analyzer and detector are mounted on a large gear wheel and are rotated about the center of the sample chamber from 45° to 120°. The apparatus is carefully shielded against stray magnetic fields and background is subtracted before β is calculated.

The SF₆ sample was obtained from Matheson Gas Products and had a stated purity of 99.8%. The energy scale was calibrated by obtaining the spectrum of a mixture of SF₆ and a small amount (less than 10%) of argon. The accuracy of the apparatus was checked by its ability to reproduce the known value [13-16] of β for production of the ²P_{3/2} state of the argon ion.

III. RESULTS

The photoelectron spectrum obtained with 584 Å radiation and a plot of β as a function of ionization potential (IP) are shown in Fig. 1. The spectrum has five peaks at 15.7, 17.0, 18.4, 18.7, and 19.8 eV (bands I through V) and a shoulder (at 17.2 eV) on the 17.0 eV peak. The peak positions and corresponding β ranges are given in Table 1. The interesting features of the spectrum are the wide range of band intensities and the vibrational structure in the band at 19.8 eV (band V).

In the plot of β as a function of IP (top panel of Fig. 1) it can be seen that band I has a value of β which decreases from -0.25 to -0.33 across the band as the IP increases. Likewise, for band II, β gradually decreases from 0.14 to -0.25. Band III, whose IP is 18.4 eV, has β values increasing from -0.27 to a maximum of 0.25 decreasing thereafter to -0.16. Band IV, whose maximum intensity occurs at 18.7 eV has β values ranging from 0.02 to -0.32. In bands III and IV the maximum value of β occurs at the same energy as do the corresponding maximum intensities. Band V has a value of β which increases from -0.57 to -0.13 as the IP increases. One interesting aspect of the plot of β as a function of IP is that for all the transitions observed its values are below 0.25. By contrast, values of $\beta \geq 0.6$ are usually obtained [10,11] for carbon-carbon π orbitals.

IV. DISCUSSION

The 90° uv photoelectron spectrum of SF_6 has been reported previously by Delwiche [17], Potts et al.[18], Turner et al.[19], and Gelius [20]. The spectrum displayed in Fig. 1 was taken at the magic angle of 54.7° at which $P_2(\cos\theta) = 0$. For this angle, the relative differential cross sections for different transitions are equal to the corresponding relative integral cross sections for those transitions. For $\beta \neq 0$, this property does not hold at other angles within our angular range. Our measured β are higher for the maxima of bands III and IV than for that of band V. For these reasons the intensities of bands III and IV relative to band V in the present spectrum are lower than the corresponding relative intensities in the spectra reported previously [17-19], except for that reported by Gelius [20].

We next discuss the possibility of autoionization at $584 \text{ \AA}$ in this molecule. Potts et al.[18] obtained the photoelectron spectrum of SF_6 using both $584 \text{ \AA}$ and $304 \text{ \AA}$ incident radiation. They found that the relative intensities of the bands are quite different at the two excitation wavelengths and attributed this to autoionization at $584 \text{ \AA}$. Codling [21] obtained the ultraviolet absorption spectrum of SF_6 from $100 \text{ \AA}$ to $630 \text{ \AA}$ and observed structure in the region of $550 \text{ \AA}$ to $600 \text{ \AA}$ (22.5 eV to 20.6 eV). Potts et al.[18] attributed this structure to an autoionizing state of symmetry $^1T_{1u}$ and argued that the relatively high intensity of band II in the photoelectron spectrum occurring at 17.0 eV is due to the presence of such an autoionizing state.

In some previous photoelectron studies of other molecules [1, 2, 22] for which bands involving autoionization occur and the corresponding β

have been measured, this parameter has been found to vary steeply and/or non-monotonically with energy. The fact that in the present case β varies monotonically and slowly with electron energy across band II suggests that autoionization does not contribute to this band. This, however, is not the only conclusion possible. Instead, the relative contribution of autoionization to its intensity may be small or, less likely, that its β shows a slow energy dependence and that no significant interference occurs between the autoionization and direct process. Similarly, the slow variation of β across band I argues against a significant presence of autoionization in that band, in spite of the small value of about -0.3 for that parameter.

Assignments of the bands in the photoelectron spectrum of SF_6 by several authors, based on a variety of techniques, are compared in Table 2. Potts et al.[18] made their assignment based on the Rydberg series observed in both the vacuum uv absorption spectrum [23] and the electron impact spectra [24], which converge to the corresponding ionic states observed in the photoelectron spectrum. Gelius [20] based his assignments mainly on the relative intensities of the bands in the X-ray photoelectron spectrum. Hay [25] did an ab initio configuration interaction calculation on the states of the SF_6^+ ion. Similarly, Von Niessen et al.[26] made their assignments on the basis of their ab initio many-body calculation of SF_6 . Gianturco et al.[27] did an ab initio SCF calculation on SF_6 and used Koopmans' theorem in their assignments of the bands in the ESCA spectrum of this molecule. Finally, La Villa [28] made assignments using the x-ray emission and absorption spectrum and considering dipole selection rules for the emission of a photon. These studies represent only a fraction of the

total number of papers dealing with the assignments of the photo-electron bands in the spectrum of SF_6 but are representative of the many different methods that can be used.

The most interesting aspect of these assignments is that the theoretical studies predict that there are five orbitals whose energies are greater than -21.2 eV but the spectrum has five peaks at 15.7, 17.0, 18.4, 18.7, and 19.8 eV, and a shoulder at 17.2 eV on the high IP side of the 17.0 eV band (see Fig. 1). Most authors assign one of the two transitions at 17.2 eV and 18.4 eV to a component of the neighboring band which is split from it by Jahn-Teller (JT) interactions and the other transition to the fifth orbital which is predicted to lie below -21.2 eV. However, as can be seen from Table 2, there is disagreement about which band represents a second JT component and which corresponds to a different orbital.

We use the results of our measurements of β for this molecule to argue that the transition at 17.2 eV is a JT component of band II and that band III corresponds to ionization from the t_{2u} orbital. Carlson and White [12] have shown that the value of β for the two components of a band which are split by JT interactions are essentially equal to one another for the halomethanes. Leng and Nyberg [29] have also found this to be true for cyclopropane. The slow monotonic change of β across band II in SF_6 is typical of the general variation of β with electron energy [10]. On this basis, we assign the shoulder on this band to a JT component.

This argument ignores any complications due to autoionization. On the other hand, we interpret the significantly more rapid and non-monotonic variation of β across bands III and IV to correspond to ionization from different initial orbitals. The overall assignments we prefer, based on these results and on the available theoretical calculations, are given in the last column of Table 2. The reasons for this preference are spelled out in the next few paragraphs.

Usually, high quality configuration interaction calculations, such as those of Hay [25], tend to predict the correct ordering of the orbital energies [30], even though their absolute values may be in error by 1 eV or more. The ordering of the *ab initio* configuration interaction [25] and many-body [26] orbitals of Table 2 is the same. The SCF calculations interchange the t_{2u} and t_{1u} orbitals, but such calculations are less reliable than the other two. It is possible that the *ab initio* calculations have predicted the wrong relative ordering of the e_g and t_{2g} orbitals since the order presented in these papers is opposite of that observed in other octahedral molecules [31]. However, this is unlikely since the energy difference between the orbital energies calculated by Hay and the experimental values would then be 2.6 eV for the t_{2g} and -0.7 eV for the e_g orbital and these differences are inconsistent with the sign and magnitude of the corresponding difference for the other orbitals in that study. For this reason, we accept as valid the orbital ordering of Hay [25] and of Von Niessen et al. [26]. This, combined with the association of the 18.4 eV and 18.7 eV features to different orbitals, leads to our assignments of the observed transitions given in the last column of Table 2. This set of assignments differs from all others in that table

by at least one orbital.

The differences between our assignments and those of Potts et al. [18] may be related to their use of Rydberg series in the vacuum ultraviolet and electron impact spectra. If the Rydberg series assignments are incorrect then the photoelectron assignments would be, too. In addition, Potts et al. [18] and Gelius [20] both use arguments that assign the photoelectron bands on the basis of a comparison of their relative intensities to the degeneracies of the orbitals. However, their spectra were obtained at $\theta = 90^\circ$ for which the differential cross sections are not proportional to the integral photoionization cross sections. In addition, this type of argument which relates orbital degeneracy to photoelectron band intensity has previously been shown [32] to be inadequate in some cases. The reasons for the discrepancy between our assignments and those of LaVilla [28] are more difficult to assess. The difference in the two assignments is the relative order of the e_g and t_{2g} orbitals. His assignment of these two orbitals is based on the vibrational structure in band V, which he interprets to be the a_{1g} totally symmetric vibration. However, Von Niessen et al. [26] argue that this vibrational assignment is not the a_{1g} . Thus it seems that the relative ordering of the e_g and t_{2g} orbitals is still an open question, but the most reliable theoretical calculations predict the order presented in the last column of Table 2.

Finally, let us analyze the fact that the value of β is less than 0.25 for all of the transitions considered in this paper. Previous work [10, 11] on systems which have π orbitals indicate that the value of β for the

corresponding π photoelectron bands exceeds 0.6. Consequently, it is somewhat surprising that this is not the case for the t bands of SF₆, all of which have some π character. As argued above, autoionization is not a likely contributor to bands I and II and therefore is not a good explanation for the low values of β we observe. This behavior may be related to the fact that the orbitals involved are primarily of fluorine 2p character. We have previously found [3, 4] that ionization of π orbitals of this type have β values around -0.2 to -0.5 for the fluoroethylenes and for fluorobenzene.

V. SUMMARY AND CONCLUSIONS

The HeI photoelectron spectrum of SF₆ obtained at 54.7° and the measurements of the asymmetry parameter β were presented. These are the first β values reported for a molecule having O_h point group symmetry. The possibility of autoionization was discussed and it was argued that its contribution to the intensity of bands I and II of Fig. I is either nonexistent or insignificant. Our data lead to the conclusion that the shoulder at 17.2 eV on the peak of band II is a Jahn-Teller component of that band and that the bands at 18.4 and 18.7 eV correspond to ionization from two different initial orbitals. Orbital assignments based on these results and on theoretical calculations are made for all of the observed transitions.

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Table 1

Ionization potentials and β values for SF_6 at 584 Å

Band (fig. 1)	Vertical IP (eV)	$\beta^{\text{a)}}$	
		Vertical	Range Across Band
I	15.7	-0.32 ± 0.04	-0.33 ± 0.16 to -0.25 ± 0.10
II	17.0	-0.14 ± 0.03	-0.25 ± 0.17 to 0.14 ± 0.07
III	18.4	0.25 ± 0.08	-0.27 ± 0.16 to 0.25 ± 0.08
IV	18.7	0.02 ± 0.05	-0.32 ± 0.17 to 0.02 ± 0.05
V	19.8	-0.57 ± 0.06	-0.57 ± 0.06 to -0.13 ± 0.12

^{a)} The uncertainties given are twice the standard deviation obtained from the linear least-squares fit of the intensity to $a + b \cos^2 \theta$.

Table 2

SF₆ photoelectron spectrum band assignments

Theoretical ^a			Experimental ^b			
Hay ^c	Von Niessen et al. ^d	Gianturco et al. ^e	Vertical IP (eV)	Potts et al. ^f	Gelius ^g	La Villa ^h Present Work
t _{1g} (16.88)	t _{1g} (16.71)	t _{1g} (14.75)	15.7	t _{1u}	t _{1g}	t _{1g}
t _{1u} (18.05)	t _{1u} (17.68)	t _{2u} (15.93)	17.0	t _{1g}	t _{2u}	t _{1u}
t _{2u} (18.09)	t _{2u} (17.91)	t _{1u} (16.40)	17.2	t _{1g} (JT)	t _{1u}	t _{1u} (JT)
e _g (18.98)	e _g (18.47)	e _g (17.25)	18.4	e _g	e _g	t _{2u}
t _{2g} (20.95)	t _{2g} (20.81)	t _{2g} (20.90)	18.7	t _{2u}	e _g (JT)	e _g
			19.7	t _{2g}	t _{2g}	t _{2g}

140

^aThe numbers in parentheses are the calculated vertical ionization potentials in eV.^bThe designation (JT) indicates assignment as a second Jahn-Teller component of the corresponding band (see text).^cRef. [25].^dRef. [26].^eRef. [27].^fRef. [18].^gRef. [20].^hRef. [28].

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Figure Legends

Fig. 1. Photoelectron spectrum (lower panel) and variation of β with ionization potential (upper panel) for SF_6 . The spectrum was obtained at a detector angle of 54.7° using 511 adjacent 12 meV wide channels and 50 scans. Total dwell time per channel was 50 seconds.

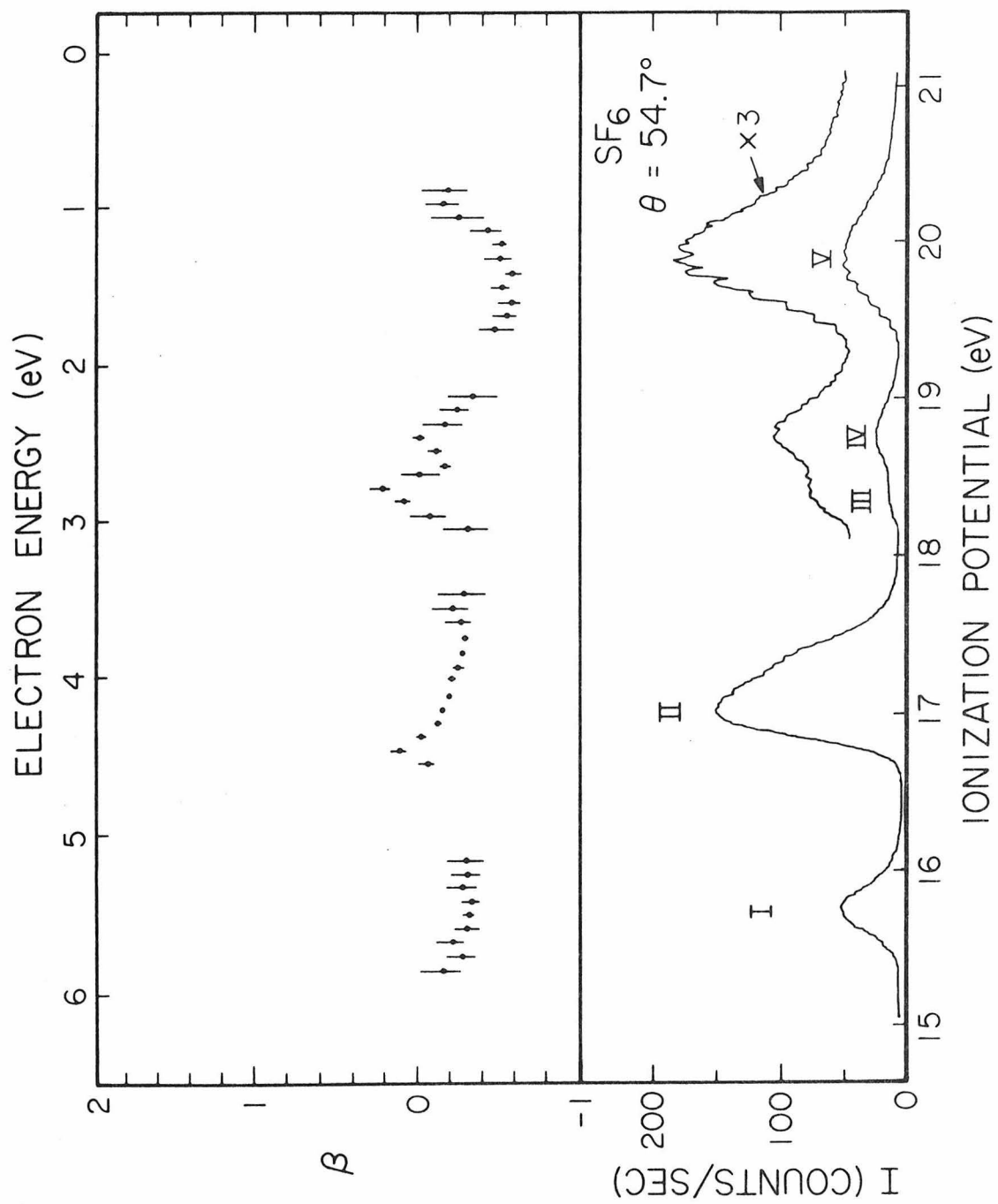


Figure 1.

CHAPTER 7: RESULTS AND DISCUSSION

Paper 4: Angular Distributions in the
Photoelectron Spectroscopy of Furan,
Thiophene, and Pyrrole

ANGULAR DISTRIBUTIONS IN THE PHOTOELECTRON
SPECTROSCOPY OF FURAN, THIOPHENE, AND PYRROLE*

Jeffrey A. SELL[†] and Aron KUPPERMANN

Arthur Amos Noyes Laboratory of Chemical Physics,[‡]

California Institute of Technology, Pasadena, California 91125, USA

Received

The photoelectron angular distributions of furan, thiophene, and pyrrole are reported. The trends in the value of the asymmetry parameter β and in the shapes and positions of bands in the spectra are used to assign the peaks that correspond to ionization from the π orbitals in these molecules.

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1. Introduction

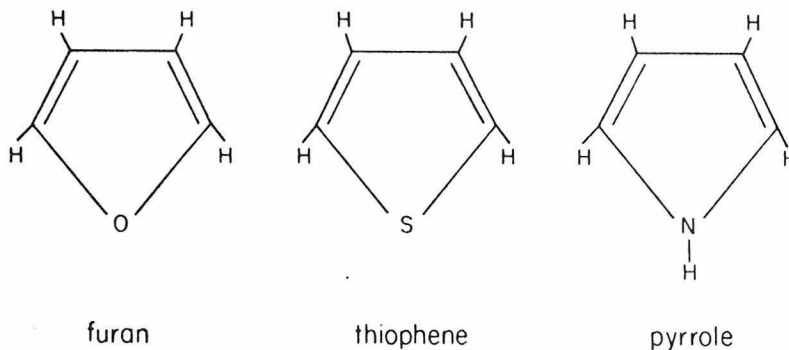
Investigations of the angular distributions in the photoelectron spectroscopy of small molecules have been recently performed in this laboratory [1-6]. These studies have shown that much information on the electronic structure of molecules which is not obtainable from fixed angle spectra alone can be obtained from the angular distribution data. This work was prompted by the early theoretical calculations of Cooper and Zare [7] and experimental data of Hall and Siegel [8] on the angular distributions of photo-detached electrons from negative atomic ions. Briefly, the differential cross section $d\sigma/d\Omega$ for photo-ionization from a given initial state i of an atom or molecule to a given final state f of the corresponding ion using unpolarized light has the form

$$\frac{d\sigma_{if}}{d\Omega} = \frac{Q_{if}}{4\pi} \left[1 - \frac{\beta_{if}}{2} P_2(\cos\theta) \right] \quad (1)$$

where Q_{if} is the integral photoionization cross section, $P_2(\cos\theta)$ is the second Legendre polynomial, θ is the angle between the momentum vector of the ejected electron and the propagation direction of the incident light, and β is the asymmetry parameter which ranges from -1 to +2. In the case of negative ions of light atoms it was found [7, 8] that β depends on the kinetic energy of the photoelectron and also on the angular momentum ℓ of the orbital from which the electron is ejected. Although in molecules this angular momentum is no longer a good quantum number, for light diatomic molecules its projection

along the molecular axis is a constant of the motion. In light polyatomic molecules, localized bond orbitals have angular momentum components along the bond which are approximate constants of the motion, permitting their characterization as σ , π , etc. orbitals. In any event, β seems to be sensitive to some of the details of the electronic structure. For example, Carlson and coworkers [9,10] have shown that the value of β for ionization of π orbitals is usually 0.2 to 1.0 units higher than for ionization of σ orbitals. We have also found this to be true for several molecules [1,4,11]. This difference in β values for π and σ orbitals has previously [4,12,14] been used to assign the peaks in the photoelectron spectra of π electron molecules.

In this paper the results of the measurements of photoelectron angular distributions in furan, thiophene, and pyrrole are reported



for the first time. The photoelectron spectra of these molecules have been published several times [15-24] but there is still uncertainty regarding the energy ordering of the σ and π orbitals. Since the understanding of their electronic structure is important to the whole field of heterocyclic chemistry, we felt that a study of their photoelectron angular distributions would provide useful information.

Complementary information about the electronic energy levels of these molecules and of their aromatic character has previously been obtained by low energy variable angle electron impact spectroscopy [25].

2. Experimental

The apparatus used in the present study is essentially the same as the one previously described in detail [1] and will therefore be reviewed here only briefly. A block diagram of the apparatus is shown in fig. 1. A helium discharge lamp produces mostly 584 Å radiation which interacts with the sample vapor in the scattering chamber. The sample pressure is typically 1 to 2 milliTorrs as monitored by a calibrated[‡] capacitance manometer. The photoelectrons produced are energy-selected by a hemispherical electrostatic analyzer and detected by a Spiraltron electron multiplier. The analyzer and detector are mounted on a large gear wheel and are rotated about the center of the sample chamber which permits scanning of scattering angles over the range of 45° to 120°. The main vacuum chamber is lined with μ metal and the apparatus is located at the center of three pairs of Helmholtz coils which reduce the residual magnetic field to about 0.3 mGauss. Background counts are subtracted before β is calculated and the performance of the instrument is checked by its ability to reproduce the value previously reported [1] of $\beta = 0.88$ for formation of the $^2P_{3/2}$ state of the argon ion. The energy resolution of the apparatus was set at about 55 meV

[‡]The manometer used in this study is an MKS Baratron Model 210 (MKS Instruments, Inc., Burlington, Mass. 01803) which has been calibrated at the factory against a CEC air dead-weight tester. The calibration is reported to be accurate to within 0.1% over 10^{-5} to one Torr pressure.

as measured from the full width at half maximum of the argon $^2P_{3/2}$ peak.

Samples of the three heterocyclic molecules were obtained from the Aldrich Company. The stated purity of pyrrole was 98% while that of thiophene and furan was > 99%. The pyrrole sample was further purified by fractional distillation under 1 atm of argon using a spinning band distillation column [26]. All three samples were subjected to three liquid nitrogen freeze-pump-thaw cycles before being loaded into the spectrometer. The energy scale was calibrated by obtaining the spectrum of a mixture of the sample molecule with a small fractional amount (< 10%) of argon.

3. Results

Furan

The photoelectron spectrum and a plot of β as a function of ionization potential (IP) and electron energy for furan are shown in fig. 2. The IP's and values of β are also listed in Table 1. The spectrum is similar to the ones reported previously by Eland [19], Derrick *et al.* [20], and Baker *et al.* [16], except that some of the relative band intensities are different. One cause of this is the energy-dependent discrimination factor of kinetic energy analyzers [27]. Our intensities, as well as those reported by others [15-19], are not corrected for this discrimination. Some authors [19-24] approximately account for this by multiplying the intensities by the retarding voltage. In our apparatus, this discrimination factor varies by less than 8% over the electron kinetic energy range of 4.2 to 5.7 eV. Another cause of the slightly different relative band intensities is that our spectra were obtained at a detector angle of 54.7° for which $P_2(\cos\theta) = 0$. At this angle, ratios of relative differential cross sections are equal to ratios of integral cross sections. Most other spectra reported for the molecules considered in this paper have been obtained at a detector angle of 90° for which a nonzero value of β causes the observed relative intensities to deviate from those obtained at 54.7° .

Bands I and II (see fig. 2) have vertical IP's of 8.9 eV and 10.4 eV respectively, and have resolved vibrational structure. Bands III through VI are fairly broad and have vertical IP's of 12.9, 13.8,

14.4, and 15.1 eV, respectively. Band VII is located at 17.5 eV and looks remarkably similar to bands I and II. Finally, band VIII is very broad and featureless and has maximum somewhere near 18.8 eV.

There are several interesting features in the plot of β as a function of IP. Band I has relative high values of β which ranges from 0.63 to 1.22. Similarly, band II has values which range from 0.43 to 1.16. If straight lines are drawn through the β points for each of these bands one finds that the slope of these lines are -1.0 eV^{-1} for both bands. These results will be discussed in section IV. Bands III through VI have lower values of β which are in the range -0.18 to 0.44 . β is again relatively high for band VII decreasing from 0.61 to 0.19 as the IP increases at an approximate rate of -0.45 eV^{-1} , and is in the range -0.20 to 0.28 for band VIII.

Thiophene

The photoelectron spectrum and a plot of β as a function of ionization potential (IP) and electron energy for thiophene are shown in fig. 3. The IP's and values of β are also listed in Table 2. Again the spectrum is similar to those reported previously by Eland [19], Derrick et al. [21], Baker et al. [16] and Rabalais et al. [24], except for minor disagreements on relative band intensities, as discussed for furan. The IP of band I is 8.9 eV, the same as in furan, but band II has moved downwards in energy from 10.4 eV to 9.5 eV. Bands III through VII are all fairly broad and have IP's of 11.9, 12.4, 13.1, 13.5, and 14.2 eV, respectively. Finally, band VIII is located at 16.4 eV.

The value of β for bands I and II ranges between 0.78 and 1.11 with no discernible systematic trends in its energy dependence. β is relatively low, from 0.23 to 0.42, for band III and then rises to a maximum of 0.74 at the maximum intensity of band IV, decreasing thereafter. For bands V, VI, and VII the value of β is in the range 0.25 to 0.46 and then varies between 0.21 and 0.46 for band VIII.

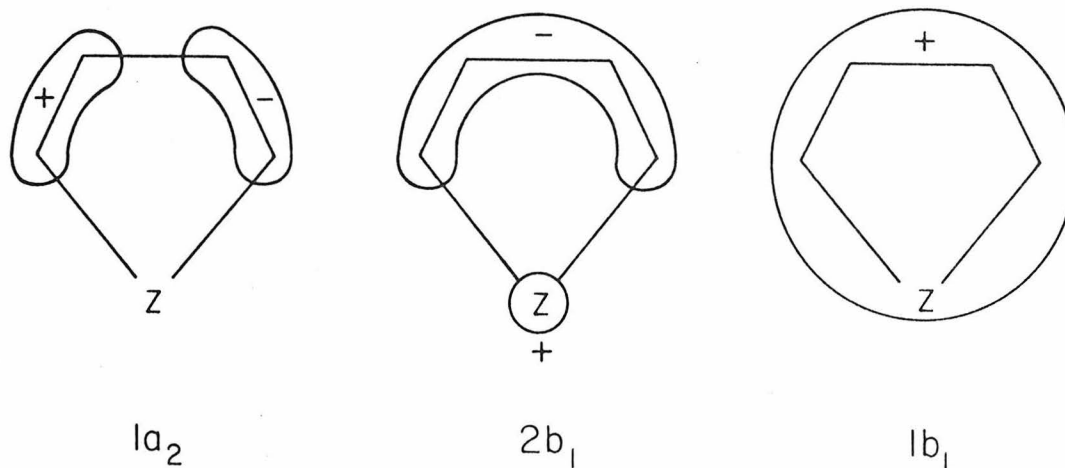
Pyrrole

The photoelectron spectrum and a plot of β as a function of IP and electron energy for pyrrole are shown in fig. 4. The IP's and values of β are also listed in Table 3. The spectrum is similar to those reported earlier [16,19,22]. The first two bands (see fig. 3) have resolved vibrational structure and have IP's of 8.2 eV and 9.2 eV. Bands III through VI overlap each other and are very broad, having IP's of 12.7, 13.7, 14.3, and 14.8 eV, respectively. Band VII is weak and extremely broad and relatively flat between 17.2 eV and 18.2 eV.

β decreases from 1.20 to 0.79 across band I at an approximate rate of -1.5 eV^{-1} . Similarly for band II, β decreases from 1.09 to 0.76 at an approximate rate of -1.5 eV^{-1} . The values of β for bands III through VI are all in the range -0.07 to +0.33 and the values for band VII range from -0.17 to 0.34.

IV. Discussion

The molecules furan, thiophene and pyrrole belong to the C_{2v} point group for which the standard coordinate system [28] designates the z and y axes to lie in the molecular plane, the first one being the C_2 axis. In all three cases the heteroatom has a lone pair of electrons in an orbital which is directed out of the molecular plane. There are six out-of-plane electrons, and previous work [25] has shown that they form a ring with aromatic character. Three of the corresponding molecular orbitals are of the π type and have a symmetry described by either the a_2 or b_1 irreducible representations. The shapes and nodal characteristics of these orbitals are shown below [15]:



The rest of the discussion will focus on our use of the angular distribution data to assign the peaks in the spectra that correspond to ionization from these orbitals and will include a comparison of our assignments to those made previously [15-24] using different techniques.

Furan

Due to the relatively high values of β for bands I, II, and VII we

assign these peaks as the ones that correspond to the three π orbitals. The assignment for band VII is slightly more uncertain than those for bands I and II since the highest value of β for this band is 0.61 which is only slightly higher than the highest value in band VI (0.44).

However, the variation of β across band VII is much more similar to that for bands I and II than for any other band. In addition, the vibrational spacing and intensity distribution of band VII is remarkably similar to those of bands I and II. These arguments suggest that the assignment of band VII to a π orbital is a reasonable one.

The $1b_1$ orbital is nodeless and therefore the most stable (lowest energy, highest IP) of the three π orbitals displayed above. The relative ordering of the $1a_2$ and $2b_1$ orbitals is more difficult to ascertain using simple arguments. However, the calculations of Derrick et al. [20-22] predict that the $2b_1$ is more stable than the $1a_2$ for all three molecules. This order is reflected in the orbital assignments given in Table 1.

One interesting aspect of the angular distribution data is that the change in β across each of the bands I, II and VIII is essentially monotonic (deviations from monotonicity are due to statistical fluctuations and are not reproducible) and the slopes of the lines drawn through the corresponding parts in fig. 2 are, as stated above, equal to -1.0 eV^{-1} , -1.0 eV^{-1} , and -0.45 eV^{-1} , respectively. Previously, values of such

slopes for π electron ionizations were typically -0.1 to -0.2 eV^{-1} for benzene [14,29], linear dienes [9,11] and methyl substituted ethylenes [30]. However, higher values for this slope have been recently observed for π ionizations in the halobenzenes [3] as well as in the non- π molecule cyclopropane [13].

Therefore, the expectation that β varies only gradually across a π photoionization band may have to be modified and this behavior may have to be taken into account when β is used to make orbital assignments. Nevertheless, the β values for bands I, II and VII are in average sufficiently high and the vibrational structure sufficiently analogous for their assignment as π bands to be reliable.

These assignments agree with those given by the experimental work and calculations of Eland [19] and also the calculations of Siegbahn [31]. However, our assignment of the 17.5 eV band (VII) to the $1b_1$ orbital does not agree with Derrick et al. [20], who associate that orbital to the band at 14.4 eV (V).

Thiophene

The relatively high values of β for bands I, II, and IV lead to the association of these bands with π orbitals. Consideration of the nodal characteristics (which are similar to those of furan) leads to the assignments given in Table 2. With the exception of the $1b_1$ orbital, these assignments agree with those of Derrick et al. [21], Gelius et al. [32], Eland [19], and Baker et al. [16]. There is essentially no agreement among these authors on the assignment of the $1b_1$ orbital, but our angular distribution data indicate that this orbital is

associated with the peak at 12.4 eV.

Pyrrole

The β values for pyrrole are relatively high only for bands I and II (see fig. 4) which are associated with the $1a_2$ and $2b_1$ orbitals, respectively, in analogy with furan and thiophene. The high negative slopes of the lines drawn through the β values across these features (-1.5 eV^{-1}) are significant for the same reason mentioned in the discussion of the corresponding bands in furan. The fact that another transition which has a relatively high value of β is not observed is very interesting since a third π orbital is expected to be accessible to 21.2 eV photons.

Tanaka et al. [33], have recently reported an ab initio SCF CI calculation for the ground and excited states of pyrrole and its positive ion. They found that although the third π state of the positive ion is formed mostly by ionization from the $1b_1$ orbital ($1b_1 \rightarrow \infty$), two shake-up transitions ($1a_2^2 \rightarrow 3b_1 \infty$ and $2b_1^2 \rightarrow 3b_1 \infty$) contribute significantly to this state. This configuration mixing would affect β [34], but since all three orbitals involved in the ionization ($1b_1$, $1a_2$ and $2b_1$) have π symmetry, the resulting value of this parameter would still be characteristic of a π ionization. Their results yield an IP of 13.3 eV for the $1b_1$ orbital. This type of calculation can give an IP which is in error by up to 1 eV, but the important consideration is that the band which corresponds to this orbital probably lies in the 12.2 to 15.5 eV region where several bands can be seen in fig. 4. The fact that there are several σ bands in this region which could overlap this π band may

explain why only relatively low values of β are observed. When two transitions overlap one another without interfering, having characteristic asymmetry parameters β_1 and β_2 , the observed β value will be a weighted average of these:

$$\beta_{\text{obs}} = \frac{Q_1 \beta_1 + Q_2 \beta_2}{Q_1 + Q_2} \quad (2)$$

where Q_1 and Q_2 are the integral photoionization cross sections for the two bands [2, 3]. Thus, depending on the ratio of cross sections, it is possible for the observed β value of an overlapped π transition to be lower than one would normally expect.

V. Summary and Conclusions

The photoelectron spectra of furan, thiophene, and pyrrole have been obtained using 584 Å light at scattering angles in the range of 45° to 120°, including the magic angle of 54.7°. The anisotropy parameters β have been determined as a function of IP for each molecule, and in some cases show a rapid variation across individual photoelectron bands. These angular distribution data are used to make assignments of the two lowest IP π bands in all of these molecules in agreement with previous identifications. In addition, they are used to label the third IP π band in furan and thiophene, for which previous assignments are in disagreement with each other. For all these eight π -bands the value of β is relatively high compared to those of the σ -bands. For pyrrole, the third IP π -band seems to occur in a region of the spectrum heavily overlapped by σ bands, making the observed values of β ineffective for determining its precise location.

Acknowledgment

We wish to thank Professor David A. Evans for assistance in the purification of the pyrrole sample.

Table 1

 β Values and ionization potentials for furan at 584 Å.

Band	Initial Orbital	Vertical IP ^a (eV)	β	
			Range across band ^b	Vertical
I	1a ₂	8.9	0.63±0.09 to 1.22±0.18	1.02±0.05
II	2b ₁	10.4	0.43±0.06 to 1.16±0.06	0.56±0.11
III		12.9	-0.18±0.06 to 0.20±0.10	-0.08±0.08
IV		13.8	0.04±0.05 to 0.36±0.11	0.25±0.07
V		14.4	0.11±0.07 to 0.30±0.07	0.26±0.03
VI		15.1	0.09±0.07 to 0.44±0.08	0.09±0.07
VII	1b ₁	17.5	0.19±0.09 to 0.61±0.05	0.49±0.13
VIII		~18.8 ^c	-0.20±0.09 to 0.28±0.09	0.13±0.19

a) This corresponds to the band maximum and has an absolute accuracy of ± 0.05 eV.

b) The first and second values quoted are respectively the lowest and highest values. The uncertainties given are twice the standard deviation (see Ref. 1).

c) The value of this IP is uncertain by ± 0.2 eV due to the low intensity and broad shape of the band.

Table 2

β Values and ionization potentials for thiophene at 584 Å.

Band	Initial Orbital	Vertical IP ^a (eV)	β	
			Range across band ^b	Vertical
I	1a ₂	8.9	0.78±0.09 to 1.11±0.09	0.99±0.07
II	2b ₁	9.5	0.89±0.07 to 1.11±0.06	1.11±0.06
III		11.9	0.23±0.04 to 0.42±0.10	0.28±0.02
IV	1b ₁	12.4	0.46±0.05 to 0.74±0.05	0.74±0.05
V		13.1	0.28±0.04 to 0.40±0.04	0.28±0.04
VI		13.5	0.35±0.04 to 0.44±0.03	0.35±0.03
VII		14.2	0.25±0.04 to 0.46±0.03	0.25±0.04
VIII		16.4	0.21±0.12 to 0.46±0.11	0.46±0.11

a) This corresponds to the band maximum and has an absolute accuracy of ± 0.05 eV.

b) The range and uncertainties have the same meaning as in Table 1.

Table 3

 β V_a lues and ionization potentials for pyrrole at 584 Å.

Band	Initial Orbital	Vertical IP ^a (eV)	β	
			Range across band ^b	Vertical
I	1a ₂	8.2	0.79±0.17 to 1.15±0.07	1.15±0.07
II	2b ₁	9.2	0.76±0.09 to 1.09±0.06	1.09±0.06
III		12.7	-0.07±0.07 to 0.18±0.09	0.11±0.07
IV		13.7	0.04±0.14 to 0.24±0.06	0.04±0.14
V		14.3	0.18±0.08 to 0.31±0.10	0.26±0.08
VI		14.8	0.09±0.16 to 0.33±0.10	0.33±0.10
VII		17.4 ^c	-0.17±0.11 to 0.34±0.16	0.00±0.12

a) This corresponds to the band maximum and has an absolute accuracy of ± 0.05 eV.

b) The range and uncertainties have the same meaning as in Table 1.

c) This band is very broad and flat making an assignment of the vertical IP quite uncertain.

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Figure Captions

Figure 1. Block diagram of the variable-angle photoelectron spectrometer. He, cylinder of ultra-high purity helium; ZT, liquid nitrogen cooled zeolite trap for lamp helium supply; RB, lamp ballast resistor; LPS, lamp dc power supply; SC, sample chamber; PC, photocathode for light flux measurements; CL, electron lens elements; ANALYZER, hemispherical electron energy analyzer; ML, electron lens element; S, Spiraltron electron multiplier; CPS, Spiraltron cathode power supply; APS, Spiraltron anode power supply; R. C., resistance and capacitance of differentiating network for Spiraltron pulses.

Figure 2. Photoelectron spectrum (lower panel) and variation of β with ionization potential and electron energy (upper panel) for furan using HeI (21.22 eV) radiation. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 60 scans. Total dwell time per channel was 60 seconds.

Figure 3. Photoelectron spectrum (lower panel) and variation of β with ionization potential and electron energy (upper panel) for thiophene using HeI radiation. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 seconds.

Figure 4. Photoelectron spectrum (lower panel) and variation of β with ionization potential and electron energy (upper panel) for pyrrole

using HeI radiation. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 40 scans. Total dwell time per channel was 40 seconds.

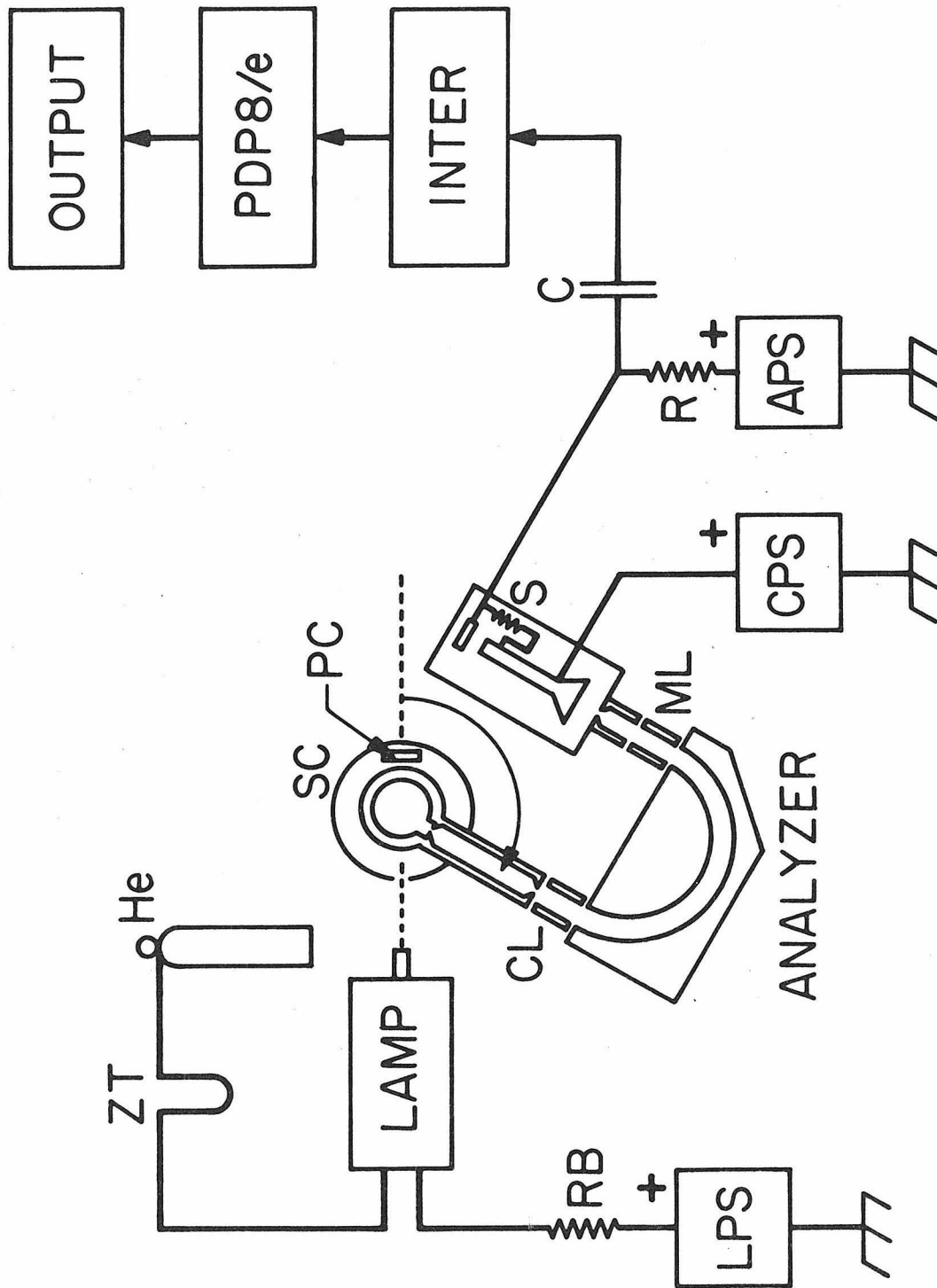


Figure 1.

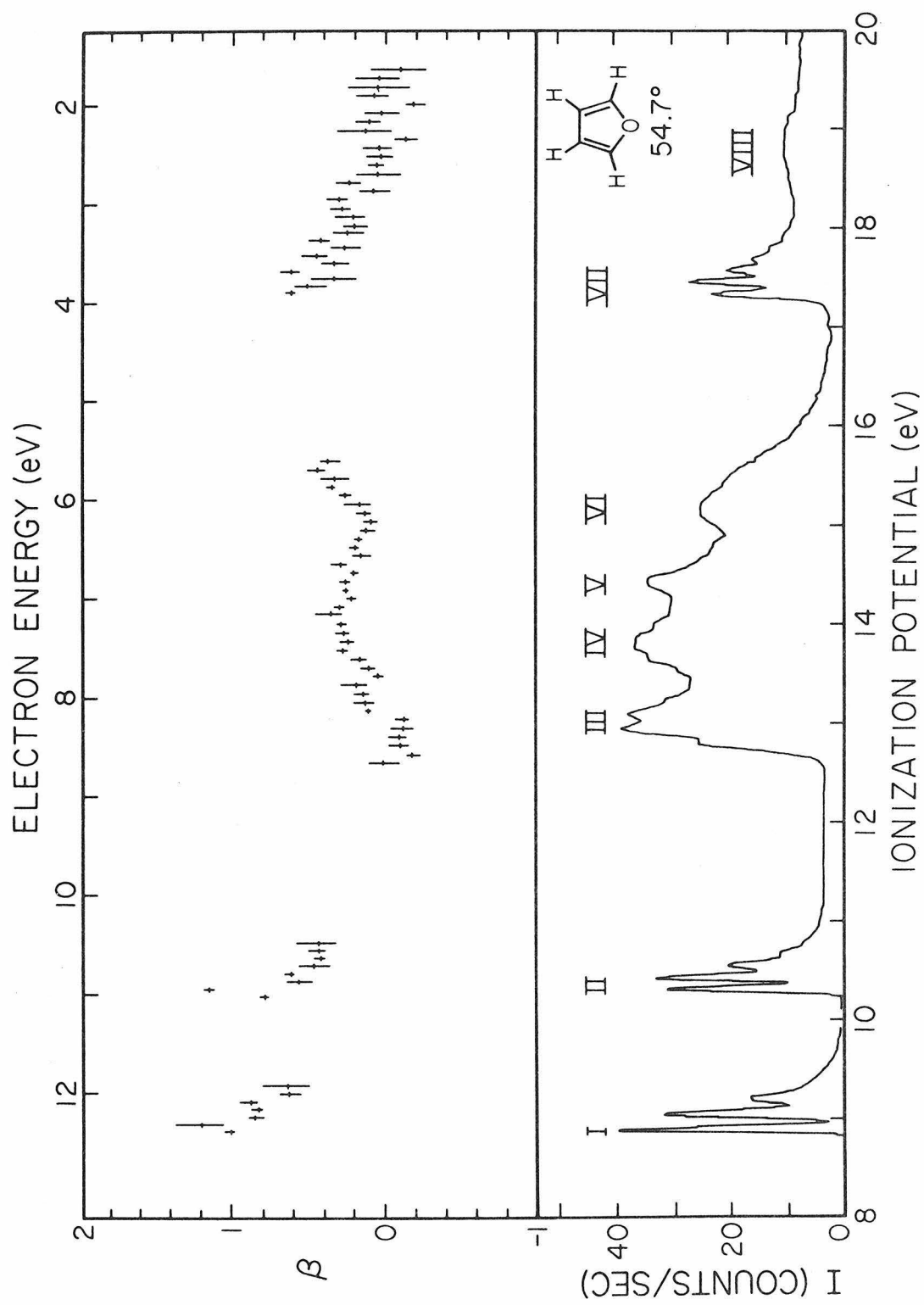


Figure 2.

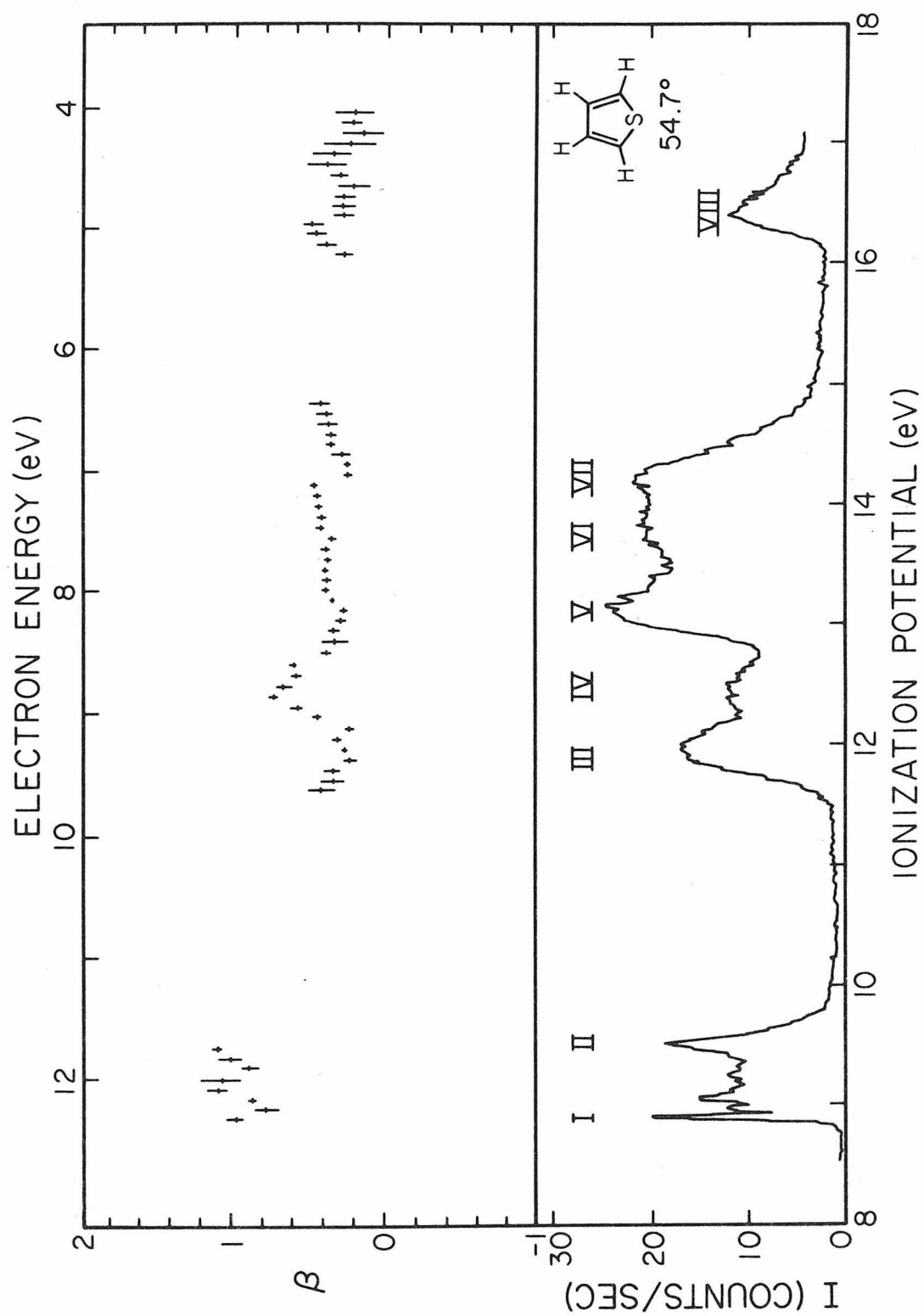


Figure 2.

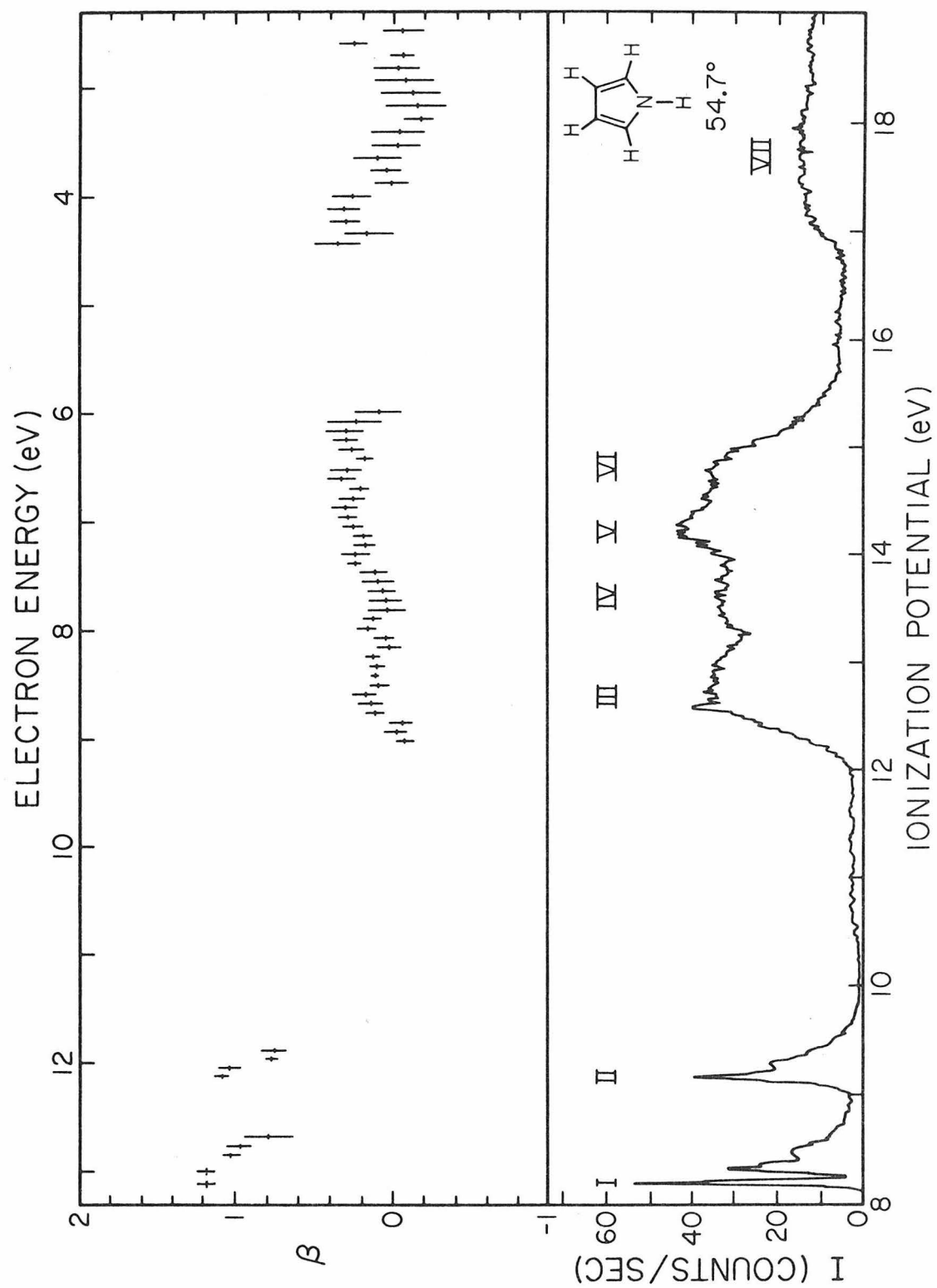


Figure 3.

CHAPTER 8: RESULTS AND DISCUSSION

**Paper 5: Photoelectron Angular Distributions
of Carbon-Carbon Pi Electrons in Ethylene,
Benzene, and their Fluorinated Derivatives**

PHOTOELECTRON ANGULAR DISTRIBUTIONS OF CARBON-CARBON
PI ELECTRONS IN ETHYLENE, BENZENE, AND THEIR FLUORINATED
DERIVATIVES*

Jeffrey A. SELL,** Donald M. MINTZ,[†] and Aron KUPPERMANN

Arthur Amos Noyes Laboratory of Chemical Physics,[‡]

California Institute of Technology, Pasadena, California 91125, USA

Received

Abstract

We have measured the anisotropy parameter β describing the angular distribution of C-C π electrons photoejected by 584 Å radiation from benzene, ethylene, and most of their fluorinated derivatives. The results indicate that in going from C₂H₄ to C₂F₄, the value of β at the maximum intensity of the C-C π band decreases from 1.25 ± 0.05 to 0.05 ± 0.04 , whereas in going from C₆H₆ to C₆F₆ it decreases from 1.23 ± 0.04 to 0.65 ± 0.04 . The differences in these variations are attributed to the differences in the interactions of the F π electrons with the C-C π electrons in these two series of molecules. If such correlations

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[†] Present address: TRW Space and Defense Systems Group, Redondo Beach, California 90278, USA.

[‡] Contribution No. 5707.

between these interactions and β values turn out to be generally valid, a determination of β could help elucidate the nature of bonding interactions in other molecules.

1. Introduction

Previously [1-15] it has been shown that the differential cross section ($d\sigma/d\Omega$) for a photoionization transition of an atom or molecule by unpolarized light has the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 - \frac{\beta}{2} P_2(\cos \theta) \right] ,$$

where σ is the integral photoionization cross section for this transition, P_2 is the second-order Legendre polynomial, θ is the scattering angle between the direction of propagation of the incident light and the momentum vector of the ejected electron, and β is the anisotropy parameter which ranges from -1 to +2. It has also been shown [7-9, 12, 15] that the β parameter contains important chemical information and that it is particularly informative to study trends in its variation over a series of related molecules.

2. Experimental

The apparatus used for measuring β has been described in detail previously [10]. Basically, the sample vapor at a pressure of 1 to 4 mTorr is irradiated by HeI radiation (mostly 584 Å), and the photoelectrons produced are energy-selected by a 180° hemispherical electrostatic analyzer and detected by a Spiraltron electron multiplier. The analyzer and detector are mounted on a gear wheel and are rotated about the center of the ionization chamber scanning the

scattering angle range from 45° to 120° . The apparatus is carefully shielded against stray magnetic fields and its performance is checked by the symmetry of the angular distributions with respect to $\theta = (\pi/2)$ and by the ability of the instrument to reproduce the value of $\beta = 0.88 \pm 0.02$ previously reported [10] for the argon $^2P_{3/2}$ peak.

3. Results and Discussion

The results of our measurements of β at maximum intensity of the C-C π bands in benzene, ethylene, and some of their fluorinated derivatives are shown in Table 1 along with those of other investigators. In addition, the photoelectron spectrum and plot of β as a function of ionization potential (IP) and electron energy for ethylene and perfluoroethylene are shown in Figs. 1 and 2, respectively.[‡] The agreement between the various measurements is good, with the exception of the values for perfluorobenzene where our results differ substantially from those of Kobayashi and Nagakura [17].^{‡‡} The main point of interest is the difference in these vertical C-C π ionization β values between the fluoroethylenes and fluorobenzenes. It can be seen that the value of β for the C-C π band in ethylene is 1.25 and decreases monotonically to 0.05 for C_2F_4 . On the other hand, this β is 1.23 for benzene and

[‡] A more detailed study of the π and the higher IP bands of ethylene and its fluorinated derivatives will be published separately [16].

^{‡‡} The trend in the variation of β as a function of fluorination fraction for the fluorobenzene series displayed in Fig. 3 indicates the self-consistency of our set of values. In spite of careful checks, we have been unable to detect any systematic errors in our apparatus.

decreases to 0.65 for C_6F_6 . In Fig. 3, the value of β for the vertical C-C π band IP for each of these molecules is plotted as a function of the fractional fluorination α , which varies from zero for ethylene and benzene to unity for perfluoroethylene and perfluorobenzene. The difference in β among the several fluoroethylenes or the several fluorobenzenes is not due to the electron energy dependence of β since the lowest C-C π IP's differ by 0.31 eV or less for the fluoroethylenes or by 0.9 eV or less for the fluorobenzenes, whereas the energy dependence of β rarely exceeds 0.4 eV^{-1} [18-20]. By the same argument, the difference in the trends of β between the fluoroethylene series and the fluorobenzene series cannot be explained by an electron energy dependence of β .

This difference must be due to the different effects of fluorination on the C-C π electrons of ethylene and benzene. Bralsford, Harris and Price [21] have previously made the same suggestion on the basis of trends in the variation of the adiabatic IP of these molecules with fluorine substitution. As can be seen from Table 1, this IP decreases monotonically from 10.51 eV in ethylene to 10.14 eV in perfluoroethylene and increases from 9.22 eV in benzene to 9.91 eV in perfluorobenzene. They argue that the decrease in IP in the fluoroethylene is due to a dominance of the resonance effect between the fluorine π electrons and the C-C π electrons (which tends to stabilize the ionic state) over the inductive effect of the fluorine atoms on the C-C σ electrons. In the fluorobenzenes, however, they argue, on the basis of the nodal structure of the C-C π orbitals, that this resonance effect is dominant only in the fluoro- and p-difluoro compounds.

If these arguments are correct, they can also help provide an explanation for the effect of fluorination on β in these molecules. The resonance effect can be thought of as donation of π -electron density by the fluorine atom to the carbon-carbon π orbitals [22-25]. This can be described in elementary concepts as the contribution of structures such as ${}^{\text{m}}\text{C}=\text{C}=\text{F}^+$ to the bonding in these molecules. The resonance effect is expected to stabilize the ionic states more than the neutral ones, thereby decreasing the IP [21]. The inductive effect is basically the withdrawal of C-C σ electron density by the highly electronegative F atom. This affects the π orbital mainly by reducing the screening of the π electrons from the nucleus, consequently increasing their IP [22-25]. The C-C π electrons have a relatively high value of β , about 1.25 in both ethylene and benzene. The value of β for the fluorine atom 2p π electrons has not been measured or calculated. It can perhaps be approximated by the value of β for the fluorine π lone-pair electrons in fluorobenzene, which is -0.52 [15]. When a bond is formed between F and C=C, the resulting C=C π orbital will acquire some F π character due to the resonance effect. This should result in a decrease of the value of β for the π electron ionization.[§] The reason that in the fluorobenzene series β decreases less rapidly with the degree of fluorination than in the fluoroethylene series is that there is less donation of π electron density by the F atom, according to Fischer-Hjalmar and

[§] Unfortunately, a simple quantitative estimate of the magnitude of this decrease is difficult to obtain because of the possible contributions from interference effects between C-C and C-F orbitals.

Meza [26]. We do not expect the inductive effect to drastically change the value of β for a C-C π orbital, since it affects the π electrons only indirectly through the σ orbitals. The situation in the fluorobenzenes is slightly complicated due to the degeneracy of the benzene πe_{1g} orbital which is lifted upon fluorine substitution (except for 1, 3, 5- $C_6H_3F_3$ and C_6F_6). For example, in fluorobenzene this orbital is split into two, the b_1 and a_2 . The β value of the b_1 orbital would be expected to be affected most by fluorine substitution since it has the same symmetry as the fluorine π lone-pair orbital and would thus have the largest resonance effect. This argument is in agreement with the fact that the fluorobenzene b_1 orbital has a value of $\beta = 0.86$ and the a_2 orbital has a value of $\beta = 1.09$.

Obviously these arguments are very crude and speculative. However, the present and previous [7, 8, 12, 14] trends in the variation of β across families of related molecules indicates that this parameter contains information about the details of the chemical bond which could be most useful if a deeper theoretical understanding of the factors which affect it were available.

Table 1

Ionization potentials and β values at 584 Å for the C-C π bands of the fluoroethylene and fluorobenzene series.

Molecule	Original Orbital	Adiabatic IP ^{a)} (eV)	Vertical IP (eV)	β , Present Work		Previous Work, β , Vertical
				Range ^{b)}	Adiabatic ^{c)}	Vertical ^{d)}
C ₂ H ₄	b _{3u}	10.51	10.51	1.00 ± 0.10 to 1.25 ± 0.05	1.25 ± 0.05	1.25 ± 0.05
C ₂ H ₃ F	a ^e	10.36	10.56	0.67 ± 0.05 to 0.85 ± 0.02	0.82 ± 0.04	0.82 ± 0.03
1,1-C ₂ H ₂ F ₂	b ₁	10.29	10.69	0.46 ± 0.05 to 0.81 ± 0.03	0.75 ± 0.04	0.64 ± 0.03
cis-1,2-C ₂ H ₂ F ₂	b ₁	10.23	10.44	0.30 ± 0.04 to 0.47 ± 0.06	0.47 ± 0.06	0.30 ± 0.03
trans-1,2-C ₂ H ₂ F ₂	a _u	10.21	10.38	0.32 ± 0.11 to 0.53 ± 0.11	0.44 ± 0.05	0.43 ± 0.04
C ₂ HF ₃	a ^e	10.14	10.54	0.26 ± 0.03 to 0.36 ± 0.05	0.36 ± 0.05	0.30 ± 0.03
C ₂ F ₄	b _{3u}	10.14	10.56	-0.25 ± 0.10 to 0.12 ± 0.09	-0.25 ± 0.10	0.05 ± 0.04
C ₆ H ₆	e _{1g}	9.22	9.22	0.86 ± 0.10 to 1.23 ± 0.04	1.23 ± 0.04	1.23 ± 0.04
C ₆ H ₅ F	b ₁	9.22	9.22	0.86 ± 0.06 to 1.03 ± 0.07	1.03 ± 0.07	0.86 ± 0.06
	a ₂		9.80	0.91 ± 0.10 to 1.09 ± 0.04		1.09 ± 0.04
p C ₆ H ₄ F ₂	b _{2g}	9.29	9.28	0.77 ± 0.09 to 0.92 ± 0.15	0.80 ± 0.07	0.89 ± 0.09
	b _{2g}	10.04	10.04	0.77 ± 0.13 to 1.29 ± 0.03	1.29 ± 0.03	1.09 ± 0.08
1,3,5-C ₆ H ₃ F ₃	e ^e	9.64	9.82	0.62 ± 0.11 to 0.90 ± 0.06	0.90 ± 0.06	0.69 ± 0.07
1,2,3,4-C ₆ H ₂ F ₄	b ₁ , a ₂	9.60	9.78	0.63 ± 0.11 to 1.20 ± 0.21	0.71 ± 0.07	0.82 ± 0.07
C ₆ HF ₅	b ₁ , a ₂	9.73	9.91	0.60 ± 0.14 to 0.76 ± 0.10	0.76 ± 0.10	0.71 ± 0.06
C ₆ F ₆	e _{1g}	9.91	10.10	0.38 ± 0.09 to 0.82 ± 0.09	0.81 ± 0.10	0.65 ± 0.04

a) These are the IP's for the maximum of the lowest resolved vibrational feature of the band being considered.

b) Minimum and maximum values over the band.

c) Values at the maximum of the vibrational peak for which corresponding IP was measured (see footnote a).

d) Value measured for the most intense feature of the band.

e) Ref. [7].

f) Ref. [6].

g) Ref. [17].

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Figure Captions

Fig. 1. Variation of photoelectron intensity I (in counts/sec) and asymmetry parameter β with ionization potential and photoelectron kinetic energy for ethylene. The spectrum was obtained at the magic scattering angle of 54.7° , using 511 adjacent 14 meV wide channels and 50 scans. Total dwell time per channel was 50 sec.

Fig. 2. Variation of photoelectron intensity I (in counts/sec) and asymmetry parameter β with ionization potential and photoelectron kinetic energy for perfluoroethylene. The spectrum was obtained at the magic scattering angle of 54.7° , using 511 adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 sec.

Fig. 3. Variation of β obtained at the maximum intensity of the C-C π bands in the fluoroethylene series (solid dots) and the fluorobenzenes (open diamonds) as a function of the fluorination fraction. Fluoroethylene series: a, ethylene; b, fluoroethylene; c, geminal difluoroethylene; d, trans-difluoroethylene; e, cis-difluoroethylene; f, trifluoroethylene; and g, perfluoroethylene. Fluorobenzene series: h, benzene; i, the a_2 state of fluorobenzene; j, the b_1 state of fluorobenzene; k, the b_{1g} state of para-difluorobenzene; l, the b_{2g} state of para-difluorobenzene; m, 1,3,5-trifluorobenzene; n, 1,2,3,4-tetrafluorobenzene; o, pentafluorobenzene; and p, perfluorobenzene. The solid curves are shown to draw attention to the main trends in the variation of β with fluorination fraction for each of the two series of molecules and are not intended to have quantitative meaning.

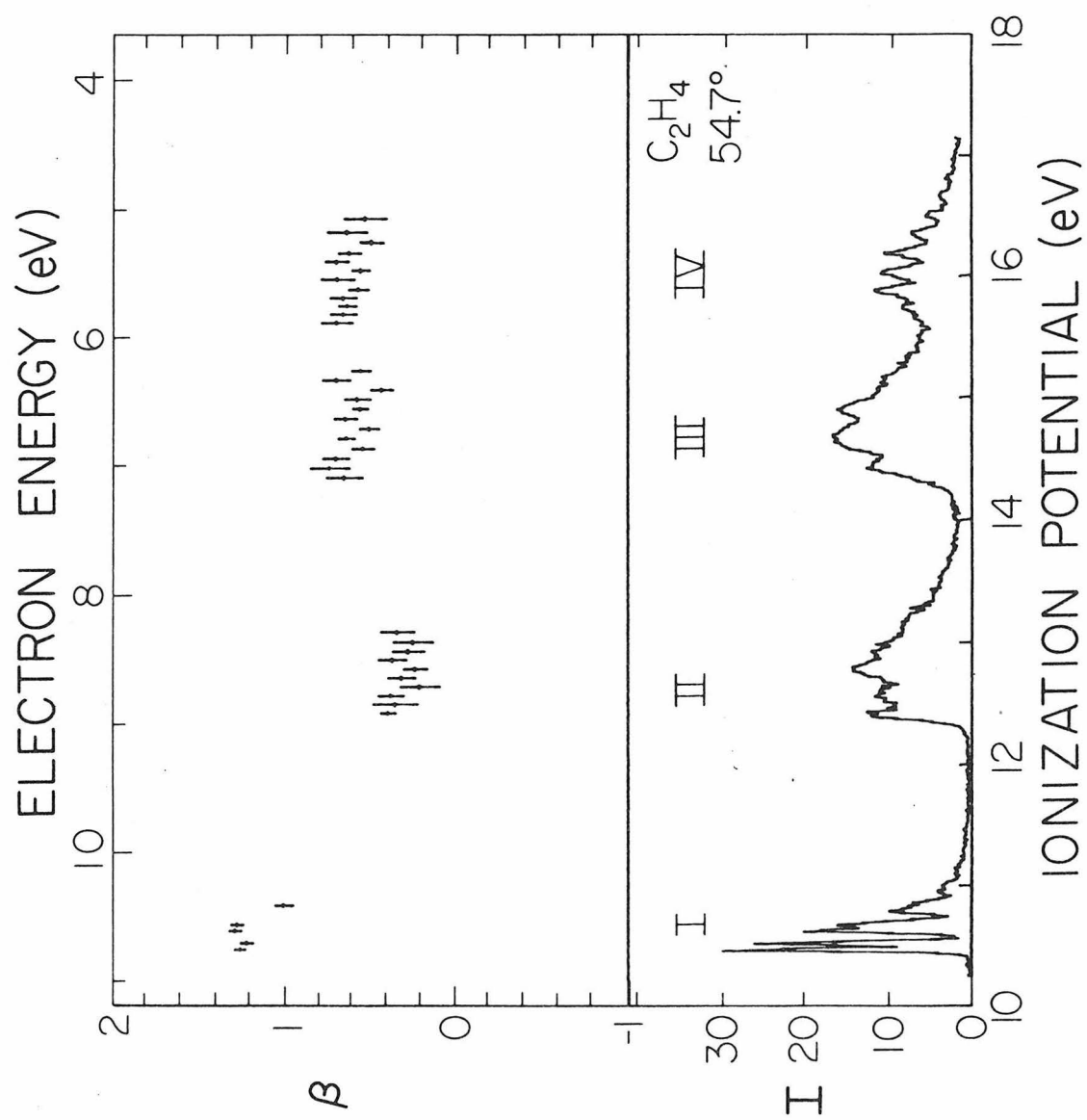


Figure 1.

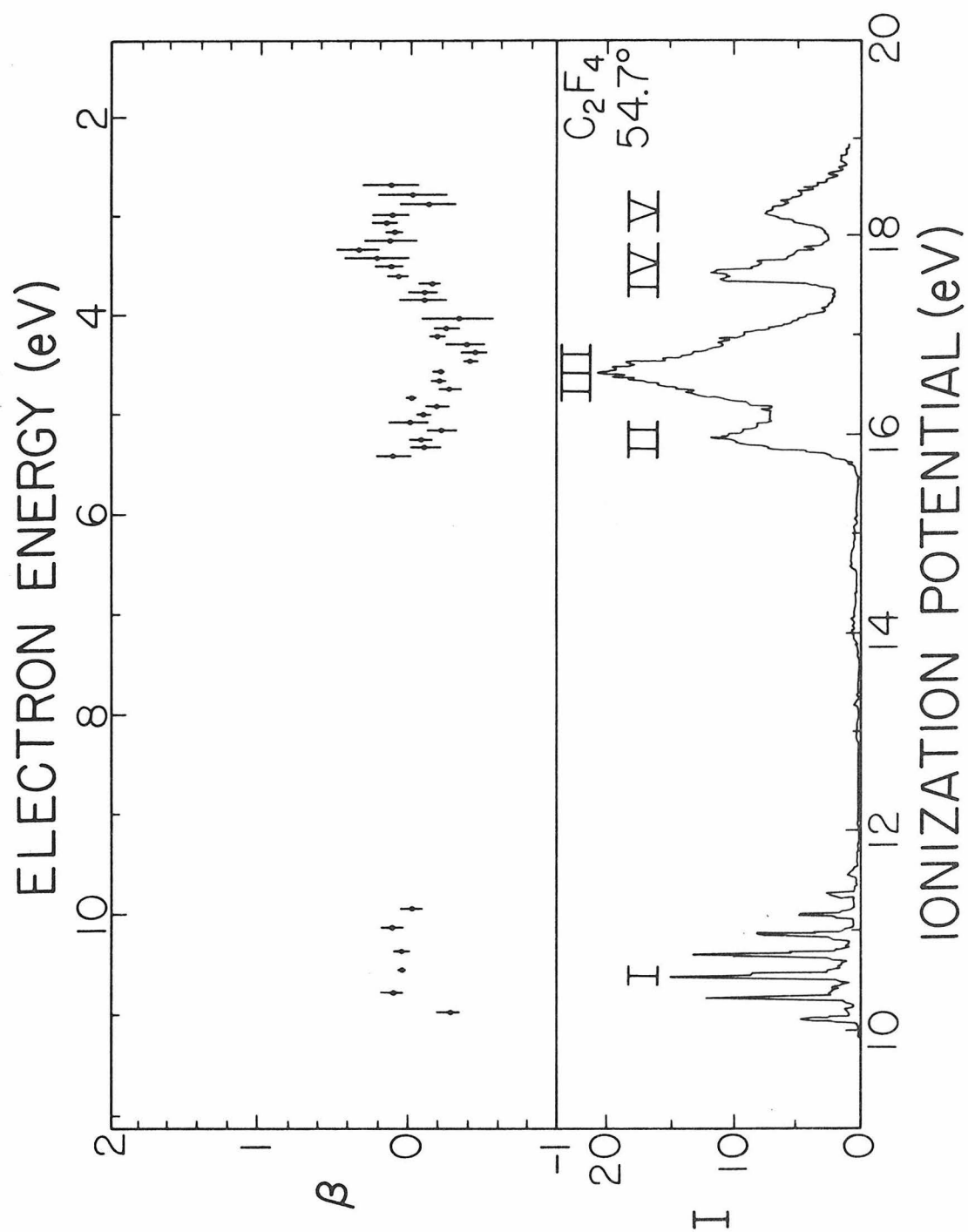


Figure 2.

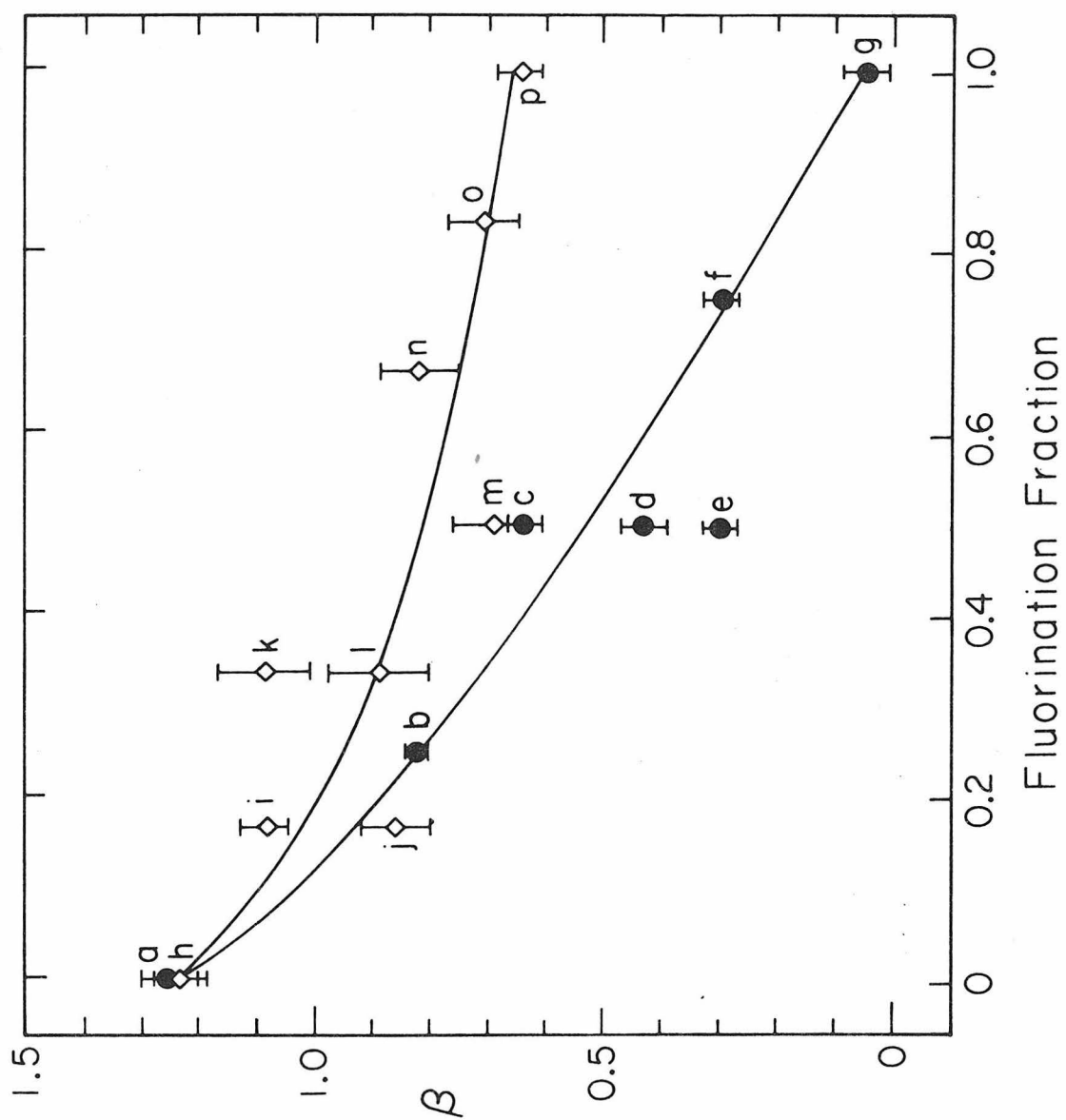


Figure 3.

CHAPTER 9: RESULTS AND DISCUSSION

Paper 6: Variable Angle Photoelectron

Spectroscopy of the Fluorethylenes

Variable angle photoelectron spectroscopy of the fluoroethylenes ^{a)}

Jeffrey A. Sell^{b)} and A. Kuppermann

Arthur Amos Noyes Laboratory of Chemical Physics, ^{c)}

California Institute of Technology, Pasadena, California 91125

(Received)

ABSTRACT

HeI photoelectron spectra of fluoroethylene, 1,1-difluoroethylene, cis-1,2-difluoroethylene, trans-1,2-difluoroethylene, trifluoroethylene and perfluoroethylene were obtained over the scattering angle range of 45° to 120° and compared with those of ethylene. Vibrational frequencies of the ionic states were measured and their symmetry modes assigned. The asymmetry parameter β as a function of the ionization potential was measured for each molecule. The value of β for the first IP band of these molecules was found to decrease monotonically with increasing fluorine substitution. This variation was interpreted as being due to resonance mixing of the lone pair $F\pi$ orbitals with C-C π orbitals. The data obtained were used to assign some of the spectral bands observed.

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I. INTRODUCTION

In the last ten years the results of measurements of the angular distributions in the photoelectron spectroscopy of atoms and molecules have been used to characterize the symmetry, energy, and bonding nature of the orbitals from which the electrons are photoejected.¹⁻⁹ They have also been used to characterize the physics of the ionization process itself.^{9e,f} Briefly, the differential cross section $\frac{d\sigma_{if}}{d\Omega}$ for photoionization of an atom or molecule by unpolarized light has been found to have the form:^{10,11}

$$\frac{d\sigma_{if}}{d\Omega} = \frac{\sigma_{if}}{4\pi} \left[1 - \frac{\beta_{if}}{2} P_2(\cos \theta) \right] \quad (1)$$

where σ_{if} is the integral cross section for photoionization from an initial state i of the atom or molecule to a final state f of the corresponding singly charged ion, P_2 is the second order Legendre polynomial, θ is the angle between the direction of the incident light beam and the momentum vector of the ejected electron, and β_{if} is the asymmetry parameter which ranges from -1 to +2. This β parameter is the main quantity of interest in the present paper since it contains useful chemical and physical information that cannot be obtained from fixed angle spectra alone. It is now possible to perform approximate calculations of β for atoms¹² and H_2 ¹³ which are in reasonable agreement with experiment, but for larger molecular systems practical computational considerations require less realistic approximations to be made. This has led to results

which are in substantial disagreement with experiment.^{13a, 14} Although the experiments are themselves difficult to perform, due to low signal intensity and perturbation by external forces such as magnetic fields, there is now fairly good agreement between the values of β obtained by various laboratories^{2b, c, 5-7, 9a, d, e, f, g} and typical error bars are currently 0.1 or less.

It has previously been shown that the value of β is usually higher by at least 0.2 for ionization from π orbitals than from σ orbitals in molecules such as ethylene,^{2d, 3, 4c, 9d} methyl substituted ethylenes,^{9g} linear dienes,^{9h} and the five membered ring heterocyclic molecules, furan, thiophene, and pyrrole.^{9c} We have previously used the trends in β in going from benzene to its mono-halogenated derivatives to extend some of the photoelectron band assignments of benzene to these molecules.^{9a} It has also been found that the value of β is roughly the same for two components of a band split by Jahn-Teller interactions.^{4b} This empirical fact has been used in cyclopropane⁸ and SF_6 ^{9b} to assign the transitions that are split by such interactions and rule out this possible splitting for other bands in the spectra. Finally, recent values of β for the lowest π band in the fluoroethylene series were compared with those obtained for some of the fluorine substituted benzenes.^{9d} It was found that β decreases upon increasing fluorine substitution but it decreases more rapidly in the ethylene series than in the benzene series. The results were attributed to the larger extent of transfer of fluorine π electron density to the C-C π bond in the ethylene series than in the benzene series.

The purpose of the present paper is to enhance the understanding of the electronic structure of the six fluoroethylenes using the technique of variable angle photoelectron spectroscopy. This is the first study of this kind for these molecules. It is hoped that these data will further the knowledge of the perfluoro effect,¹⁵ which is frequently used to make photoelectron band assignments. These molecules are furthermore sufficiently small to permit a systematic study of their electronic structure by ab initio calculations,^{15a,16,17} which would complement the information presented here. An additional source of interest in them is the fact that they are the molecular building blocks of many polymeric systems.

In Section II we outline the experimental method. We present a general discussion of the results in Section IIIA, an analysis of vibrational structure in IIIB, an analysis of trends in β in IIIC, a discussion of the initial orbital assignments in IIID, and finally, a summary and conclusion in Section IV.

II. EXPERIMENTAL

The apparatus used is summarized only briefly since it was described in detail previously.¹⁸ A helium discharge lamp produces HeI radiation (wavelengths of 584, 537, and 522 Å at relative intensities of 100:2:0.5) which interacts with the sample vapor in a cylindrical scattering chamber. The pressure of the sample (typically 1 to 2 mTorr) is monitored by a calibrated capacitance manometer¹⁹ in the case of C₂F₄ and by a Schulz -Phelps²⁰ ionization gauge for all other samples. The photoelectrons produced are energy-dispersed by a 180° hemispherical electrostatic analyzer and detected by a Spiraltron electron multiplier. The analyzer and detector are mounted on a gear wheel and can be rotated about the center of the scattering chamber thereby scanning scattering angles from 45° to 120°. The instrument is surrounded by a μ metal shield and is located at the central region of three pairs of Helmholtz coils over which the residual magnetic field is about 0.3 m Gauss or less. The background signal is subtracted from the spectra before β is calculated. The performance of the apparatus is verified by its ability to reproduce the known value of $\beta = 0.88 \pm 0.02$ for the formation of the $^2P_{3/2}$ state of the argon ion by 584 Å radiation.¹⁸ The energy resolution of the apparatus is measured by the full width at half maximum of that $^2P_{3/2}$ peak. The full spectra (Figs. 1 through 7) and angular distributions were obtained with the resolution set at 55 m eV. Spectra of bands which have vibrational structure were also obtained at the higher resolution of 20 meV (Figs. 8 through

20). The energy scale was calibrated by adding a small fractional amount ($<10\%$) of argon to the samples.

The commercial sources and stated minimum purities of the samples are as follows: C_2F_4 , Peninsular Chem Research (PCR), 97%; C_2HF_3 , PCR, 97%; cis-1,2- $C_2H_2F_2$, PCR, 97%; trans-1,2- $C_2H_2F_2$, PCR, 97%; 1,1- $C_2H_2F_2$, Matheson, 99%; C_2H_3F , Matheson, 99.9%; C_2H_4 , J. T. Baker, Chemical Purity (typically 99.5%). These samples were used without further purification.

III. RESULTS AND DISCUSSION

A. General features of photoelectron and β spectra

We have obtained the photoelectron spectra and measured β as a function of ionization potential (IP) and photoelectron kinetic energy (hereafter called β -spectra) for ethylene, fluoroethylene, 1,1-difluoroethylene, cis-1,2-difluoroethylene, trans-1,2-difluoroethylene, trifluoroethylene, and perfluoroethylene. The spectra shown in the bottom panel of Figures 1 through 7 were acquired at the "magic" detector angle of 54.7° , for which P_2 vanishes. It can be seen from Eq. (1) that, at this angle, the ratio of the differential cross sections for two transitions is independent of their respective β 's and is equal to the ratio of the corresponding integral cross sections.^{21,22}

1. C_2H_4

The ethylene photoelectron and β -spectra are reproduced in Fig. 1 from ref. 9g for comparison with those of its fluorine derivatives. The values of the vertical IP and of β for ethylene obtained in previous studies^{4c,9g} are listed in Table I for similar reasons. The ethylene spectrum and assignments of the bands to the corresponding orbitals are well known.^{23,24} The important feature of the values of β for this molecule is that they are noticeably higher for the π band than for the σ bands. This behavior has been noticed not only for ethylene^{3,4c,9d,g} but for other molecules as well.^{9a,c,g,h}

2. C₂H₃F

The photoelectron and β spectra of fluoroethylene are displayed in Fig. 2. The values of the vertical IP's and of β for this molecule are listed in Table II. Previous measurements of these IP's are included,²⁵⁻²⁷ and show reasonable agreement with the present ones. Assignment of the initial orbitals for this and the other molecules in the series will be discussed later in this section. The only band in the spectrum of Fig. 2 showing pronounced vibrational structure is band I, which is associated with the C-C π bond (see Section III D). The most interesting feature of this spectrum is the lack of a sharp peak associated with ionization from a fluorine lone pair orbital.^{9a} In the β -spectrum it can be seen that the values of β for band I have decreased to the range 0.67 to 0.85 compared to the corresponding 1.00 to 1.25 range for ethylene. This trend towards lower β for the C-C π ionization continues in the rest of the molecules in this series and is discussed in detail in Section IIIC. Also striking is the lack of significant variation of the band-average β among bands II through V. The β values for bands II and IV are somewhat lower than the corresponding ones for ethylene.

3. 1,1-C₂H₂F₂

The photoelectron and β -spectra of 1,1-difluoroethylene are given in Fig. 3. The corresponding IP's and values of β are listed in Table III, together with IP's previously published.^{26,28} Orbital assignments previously made^{29,30} are also included in the table.

There is a larger disagreement than expected among the several measurements of the vertical IP of band I. The photoelectron spectrum shows a significant vibrational progression in band I and the values of β for this band are lower than those of the previous molecules. There is also some resolvable structure on the rising side of band II. Band III has a relatively high intensity, and there is a substantial decrease in β across this band. This indicates that more than one transition may be involved in this feature. The intensities and overall shapes of bands IV and V are similar to those of band II.

4. cis-1,2-C₂H₂F₂

The photoelectron and β -spectra of cis-1,2-difluoroethylene are displayed in Fig. 4. The values of β and vertical IP's for this molecule are listed in Table IV, together with previously published IP values.^{15a} Agreement with the latter is good. The interesting features in the β -spectrum are the low value of β (0.30 to 0.47) for band I compared to ethylene and the low value (-0.17) for band III compared to the other bands.

5. trans-1,2-C₂H₂F₂

The photoelectron and β -spectra of trans-1,2-difluoroethylene are displayed in Fig. 5. The corresponding values of β and vertical IP's are given in Table V together with previously published^{15a} IP's. The most striking aspect of the photoelectron spectrum is its similarity to that of the cis isomer (Fig. 4). The shapes and

relative intensities of each of the bands is similar in the two molecules, the largest difference being the vibrational structure of bands II and VI. The corresponding vertical IP's do not differ by more than 1/4 eV in the two isomers. This is significant because the photoelectron spectra of the cis and trans isomers of compounds such as dichloro,^{26,31} dibromo,^{31,32} diiodo,³³ and dimethylethylene (cis and trans 2 butene)³⁴ differ from each other to a greater extent. The reason for this difference in behavior may be the small size of the fluorine atom which would lead to weaker through-space substituent interactions in the corresponding cis isomer. (One interesting parenthetical remark is that the electronic energy of the cis difluoroethylene is actually lower (i.e., more negative) than that of the corresponding trans isomer,^{35,36} contrary to a naive chemical intuition based on the assumption that the fluorine fluorine interactions are repulsive.) The values of β for the two isomers are generally equal to each other within experimental error, which indicates the similarity of the corresponding orbital characteristics.

6. C₂HF₃

The photoelectron and β -spectra of trifluoroethylene are given in Fig. 6. The corresponding values of β and vertical IP's are listed in Table VI together with previously published IP values.^{15a} The photoelectron spectrum of these molecules is more complex than those of the previous fluoroethylenes, having eight discernible bands. Again, band I has a resolvable vibrational progression, and a very low value of β (0.26 to 0.36) for a π band. There is interesting structure in the β -spectrum: in going from band I to band V, the value of β

decreases from 0.48 to -0.14 and then rises to a maximum of 0.51 for band VI, decreasing thereafter to a minimum of -0.10 across band VIII.

7. C_2F_4

The photoelectron and β -spectra of tetrafluoroethylene are displayed in Fig. 7. The corresponding values of β and vertical IP's are listed in Table VII, together with previously published IP values.^{15a,26} The photoelectron spectrum shows an unusually large gap of almost 5.5 eV between the vertical IP of bands I and II (the weak features between 14 and 15 eV are satellites of bands II and III due to ionization by the low intensity 537 Å line of our lamp). Theoretical calculations indicate the presence of at least 8 transitions^{15a,17,37} from band II through 21.2 eV. The value of β for band I is in the range -0.25 to 0.12 which is very low for a C-C π band.^{4a,9c,g,h}

B. Vibrational Analysis

The high resolution spectra (20 meV) of the bands in Figs. 1 through 7 that have resolvable structure are shown in Figs. 8 through 20. Each of these spectra have been convoluted by the 5-channel smoothing procedure of Savitzky and Golay.³⁸ The vibrational frequencies derived from these spectra are listed in Table VIII where they are compared to frequencies previously obtained for the positive ions by photoelectron spectroscopy^{15a,24-28,39} and for the neutrals by infrared and Raman spectroscopy.⁴⁰⁻⁴⁴

Assignments of the vibrational bands of the ions are also listed in Table VIII. These assignments are made by comparison with corresponding neutral molecule frequencies and consideration of the nature of the electron removed (bonding, non-bonding or anti-bonding) in going from the neutral molecule to the ion. The assignments with a greater degree of uncertainty (involving particularly large differences between the frequencies of the ion and the neutral molecule or closeness to two different frequencies of the neutral molecule) are depicted between square brackets in Table VIII.

The spectra of band I in all of these molecules (Figs. 8, 10, 11, 13, 15, 19 and 20) consists of a main progression associated with excitation of the C=C stretching vibration plus combination bands for which one or more additional modes are excited. In the ethylene case (Fig. 8) the additional mode is a $\nu_4(\tau\text{CH}_2)a_u$ twisting torsion; possibly one more mode is involved.²³ That the torsional mode is excited is reasonable since, in the ground electronic state of C_2H_4^+ , the two methylene planes are twisted by 27° with respect to each other.^{15a, 24, 39, 44} The decrease in $\nu_2(\nu\text{C}=\text{C})a_g$ in going from the neutral to the ion shows that band I corresponds to ionization from a strongly bonding orbital, which according to theoretical calculations^{15a, 16} should be the b_{3u} one. Our vibrational frequencies agree well with those published earlier²⁴ for ethylene. In band I of fluoroethylene (Fig. 10), several modes are excited in addition to the main $\nu_4(\nu\text{C}=\text{C})a_g$ progression. Our frequencies

agree well with the previously published^{25,26} ones. In addition, we see a progression with a frequency spacing of $1.4_2 \times 10^3 \text{ cm}^{-1}$ which had not been noticed before. The fact that the CF stretching frequency in band I of $\text{C}_2\text{H}_3\text{F}$ increases from $1.1_5 \times 10^3 \text{ cm}^{-1}$ in the neutral molecule to $1.2_7 \times 10^3 \text{ cm}^{-1}$ in the ion (see Table VIII), indicates that some CF antibonding character is mixed into the ground state orbital.

The high resolution spectra of 1,1- $\text{C}_2\text{H}_2\text{F}_2$ are given in Figs. 11 and 12. As seen from Table 8, the agreement between our vibrational frequencies and those previously published²⁶ is good, with the exception of the $1.0_5 \times 10^3 \text{ cm}^{-1}$ mode in band II. The spectrum of cis-1,2- $\text{C}_2\text{H}_2\text{F}_2$ is particularly rich in vibrational structure: at least two modes contribute to each of bands I (Fig. 13), II (Fig. 14), and III (Fig. 14). One interesting aspect of this molecule is that the $\nu_2(\nu\text{C}=\text{C})a_1$ vibrational mode is observed for two different electronic states of the ion. As expected, the value of its frequency is different for these two states: $1.5_7 \times 10^3 \text{ cm}^{-1}$ and $1.4_2 \times 10^3 \text{ cm}^{-1}$ for bands I and II respectively. This is due to the different bonding characteristics of the electron which is removed in producing the corresponding states of the ion. The high-resolution spectra of trans-1,2- $\text{C}_2\text{H}_2\text{F}_2$ are also rich in vibrational structure (Figs. 15 through 18). Band I is rather complex, consisting of a main progression associated with excitation of the $\nu_2(\nu\text{C}=\text{C})a_g$ stretching vibration ($1.6_0 \times 10^3 \text{ cm}^{-1}$) plus combination bands associated with the $\nu_3(\delta\text{CHF})a_g$ ($1.2_3 \times 10^3 \text{ cm}^{-1}$), $\nu_4(\nu\text{CF})a_g$ ($0.8_5 \times 10^3 \text{ cm}^{-1}$) and

$\nu_5(\delta\text{CHF})a_g$ ($0.5_5 \times 10^3 \text{ cm}^{-1}$) modes, as indicated in Fig. 15. The analysis of bands II, III and VI is displayed in Figs. 16 through 18 respectively. This molecule also contains the lowest ($0.1_5 \times 10^3 \text{ cm}^{-1}$) and highest ($2.8_2 \times 10^3 \text{ cm}^{-1}$) frequencies observed in this series of seven molecules.

In the high resolution spectra of $\text{C}_2\text{F}_3\text{H}$ and C_2F_4 only band I has vibrational structure (Fig. 19 and 20). Two vibrational frequencies are seen in $\text{C}_2\text{F}_3\text{H}$, one of which corresponds to the $\nu_2(\nu\text{C}=\text{C})a'$ stretching mode. In C_2F_4 three modes are observed. The ν_2 frequency is relatively high ($1.7_1 \times 10^3 \text{ cm}^{-1}$) and the $\nu_1(\nu\text{C}-\text{F})a_g$ frequency is higher in the ion than in the neutral molecule, in agreement with an anti-bonding assignment of the orbital from which the electron was removed.^{15a} The lack of an observation of the torsional mode may indicate that the ground state of C_2F_4^+ is planar,^{15a} unlike the ethylene ion. Also, since the band maximum occurs for $v' = 2$ in band I of perfluoroethylene (Fig. 20), there must be a larger increase in the C-C bond distance in going from the neutral molecule to the ion in C_2F_4 than in C_2H_4 .^{15a}

C. Analysis of trends in β -spectra

1. First π band

A cursory observation of Figs. 1 through 7 indicates that the value of β for the lowest IP π band of the series of ethylenic molecules being considered depends rather significantly on the degree of fluorine substitution. Let us examine this phenomenon

in greater detail. To this effect, we display in Fig. 21 the value of β for this band as a function of the number n_F of fluorine substituents. In order to eliminate the effect on β of photoelectron energy, we used the value of β corresponding to the same photoelectron energy for all of these molecules, namely 10.71 eV. This is the energy with which the "vertical" photoelectron of ethylene is ejected. The β values in Fig. 21 were obtained by appropriately interpolating the values of Figs. 1 through 7. The extent of this interpolation is rather small, since the vertical IP's of these molecules are all within 0.2 eV of the value for ethylene. In the absence of autoionization, this procedure is expected to be almost equivalent to the measurement of the vertical β 's using a variable wavelength excitation source tuned to produce photoelectrons of the same kinetic energy for each molecule.^{9f}

It can be seen from Fig. 21 that β decreases monotonically with n_F from 1.25 in ethylene to 0.05 in perfluoroethylene. This decrease is interpreted^{9d} as due to the resonance mixing⁴⁵ of the fluorine lone pair π electrons with the C-C π electrons. A quantitative analysis of this effect is not presently feasible due to the difficulty in performing accurate ab initio calculations of β for polyatomic molecular systems and the consequent lack of detailed theoretical understanding of factors affecting molecular photoelectron angular distributions. We nevertheless suggest a qualitative explanation of this behavior of β .

The resonant mixing of the π fluorine lone pair electrons and the π C-C electrons can be crudely described by writing the resulting hybrid orbital ψ as a linear combination of the fluorine lone pair orbitals ϕ_1 and the C-C π orbital ϕ_2 :

$$\psi = C_1\phi_1 + C_2\phi_2 . \quad (2)$$

Within the single configuration LCAO-MO approximation, the angular dependence of the photoelectron differential cross section comes from the square of the absolute value of the matrix element $\langle \psi_e | \hat{\epsilon} \cdot \mathbf{r} | C_1\phi_1 + C_2\phi_2 \rangle$ where ψ_e is the wavefunction of the ejected photoelectron, $\hat{\epsilon}$ is the unit vector in the polarization direction of the light beam, and $\mathbf{r}$ is the position vector of the electron.^{9a, 14h} Multiplying this transition amplitude by its complex conjugate leads to four terms, two of which are interference cross terms which we ignore in this simplified analysis. Of the other two terms, one contains the angular dependence parameter β_1 of the photoelectrons ejected from the ϕ_1 orbital and the other contains β_2 which is associated with photoionization from the ϕ_2 orbital. The resulting value of β from this hybrid orbital ψ will, as a result, be a linear combination of these two β 's:

$$\beta = \frac{|C_1|^2 \sigma_1 \beta_1 + |C_2|^2 \sigma_2 \beta_2}{|C_1|^2 \sigma_1 + |C_2|^2 \sigma_2} \quad (3)$$

where σ_1 and σ_2 are the corresponding integral photoionization cross sections corresponding to the orbitals ϕ_1 and ϕ_2 . We take for β_2 the value for the vertical C-C π band in ethylene which is 1.25. The value of β_1 for the atomic fluorine lone pair orbital has not been measured or calculated accurately. We approximate it by the value for the π fluorine lone pair orbital ionization in fluorobenzene which is -0.52.^{9a} Since, in Eq. (3), the quantities σ_1 , $|C_1|^2$, σ_2 , and $|C_2|^2$ are all positive, the resulting β will be lower than that for ethylene. This prediction is a consequence of the neglect of the interference terms mentioned above, and it is in agreement with our observations for all of the fluoroethylenes. It seems physically reasonable that increasing the degree of fluorine substitution would increase the fluorine character of the hybrid orbital and lower the value of β (as long as interference terms are unimportant), as Eq. (2) predicts and as observed in Fig. 21.

We have also measured β for the highest π bands in some of the fluorobenzenes and found a decrease in β upon increased fluorine substitution, but the decrease was less pronounced than in the ethylene series.^{9d} This is probably due to a smaller extent of resonance mixing in the benzene series.⁴⁶

If Fig. 21 could be reproduced theoretically, more detailed information could be obtained about the bonding in these molecules. Theoretical descriptions should also strive to account for the differences in β among the geometrical isomers of difluoroethylene.

They may be due to the differences in the fluorine π electron donation to the C=C bond, depending on whether one or two fluorine atoms are bonded to the same carbon atom, and to the presence of fluorine-fluorine interactions. Another possible explanation is the occurrence of autoionization in these molecules. One indication of autoionization is rapid and/or nonmonotonic variation of β with vibrational quantum number across a photoelectron band.^{9e,f} There is some indication of this as can be seen for band I in Figs. 3 and 5. This should be further investigated by examining the photoelectron angular distribution using a synchrotron radiation light source.

2. Higher bands

The trends in the β -spectra for bands above 12 eV in this series are more difficult to follow than the trends for band I discussed above. The values of β for bands II through V in C_2H_3F are lower than the values for bands II through IV in C_2H_4 . This decrease may be related to the mixing of some fluorine σ electron density into the C-C and C-H σ bonds. In 1,1- $C_2H_2F_2$ the decrease is even more pronounced for bands IV and V than in CH_3F . The sharp decrease in β from 0.69 to -0.05 across band III (Fig. 3) may indicate the presence of two transitions. In cis (Fig. 4) and trans (Fig. 5) 1,2- $C_2H_2F_2$, band III is particularly sharp and has a low value of β , roughly -0.2. In analogy with band IV of fluorobenzene,^{9a} these transitions could correspond to ionization mainly from the fluorine lone pair orbitals.

Also, the variation of β across band VI in these two molecules may indicate the presence of two transitions. The low value (-0.14) of β in C_2HF_3 (Fig. 6) for the moderately sharp band V may indicate some fluorine lone pair character in the corresponding orbital. Finally, for C_2F_4 , the interesting aspect of β is its low value for band III, which might be indicative of fluorine lone pair ionization.

D. Initial Orbital Assignments

Hayashi and Nakajima⁴⁷ have recently published the results of semi-empirical CNDO/2 calculations on the fluoroethylenes. In Fig. 22 we compare the energy level diagrams for this series of molecules based on their results (dotted lines) and our measured ionization potentials (solid lines). This type of calculation is used³⁷ to make orbital assignments in photoelectron spectra, with the assumption that Koopmans' theorem⁴⁸ is valid. The parameters associated with the fluorine atom which are needed to perform these semi-empirical calculations were selected⁴⁷ to reproduce a wide range of observed ionization potentials for mono-, 1,1-di-, and perfluoroethylene. Therefore, an assessment of the reliability of these calculations should be based mainly on the remaining molecules. From Fig. 22 it can be seen that the correlation between the calculations and measurements is good only for the highest two orbital energies of each molecule. An analysis of that figure indicates that this type of calculation is very unreliable for making orbital assignments for bands beyond the two lowest IP photoelectron bands. A further indication of this lack

of reliability is obtained by comparing the results for cis and trans 1,2-difluoroethylene. The theoretical energies of the bands in these two isomers are quite different whereas the corresponding experimental values differ by less than $1/4$ eV from each other for the whole set of measured ionization potentials. Therefore, none of the assignments in the present paper are based upon the results of those CNDO/2 calculations.

1. C₂H₄

As mentioned previously, the assignments for ethylene are well-known and are listed in Table I.

2. C₂H₃F

Band I has previously been assigned²⁵ to the 2a" lowest IP π orbital on the basis of its vibrational structure and on the ab initio calculations of Meza and Wahlgren.¹⁶ The high values of β which we obtained for this band are consistent with this assignment. Bands II through V are more difficult to assign due to the lack of vibrational structure and lack of distinctive characteristics in the variation of β across these different bands. One method of making these assignments is to compare the spectrum of fluoroethylene to those of chloro-³¹, bromo-,³² and iodoethylene³³ obtained previously. Figure 23 shows the vertical IP's of these molecules arranged as an orbital energy level diagram. For IP's below 18 eV there are six bands each for chloro-, bromo- and iodo-ethylene but only

five for fluoroethylene. Correlation (dashed) lines are drawn between the four molecules; the correlations between chloro-, bromo-, and iodoethylene are straightforward, but those between chloro- and fluoroethylene are less clear. It seems reasonable that the $4a'$, $5a'$, and $6a'$ orbitals of fluoroethylene would correlate with the corresponding ones in the other monohaloethylenes as shown in that figure, since these are σ orbitals. Fluorine tends to shift σ orbitals to a higher IP than the other halogens due to its greater inductive (electron withdrawal) effect.⁴⁹ The correlation between the fluoroethylene $1a''$ and $7a'$ orbitals and the corresponding ones in the other monohaloethylenes is less certain due to the lack of a peak in the fluoroethylene spectrum near 12.4 eV, which would correspond to the $7a'$ orbital. A peak in this region might be expected on the basis of a smooth extrapolation of the corresponding I, Br and Cl levels in Fig. 23. In the absence of such a peak, one possibility is to assign the $1a''$ and $7a'$ orbital to the 13.80 eV band. Another is to assign the $7a'$ orbital to the 13.80 eV band and the $1a''$ one to band III at 14.54 eV, together with the $6a'$ orbital (as indicated by the dotted line on that figure). Unfortunately, the mild structure in the β -spectrum in the region of bands II and III does not help us to distinguish between these alternatives. In addition, since the $7a'$ orbital is a fluorine nonbonding one we would expect to see a sharp intense band, which is not observed for bands II or III. Finally, adding to the confusion are the two previous conflicting assignments of the $1a''$ orbital to band IV¹⁶ and band V.²⁵ These

assignments seem unreasonable to us based on the above correlations with the other monohaloethylenes and the assignment of the equivalent orbital in fluorobenzene to a band at 13.89 eV.^{9a} The only argument for an assignment of the $1a''$ orbitals to band II (13.80 eV) rather than band III (14.54 eV), is that the intensity of band II is larger than the other bands in the spectrum as could be expected if both the $7a'$ and $1a''$ ionizations were contributing to it. This point could be clarified by performing accurate ab initio calculations of the corresponding states of the positive fluoroethylene ion, as well as of the ground state of the neutral molecule.

3. cis and trans 1,2-C₂H₂F₂

The orbital assignments for these molecules are assumed to be the same since, as discussed in Section III, the spectra are so similar to each other. There is no question that band I corresponds to the highest occupied π orbital based on its low IP and the large separation of its vibrational components which yield a vibration frequency characteristic of C=C bonds. This orbital would be the $2a_u$ in the trans isomer and the $2b_1$ in the cis isomer. The low value of β for band III indicates that it is a nonbonding fluorine orbital, of unknown symmetry, in analogy with the nonbonding orbitals in fluorobenzene.^{9a} It is somewhat surprising that this band shows vibrational structure. For a pure lone pair ionization one would expect such structure to be absent and the band to consist of a single, very sharp peak, as in chloro-, bromo- and iodobenzene.^{9a} Since, as indicated in Table 8,

both C-F and C-H vibrations contribute to that band, one concludes that the orbital involved has not only some C-F character but, more surprisingly, some C-H character also.

The correlations between the energy levels of the *trans* dihaloethylenes can be of similar usefulness as those between the vinyl compounds. These correlations between *trans* 1,2-diiodo-, dibromo-, dichloro-, and difluoroethylene are shown in Fig. 24. Also indicated on that figure are assignments based on those correlations and on the arguments presented below. The orbital designations are those for the *trans* isomer symmetry. The correlation of the $4b_u$ and $5a_g$ fluorine nonbonding orbitals with the corresponding ones in the other dihalo compounds seems reasonable, based on the trend toward higher IP as one goes from diiodo- to dichloroethylene. Thus, band II in *trans* 1,2-difluoroethylene is very tentatively assigned to the $4b_u$ and $5a_g$ orbitals; in *cis* 1,2-difluoroethylene it is assigned to the $5a_1$ and $4b_2$ orbitals. It is not clear why the vibrational structure for this band is so different in these two isomers. It is also surprising that band II of *cis* 1,2-difluoroethylene has only one main vibrational progression (the $\nu_2(\nu C=C)a_1$ one), as shown in Fig. 14, if it indeed corresponds to ionization from two different orbitals. The assignment of band III in *trans* 1,2-difluoroethylene is to the $1b_g$ fluorine nonbonding orbital and to the $1a_2$ one in *cis* 1,2-difluoroethylene. This assignment is more certain than those for band II since band III has the expected sharpness of a nonbonding orbital, and a low value of β in analogy with fluorobenzene.^{9a} The assignments for bands IV and V are based solely on the

correlations with the other dihalo compounds as shown in Fig. 24 and should, therefore, be regarded as tentative. Finally, band VI in each compound can be assigned to two orbitals ($3a_g$ and $3b_u$ in the trans and $3a_1$ and $4a_1$ in the cis isomer) based on the correlation diagrams and on the β -spectra. The rapid variation of β across this band in each molecule suggests the presence of more than one underlying transition.

4. 1, 1-C₂H₂F₂

The only orbital assignment that can be made with any certainty at this time is that band I corresponds to the $2b_1$ π orbital. In addition, from the variation of β across band III, one may conclude that this band probably corresponds to ionization from at least two orbitals. There is no resolved vibrational structure in Fig. 3, except for that of bands I and II, to help us in making assignments. Correlations between this molecule and 1,1-dichloro-, dibromo-, and diiodoethylene are not at all clear, possibly due to the high degree of interactions between the two halogen atoms in these molecules.

5. C₂HF₃

The only orbital assignment that can be made is that band I corresponds to ionization from the least bound π orbital, based upon its IP, its vibrational frequencies, and the variation of β with the degree of fluorine substitution of Fig. 21.

6. C₂F₄

Band I can be assigned to the least bound π orbital, $2b_{3u}$, in analogy with the other molecules and based on its IP, its vibrational frequencies, the variation of β with the degree of fluorine substitution of Fig. 21, and calculations.^{15a,17} There are so many transitions associated with the C-F and nonbonding F orbitals that correspond to bands II through V that there is little hope of making these assignments at the present level of resolution.

IV. SUMMARY AND CONCLUSIONS

The HeI photoelectron spectra of the six fluorine derivatives of ethylene have been obtained at a detector angle of 54.7° and compared to that of ethylene. The spectral bands which had vibrational structure were measured under high resolution (20 meV) and the vibrational frequencies and corresponding modes were assigned. Most importantly, the asymmetry parameter β was measured across each band of these spectra. It was noticed that there was a monotonic decrease in β upon increasing fluorine substitution for the lowest IP π band which was interpreted as due to the resonant mixing of the fluorine lone pair π electrons with the C=C π electrons. The IP's of monofluoro, cis 1,2-difluoro and trans 1,2-difluoroethylene were correlated with those in the corresponding chloro-, bromo-, and iodoethylenes published previously. All of the above data were used to make some assignments of the spectral bands of these fluoroethylenes to the corresponding orbitals.

The information available so far does not permit reliable assignments to be made for most of the ionization bands of the remaining molecules considered. Nevertheless, the photoelectron and β -spectra obtained, together with future experimental and theoretical work, may eventually lead to such assignments.

TABLE I. β values and ionization potentials for ethylene at 584 Å^a

Band	Initial ^b Orbital	Orbital Description	Vertical IP (eV) ^c	β		
				Range ^d	Ref 9g	Vertical ^e Ref. 4c
I	1 b _{3u}	π C-C	10.51	1.0 $\pm$ 0.10 to 1.25 $\pm$ 0.05	1.25 $\pm$ 0.05	1.20
II	1 b _{3g}	σ C-H	12.82	0.23 $\pm$ 0.10 to 0.40 $\pm$ 0.09	0.30 $\pm$ 0.05	0.35
III	3 a _g	σ C-C	14.69	0.48 $\pm$ 0.05 to 0.73 $\pm$ 0.07	0.60 $\pm$ 0.10	0.60
IV	1 b _{2u}	σ C-H	15.90	0.41 $\pm$ 0.15 to 0.75 $\pm$ 0.08	0.65 $\pm$ 0.05	0.65

^a All the numbers reported in this table, except those in the last column, are taken from Ref. 9g.

^b We use the standard coordinate system for which the z axis lies along the C=C bond and the y axis is in the plane of the molecule (R. S. Mulliken, J. Chem. Phys. 23, 1997 (1955)).

^c Measured at the band maximum and having an absolute uncertainty of ± 0.02 eV.

^d The first and second values given for each band are, respectively, the corresponding lowest and highest values of β . The variation of β across electronic bands is discussed in Section III C. The uncertainties in β are obtained from the goodness-of-fit of the data to Eq. (1) (see Ref. 18).

^e Obtained at the vertical IP.

TABLE II. β values and ionization potentials for fluoroethylene at 584 Å.

Band	Initial Orbital		Orbital Description	This Work ^b		Vertical IP (eV)			β^a	
	Ref. 25	Ref. 16		This Work	Ref. 25	Ref. 26	Ref. 27 ^c	Range	Vertical	
I	2 a''	2 a''	2 a''	10.56	10.57	10.58	10.5	0.67±0.05 to 0.85±0.02	0.82±0.02	
II	7 a'	7 a'	(1 a'', 7 a')	13.80	13.80	13.79	13.8	0.21±0.06 to 0.33±0.05	0.31±0.07	
III	6 a'	6 a'	6 a'	14.54	14.56	14.51	14.6	0.22±0.05 to 0.36±0.11	0.31±0.05	
IV	5 a'	1 a''	5 a'	16.68	16.76	16.77	16.9	0.10±0.07 to 0.40±0.10	0.38±0.05	
V	1 a''	5 a'	4 a'	18.00	17.97	17.97	18.2	0.29±0.13 to 0.59±0.07	0.54±0.06	

^a The meaning of the uncertainties and of "range" and "vertical" are the same as in Table I.^b The absolute uncertainties are ± 0.02 eV.^c Values estimated from Figure 8.33 of Ref. 27.

TABLE III. β values and ionization potentials for 1,1-difluoroethylene at 584 Å.

Band	Initial Orbital		Orbital Description	Vertical IP (eV)		β^a	
	This Work	Ref. 29, Ref. 30		This Work	Ref. 28, Ref. 26	Range	Vertical
I	2 b ₁	b ₁	π C-C	10.69	10.84	0.46±0.05 to 0.81±0.03	0.64±0.03
II	a ₁ , b ₂	b ₂		14.83	14.85	0.19±0.17 to 0.56±0.07	0.39±0.11
III	(two orbitals) ^d	b ₂ , a ₂	a, b ₂ , a ₂	15.73	15.75	-0.05±0.17 to 0.69±0.04	0.55±0.05
IV		a ₁		18.18	18.20	-0.19±0.20 to 0.15±0.13	-0.07±0.11
V	b ₁			19.74	19.65	-0.04±0.07 to 0.25±0.18	0.18±0.09

^a The meaning of the uncertainties and of "range" and "vertical" are the same as in Table I.

^b The absolute uncertainties are ±0.02 eV.

^c The values given are estimated from the Figure 8.36 of Ref. 8.

^d See Section III D.4.

TABLE IV. β values and ionization potentials for cis-1,2- $\text{C}_2\text{H}_2\text{F}_2$ at 584 Å.

Band	Initial Orbital	Orbital Description	Vertical IP (eV)		β^a	
			This Work ^b	Ref. 15a	Range	Vertical
I	2 b ₁	π C-C	10.44	10.43	0.30±0.04 to 0.47±0.06	0.30±0.03
II	(5a ₁ , 4b ₂)	σ n _F , σ n _F	13.97	13.97	0.39±0.03 to 0.49±0.03	0.47±0.03
III	1 a ₂	σ n _F	14.87		-0.17±0.03	-0.17±0.03
IV	(1 b ₁)	π n _F	16.15		0.17±0.09 to 0.57±0.07	0.42±0.09
V	(3 b ₂)	σ CF	17.05		0.33±0.17 to 0.62±0.11	0.47±0.08
VI	3 a ₁ , 4 a ₁	σ CH, σ CF	18.79		0.02±0.11 to 0.66±0.07	0.46±0.03

^a The meaning of the uncertainties and of "range" and "vertical" are the same as in Table I.

^b The absolute uncertainties are ±0.02 eV.

TABLE V. β values and ionization potentials of trans-1, 2-difluoroethylene at 584 Å.

Band	Initial Orbital	Orbital Description	Vertical IP (eV)		β^a	
			This Work ^b	Ref. 15a	Range	Vertical
I	2 a _u	π C-C	10.38	10.38	0.32±0.11 to 0.53±0.11	0.48±0.06
II	(4b _u , 5a _g)	σ n _F , σ n _F	13.97	13.90	0.13±0.09 to 0.52±0.06	0.39±0.05
III	1 b _g	σ n _F	15.08		-0.20±0.11 to 0.04±0.20	0.02±0.07
IV	(1 a _u)	π n _F	16.38		0.12±0.06 to 0.33±0.10	0.21±0.04
V	(4 a _g)	σ CF	17.00		0.10±0.05 to 0.49±0.07	0.39±0.05
VI	3 a _g , 3b _u	σ CH, σ CF	18.77		-0.07±0.11 to 0.50±0.13	0.36 ±0.06

^a The meaning of the uncertainties and of "range" and "vertical" are the same as in Table I.

^b The absolute uncertainties are ± 0.02 eV.

TABLE VI. β values and ionization potentials for trifluoroethylene at 584 Å.

Band	Initial Orbital	Orbital Description	Vertical IP (eV)		β^a	
			This Work ^b	Ref. 15a	Range	Vertical
I	a''	π C-C	10.54	10.53	0.26 $\pm$ 0.03 to 0.36 $\pm$ 0.05	0.30 $\pm$ 0.03
II			14.62	14.64	0.16 $\pm$ 0.12 to 0.48 $\pm$ 0.06	0.41 $\pm$ 0.05
III			15.90		-0.06 $\pm$ 0.06 to 0.24 $\pm$ 0.05	-0.06 $\pm$ 0.06
IV			16.36		-0.11 $\pm$ 0.10 to 0.09 $\pm$ 0.06	-0.11 $\pm$ 0.10
V			16.69		-0.14 $\pm$ 0.08 to 0.04 $\pm$ 0.11	-0.08 $\pm$ 0.03
VI			18.06		0.25 $\pm$ 0.07 to 0.51 $\pm$ 0.06	0.36 $\pm$ 0.07
VII			18.56		0.14 $\pm$ 0.06 to 0.45 $\pm$ 0.04	0.18 $\pm$ 0.06
VIII			20.14		-0.10 $\pm$ 0.04 to 0.10 $\pm$ 0.09	0.06 $\pm$ 0.03

^a The meaning of the uncertainties and of "range" and "vertical" are the same as in Table I.

^b The absolute uncertainties are ± 0.02 eV.

TABLE VII. β values and ionization potentials for perfluoroethylene at 584 Å.

Band	Initial Orbital ^a					Orbital Description	Vertical IP (eV)		β^b		
	Ref. 41	Ref. 17	Ref. 15a	Ref. 37	This Work		This Work ^c	Ref. 15a	Ref. 26	Range	Vertical
I	b_{1u}	b_{2u}	b_{2u}	b_{1u}	b_{3u}	π C-C	10.56	10.52	10.54	-0.25±0.10 to 0.12±0.09	0.05±0.04
II	a_g			a_g			15.95	15.95	15.93	-0.21±0.12 to 0.11±0.13	-0.10±0.12
III	b_{1g}, b_{2u}, a_u			b_{1g}, b_{2u}, a_u			16.63	16.60	16.64	-0.42±0.11 to 0.00±0.05	-0.26±0.09
IV	b_{3g}			b_{3g}			17.60	17.60	17.57	-0.13±0.09 to 0.35±0.16	-0.13±0.09
V	b_{3u}			b_{3u}			18.22	18.21	18.45	-0.12±0.12 to 0.17±0.10	0.17±0.10

^a Different authors use different coordinate systems; for our convention, see Table I, footnote b.^b The meaning of the uncertainties and of "range" and "vertical" is the same as in Table I.^c The absolute uncertainties are ±0.02 eV.

TABLE VIII. Vibrational Frequencies

Molecule	Band	Vibrational Assignment ^a	Frequency (10 ³ cm ⁻¹)		
			Ion This ^b Work	Previous Work	Neutral, Previous Work
C ₂ H ₄	I	ν ₂ (νC=C)a _g	1.2 ₆	1.2 ₃ ^c	1.62 ₃ ^d
		ν ₄ (τCH ₂)a _u	0.4 ₂	0.4 ₃ ^c	0.82 ₅ ^d
	IV	ν ₃ (δCH ₂)a _g	1.1 ₁	~1.2 ₄ ^c	1.34 ₂ ^d
C ₂ H ₃ F	I	ν ₄ (νC=C)a'	1.5 ₃	1.5 ₃ ^e , 1.5 ₇ ^f	1.65 ₅ ^g
			1.4 ₂		
		ν ₇ (νCF)a'	1.2 ₇	1.3 ₃ ^e , 1.3 ₉ ^f	1.15 ₅ ^g
		ν ₉ (δCHF)a''	0.4 ₈	0.5 ₁ ^e , 0.5 ₀ ^f	0.48 ₈ ^g
1,1-C ₂ H ₂ F ₂	I	ν ₂ (νC=C)a ₁	1.5 ₃	1.6 ₀ ^e	1.72 ₈ ^h
		ν ₄ (νCF)a ₁	0.7 ₀	0.7 ₂ ^e	0.92 ₅ ^h
	II	[ν ₃ (δCH ₂)a ₁]	1.0 ₅	1.1 ₈ ^e	1.41 ₄ ^h
cis-1,2-C ₂ H ₂ F ₂	I	ν ₂ (νC=C)a ₁	1.5 ₇		1.71 ₆ ⁱ
		ν ₃ (δCHF)a ₁	1.3 ₉		1.26 ₃ ⁱ
		ν ₅ (δCHF)a ₁	0.2 ₅		0.23 ₇ ⁱ
	II	[ν ₂ (νC=C)a ₁]	1.4 ₂		1.71 ₆ ⁱ
		ν ₄ (νCF)a ₁	0.9 ₇		1.01 ₅ ⁱ
			0.6 ₅		
	III	ν ₁ (νCH)a ₁	2.6 ₁		3.12 ₂ ⁱ
		[ν ₄ (νCF)a ₁]	1.1 ₀		1.01 ₅ ⁱ
trans-1,2-C ₂ H ₂ F ₂	I	ν ₂ (νC=C)a _g	1.6 ₀		1.69 ₄ ⁱ
		ν ₃ (δCHF)a _g	1.2 ₃		1.28 ₆ ⁱ
		[ν ₄ (νCF)a _g]	0.8 ₅		1.12 ₃ ⁱ
		[ν ₅ (δCHF)a _g]	0.5 ₅		0.54 ₈ ⁱ
	II	[ν ₅ (δCHF)a _g]	0.5 ₀		0.54 ₈ ⁱ
			0.1 ₅		
	III	ν ₁ (νCH)a _g	2.8 ₂		3.11 ₁ ⁱ
		ν ₄ (νCF)a _g	1.1 ₈		1.12 ₃ ⁱ
	VI		0.9 ₂		
		ν ₅ (δCHF)a _g	0.4 ₅		0.54 ₈ ⁱ
C ₂ HF ₃	I	ν ₂ (νC=C)a	0.6 ₁		0.78 ₈ ^j
			0.5 ₆		
C ₂ F ₄	I	ν ₂ (νC=C)a _g	1.7 ₁	1.6 ₆ ^k , 1.6 ₉ ^l	1.87 ₂ ^l
		ν ₁ (νCF)a _g	0.8 ₂	0.7 ₉ ^k , 0.7 ₄ ^l	0.77 ₈
		ν ₃ (δCF ₂)a _g	0.4 ₀	0.3 ₇ ^k	0.39 ₄ ^l

TABLE VIII, Continued

- ^a The notation follows the recommendation given by R. S. Mulliken, J. Chem. Phys. 23, 1997 (1955).
- ^b The absolute uncertainties are estimated to be $\pm 0.08 \times 10^3 \text{ cm}^{-1}$.
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- ^d Values given in Ref. 24 and Ref. 25a without reference to the original work.
- ^e Ref. 26.
- ^f Ref. 25.
- ^g Ref. 40.
- ^h Ref. 41.
- ⁱ Ref. 42.
- ^j Ref. 43.
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FIGURE CAPTIONS

Figure 1. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for ethylene. The spectrum was obtained at a detector angle of 54.7° . This figure is reproduced from Ref. 9g. [The ordinate of the photoelectron spectrum of that reference was rescaled to correspond to the conditions of the other spectra in the present paper.]

Figure 2. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for fluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 60 scans. Total dwell time per channel was 60 s.

Figure 3. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for 1,1-difluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 30 scans. Total dwell time per channel was 30 s.

Figure 4. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for cis-1,2-difluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 60 scans. Total dwell time per channel was 60 s.

Figure 5. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for trans-1,2-difluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 40 scans. Total dwell time per channel was 40 s.

Figure 6. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for tribluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 40 scans. Total dwell time per channel was 40 s.

Figure 7. Photoelectron spectrum (lower panel) and β -spectrum (upper panel) for perfluoroethylene. The spectrum was obtained at a detector angle of 54.7° using adjacent 18 meV wide channels and 50 scans. Total dwell time per channel was 50 s.

Figure 8. High resolution (20 meV) photoelectron spectrum of band I of ethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 80 scans. Total dwell time per channel was 80 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 9. High resolution (20 meV) photoelectron spectrum of band IV of ethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 100 scans. Total dwell time per channel was 100 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 10. High resolution (20 meV) photoelectron spectrum of band I of fluoroethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 100 scans. Total dwell time per channel was

100 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 11. High resolution (20 meV) photoelectron spectrum of band I of 1,1-difluoroethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 12. High resolution (20 meV) photoelectron spectrum of band II of 1,1-difluoroethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 13. High resolution (20 meV) photoelectron spectrum of band I of cis-1,2-difluoroethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 100 scans. Total dwell time per channel was 100 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 14. High resolution (20 meV) photoelectron spectrum of bands II and III of cis-1,2-difluoroethylene obtained at a detector angle of 54.7°

using adjacent 4 meV wide channels and 80 scans. Total dwell time per channel was 80 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 15. High resolution (20 meV) photoelectron spectrum of band I of trans-1,2-difluoroethylene obtained at a detector angle of 54.7° using adjacent 3 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 16. High resolution (20 meV) photoelectron spectrum of band II of trans-1,2-difluoroethylene obtained at a detector angle of 54.7° using adjacent 2 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 17. High resolution (20 meV) photoelectron spectrum of band III of trans-1,2-difluoroethylene obtained at a detector angle of 54.7° using adjacent 2 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 18. High resolution (20 meV) photoelectron spectrum of band VI of trans-1,2-difluoroethylene obtained at a detector angle of 54.7°

using adjacent 3 meV wide channels and 70 scans. Total dwell time per channel was 70 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 19. High resolution (20 meV) photoelectron spectrum of band I of trifluoroethylene obtained at a detector angle of 54.7° using adjacent 4 meV wide channels and 100 scans. Total dwell time per channel was 100 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 20. High resolution (20 meV) photoelectron spectrum of band I of perfluoroethylene obtained at a detector angle of 54.7° using adjacent 4 meV wide channels and 80 scans. Total dwell time per channel was 80 s. The position of the vibrational lines, the assignment of the corresponding vibrational modes and the values of their frequencies are given at the top of the figure.

Figure 21. Plot of β for the C-C π orbitals as a function of the number of fluorine atoms n_F in the fluoroethylene series. The values of β in this figure were obtained at an electron kinetic energy of 10.71 eV (see text).

Figure 22. Orbital energy level diagrams for the fluoroethylene series derived by photoelectron spectroscopy in the present work (solid lines) and by CNDO/2 calculations (dotted lines) from Ref. 47.

Figure 23. Correlation of energy levels for the monohalo-substituted ethylenes derived by photoelectron spectroscopy. The orbital energies and assignments for iodoethylene are taken from Ref. 33 and for bromo- and chloroethylene from Ref. 31. The orbital energies of fluoroethylene are those of the present experiments; the assignments for it are derived on the basis of these correlations, the β values, and vibrational structure in the spectra (see text).

Figure 24. Correlation of energy levels for the trans dihalogenated ethylenes derived by photoelectron spectroscopy. The orbital energies and assignments for trans-1,2-C₂H₂I₂ are taken from Ref. 33 and for trans-1,2-C₂H₂Br₂ and trans-1,2-C₂H₂Cl₂ from Ref. 31. The orbital energies of trans-1,2-C₂H₂F₂ are those of the present experiments; the assignments for it are derived on the basis of these correlations, the β values, and vibrational structure in the spectra (see text).

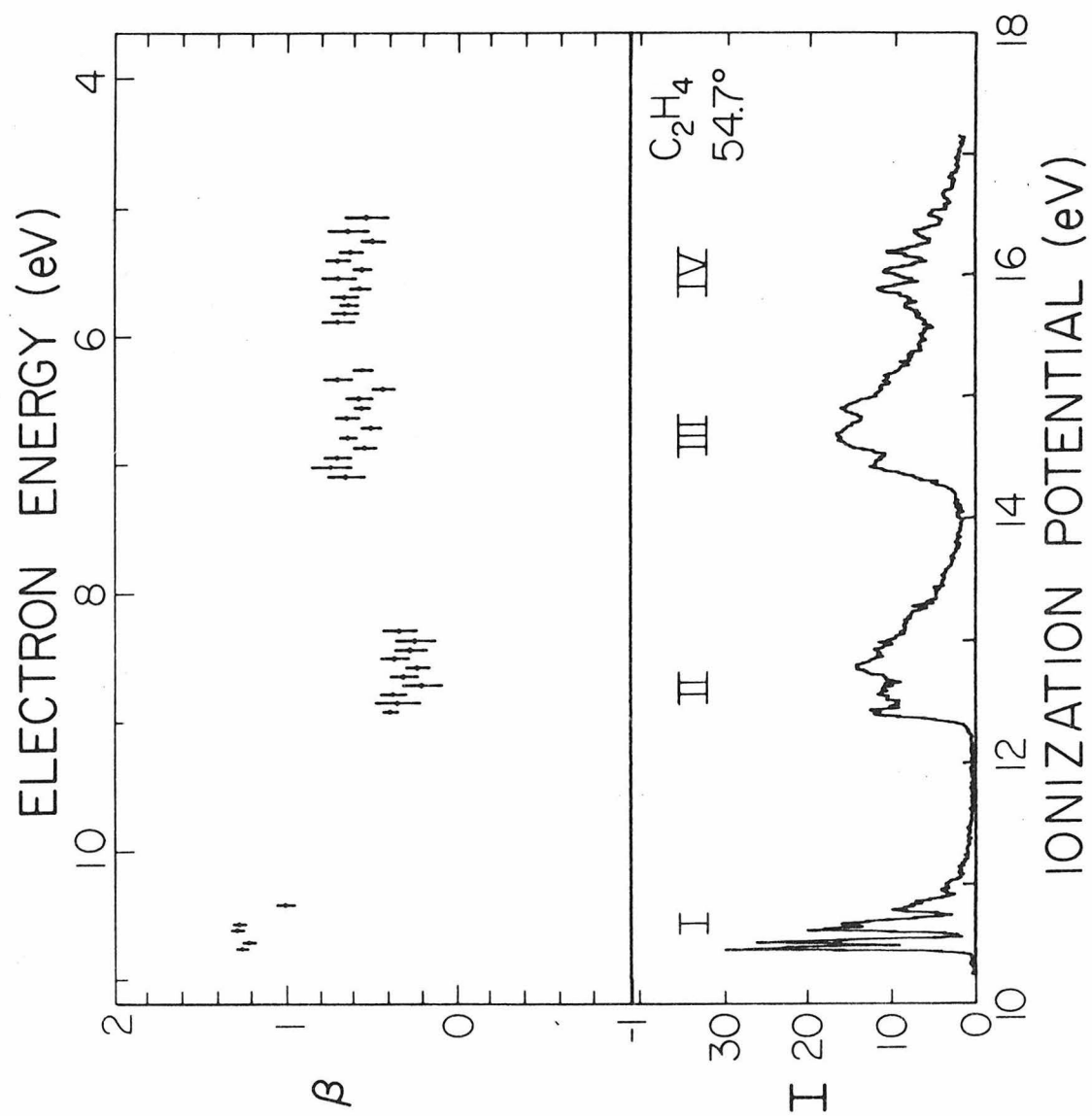


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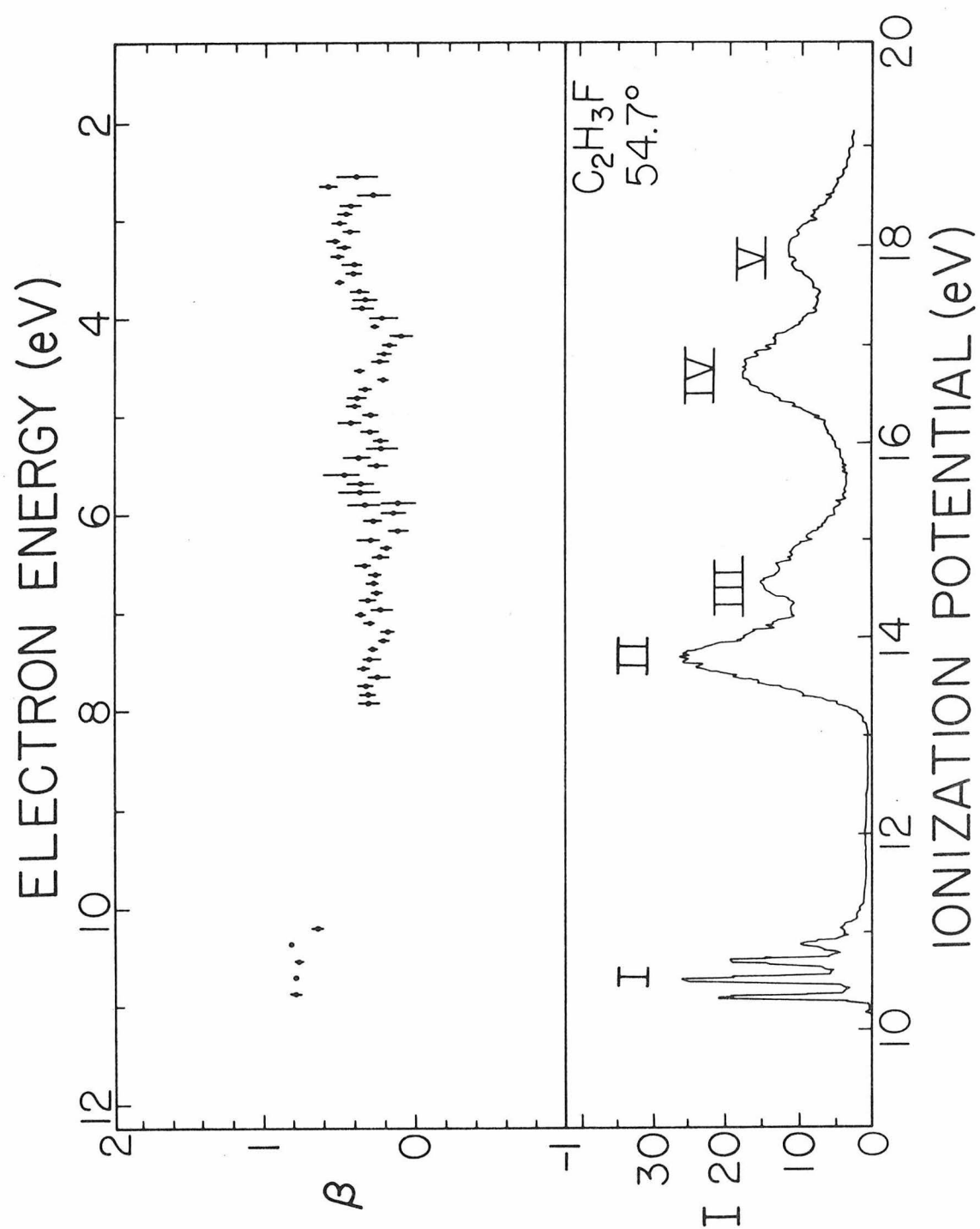


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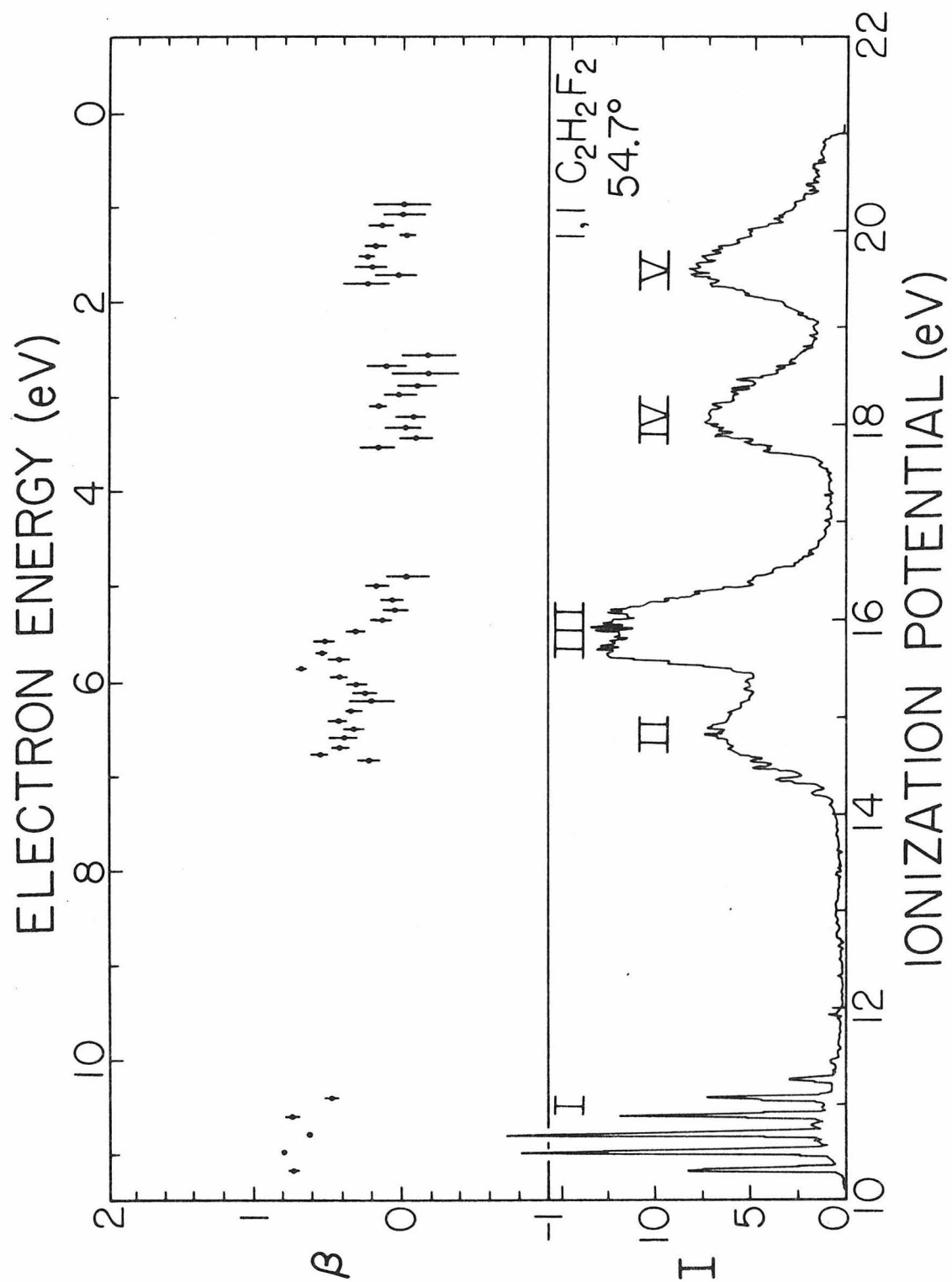


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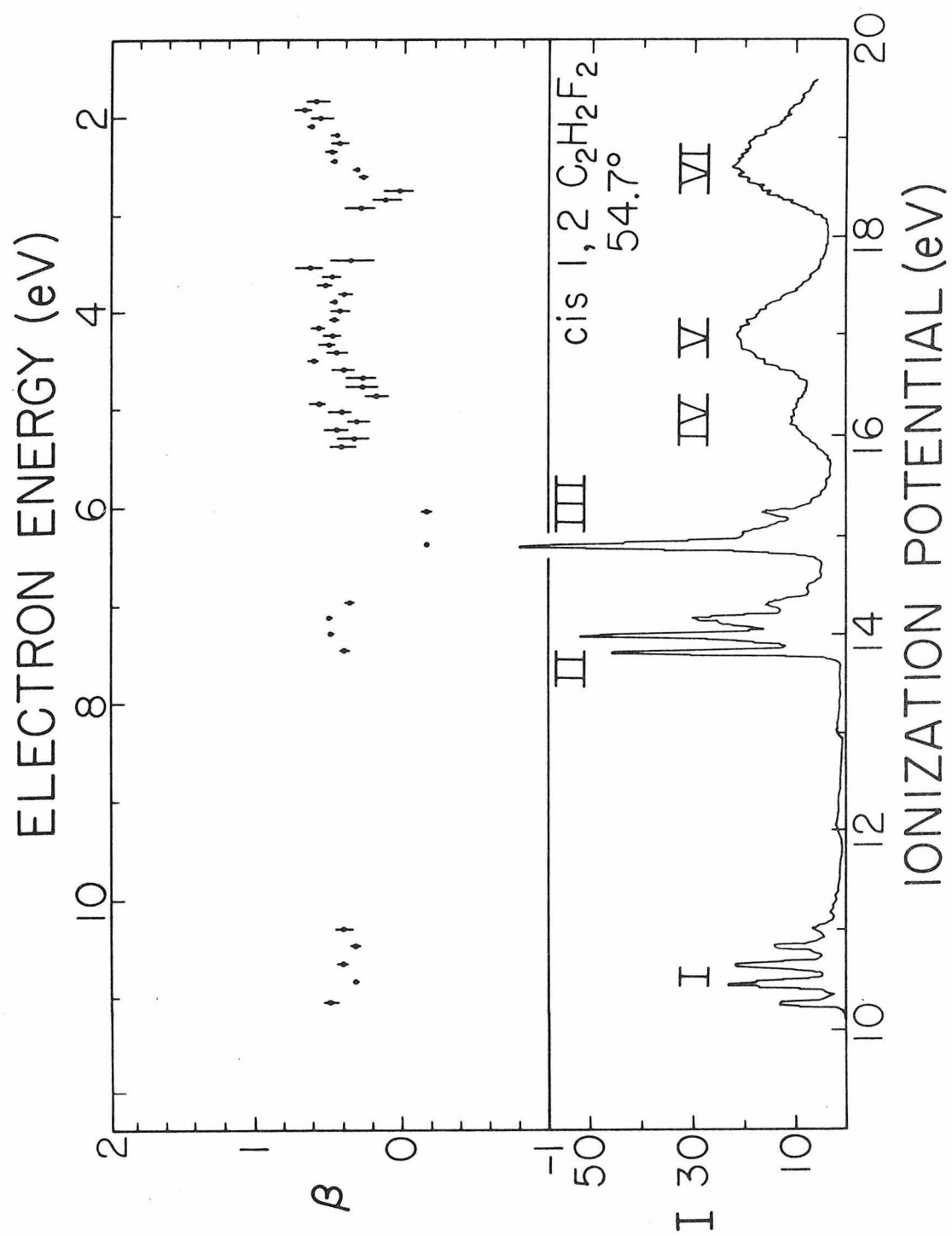


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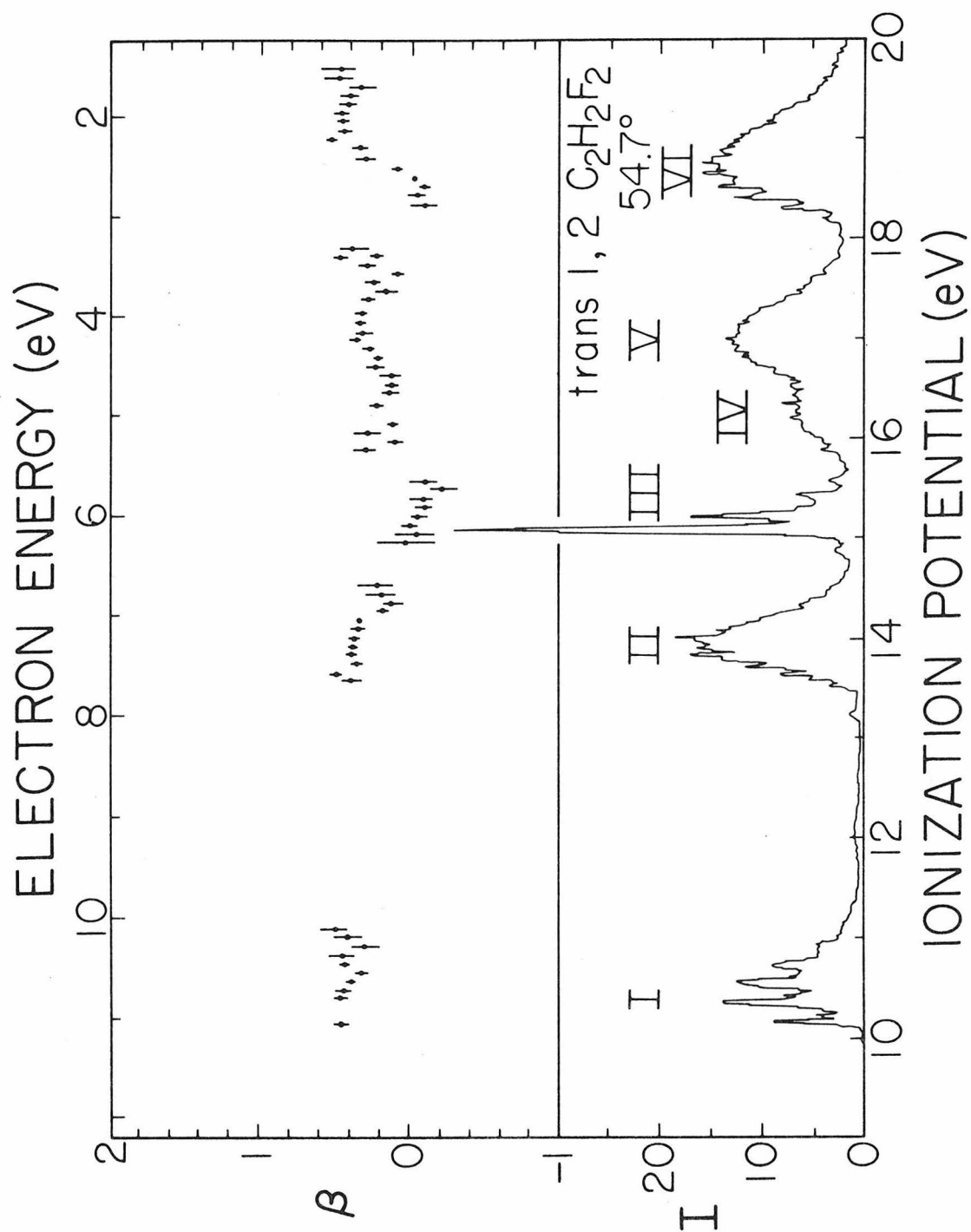


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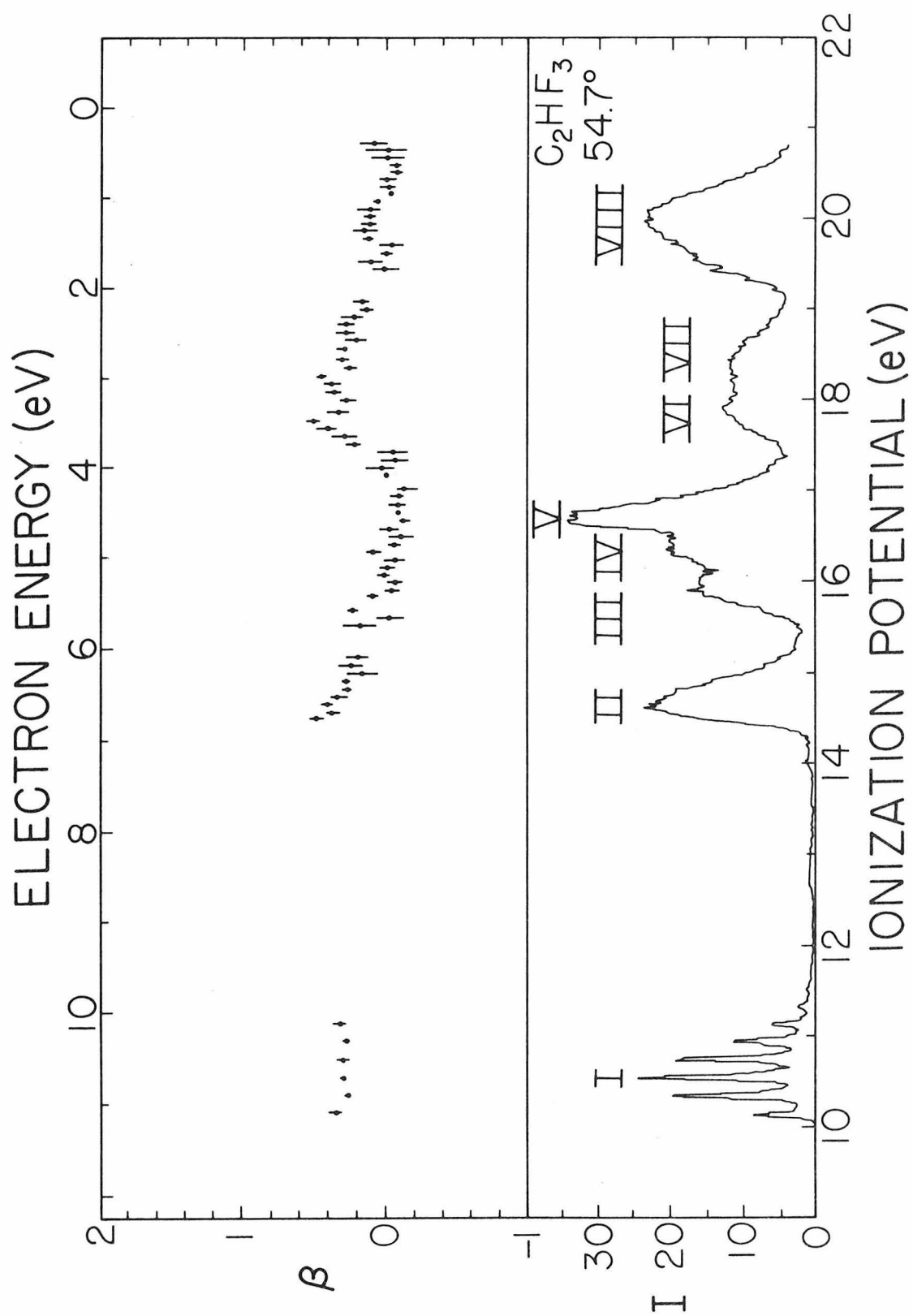


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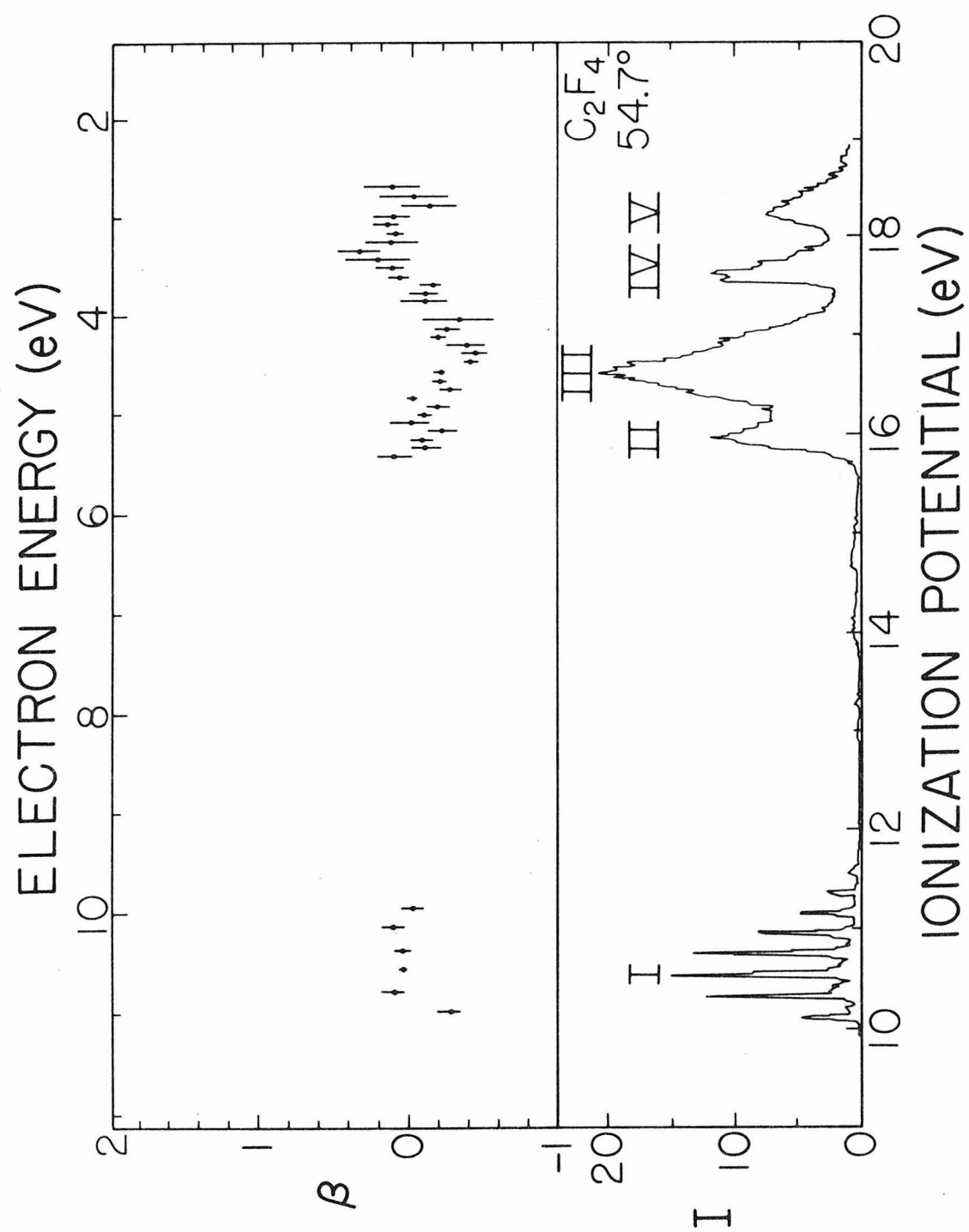


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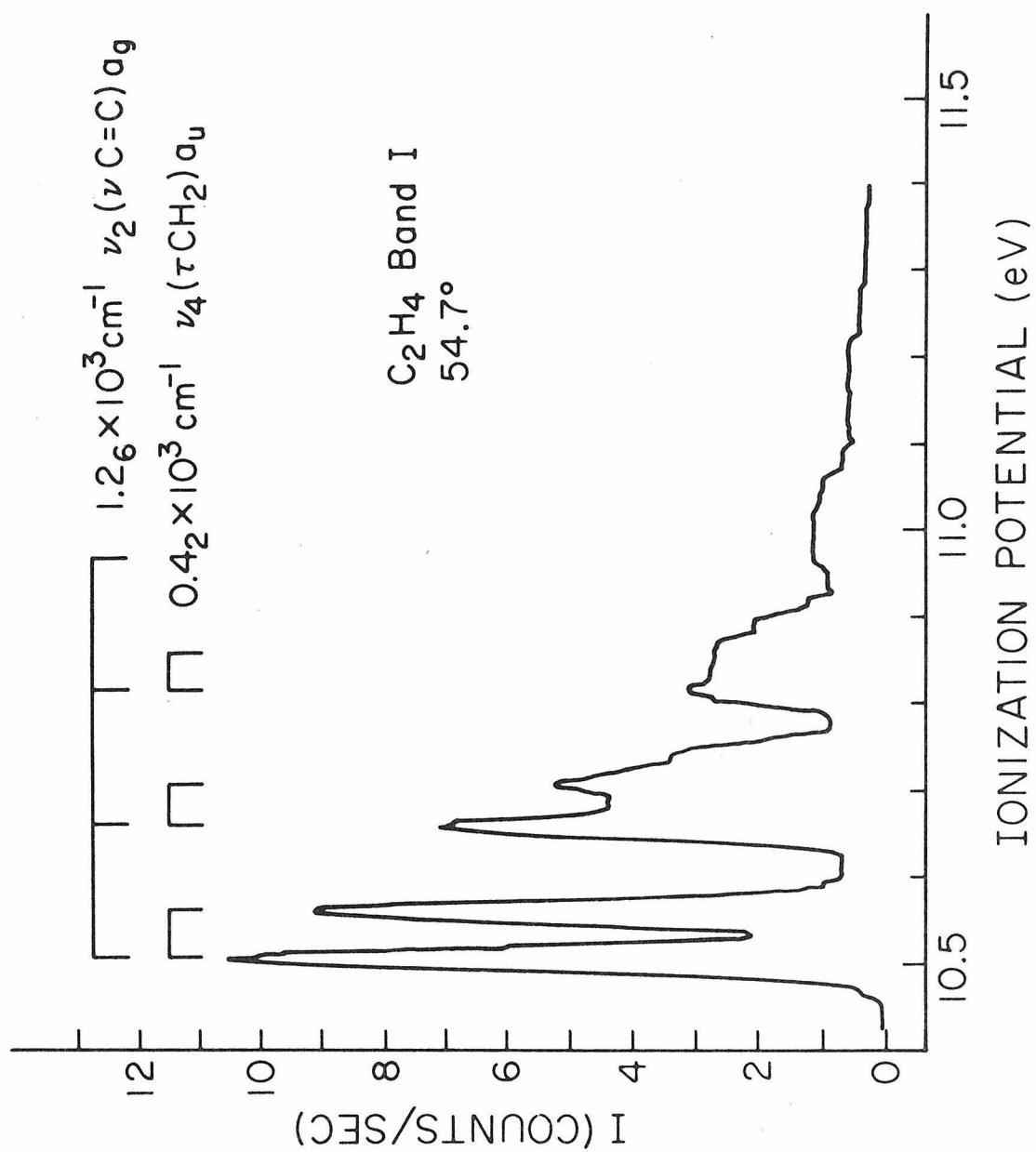


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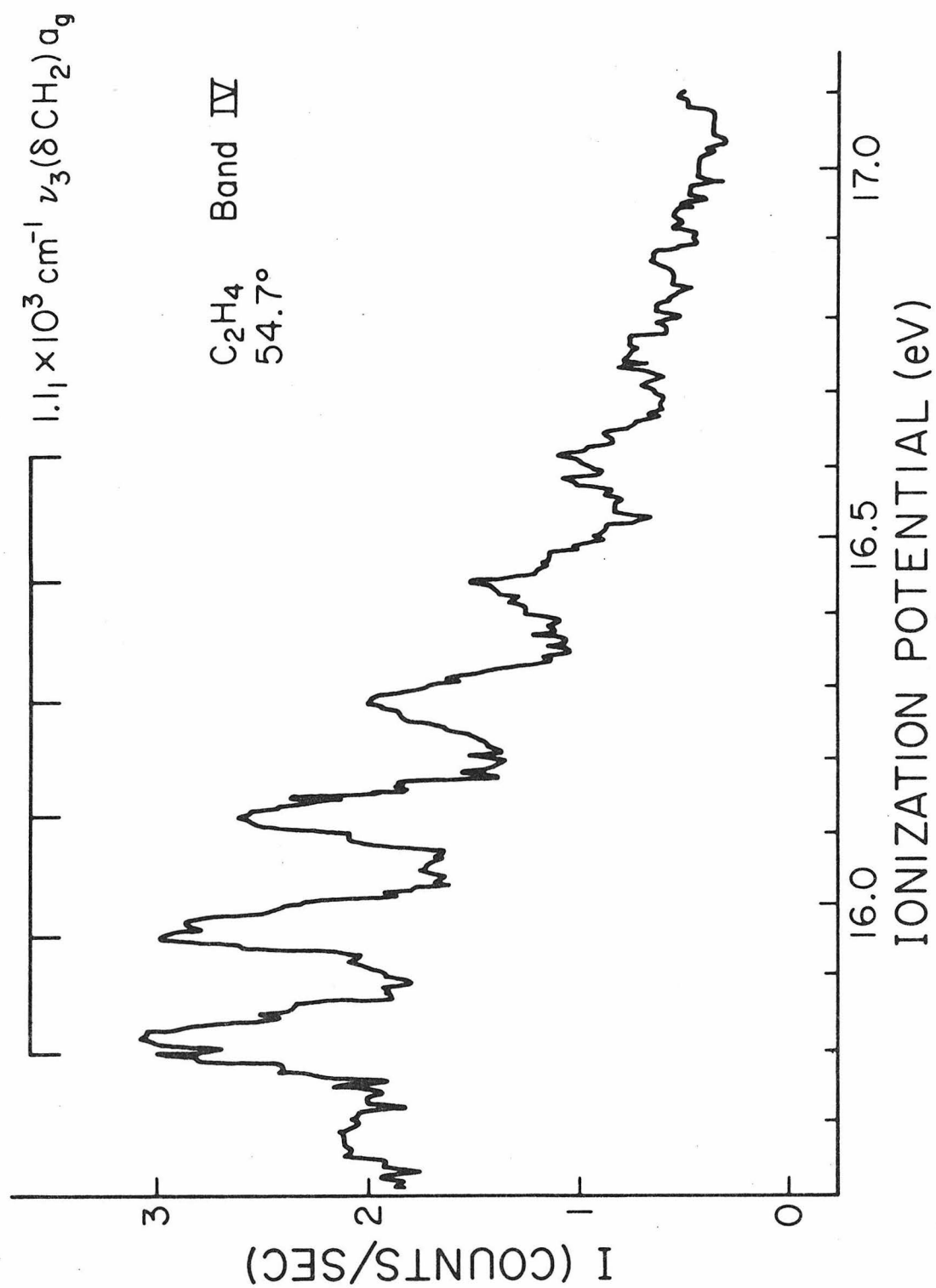


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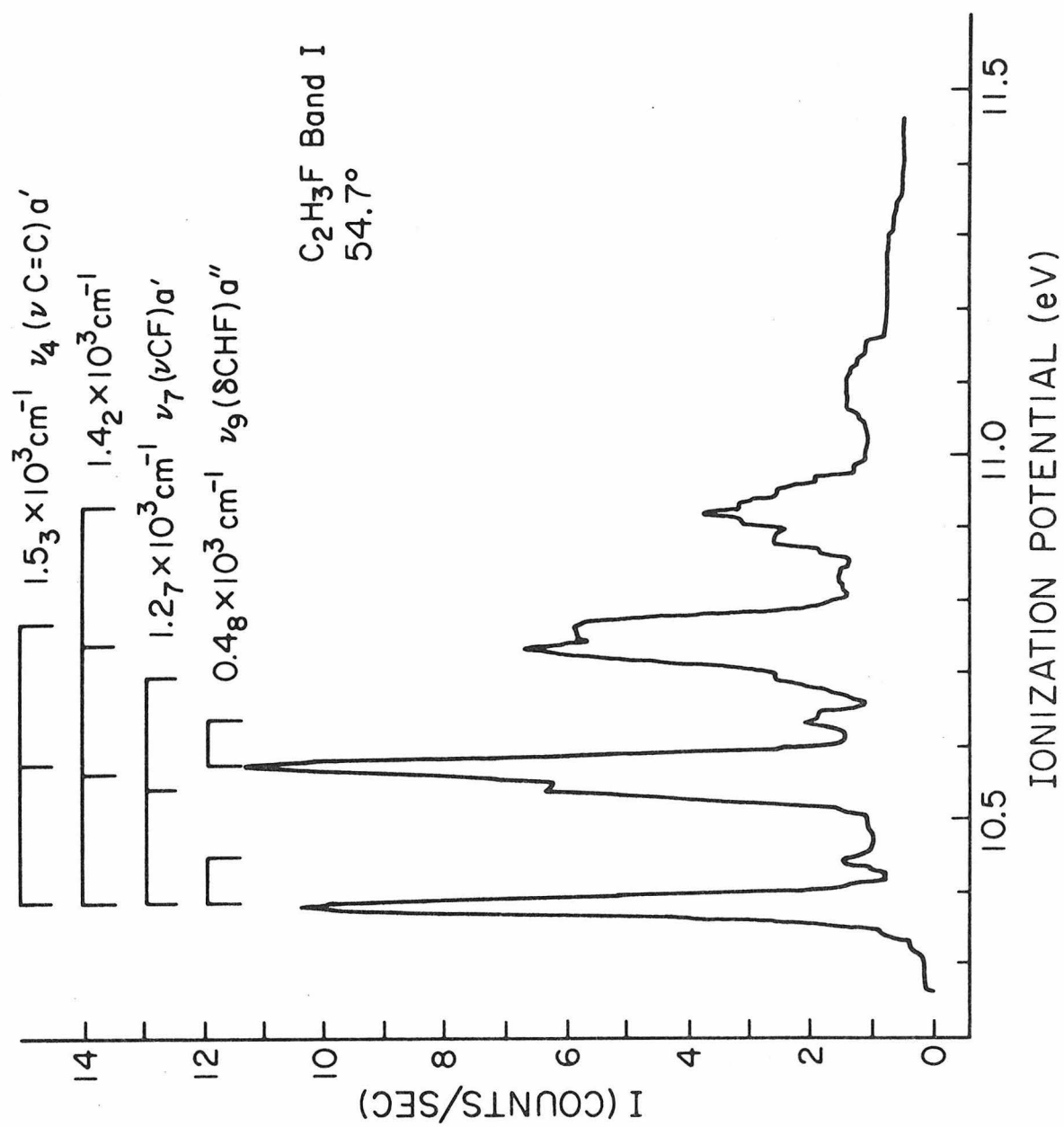


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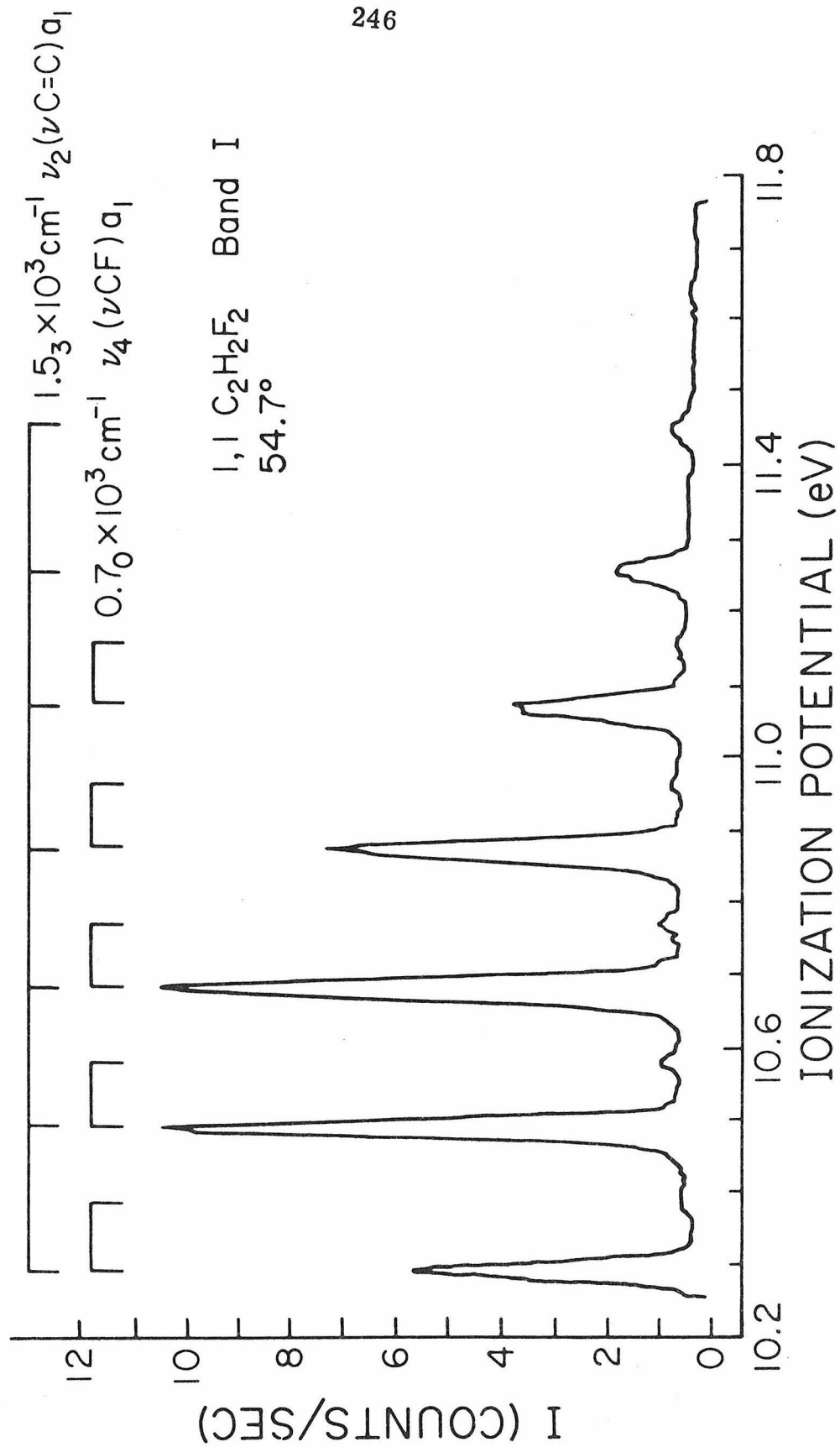


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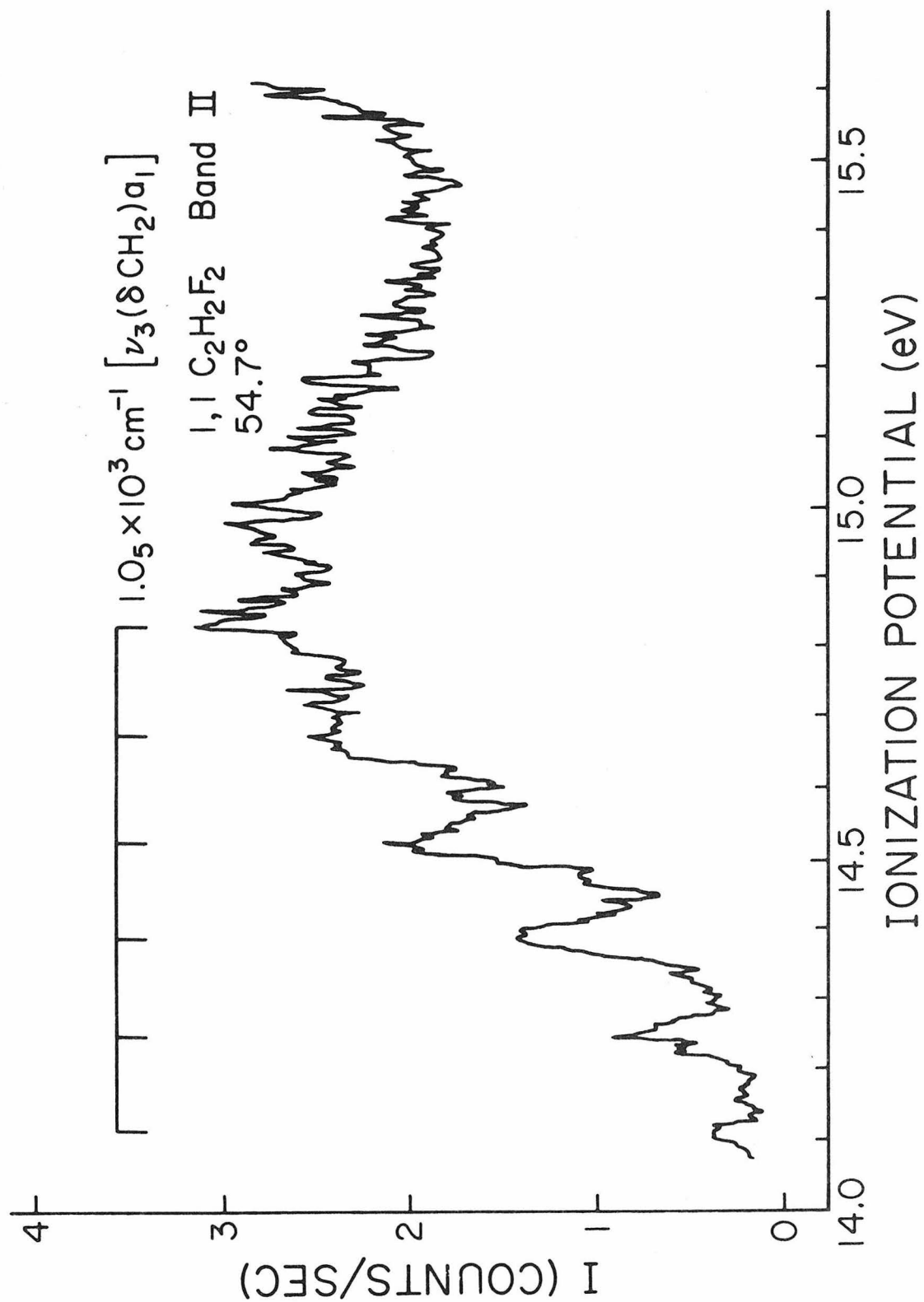


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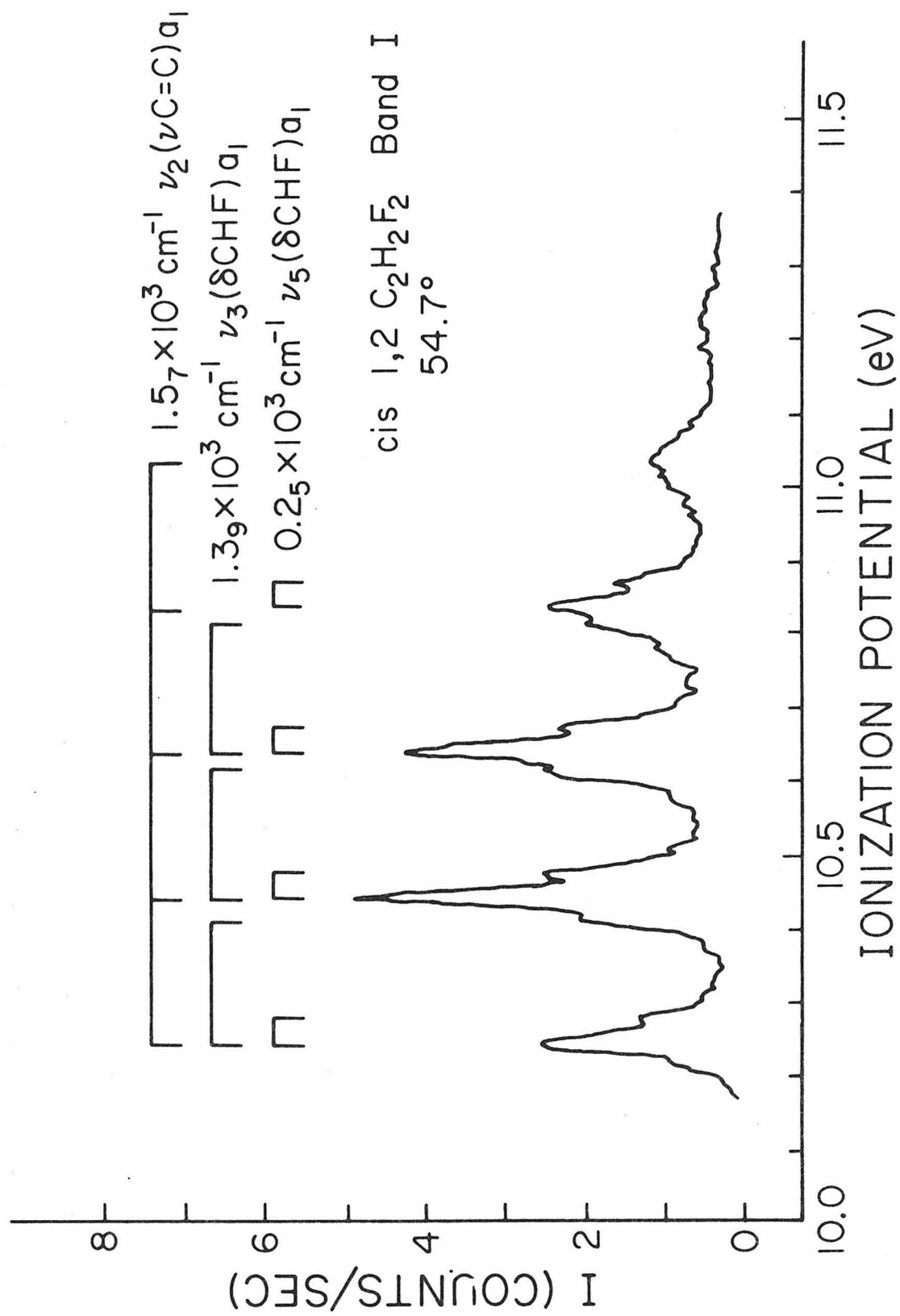


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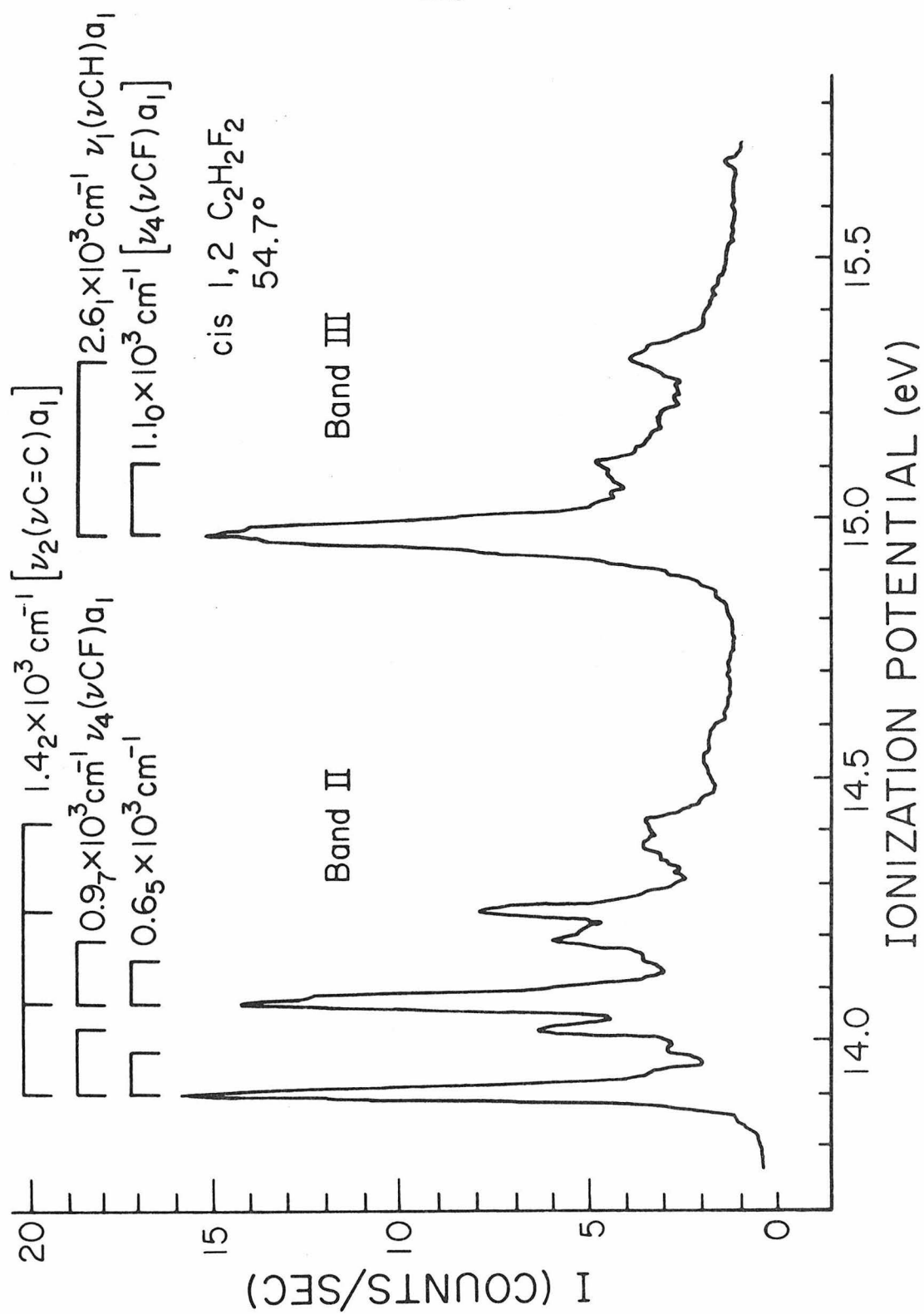


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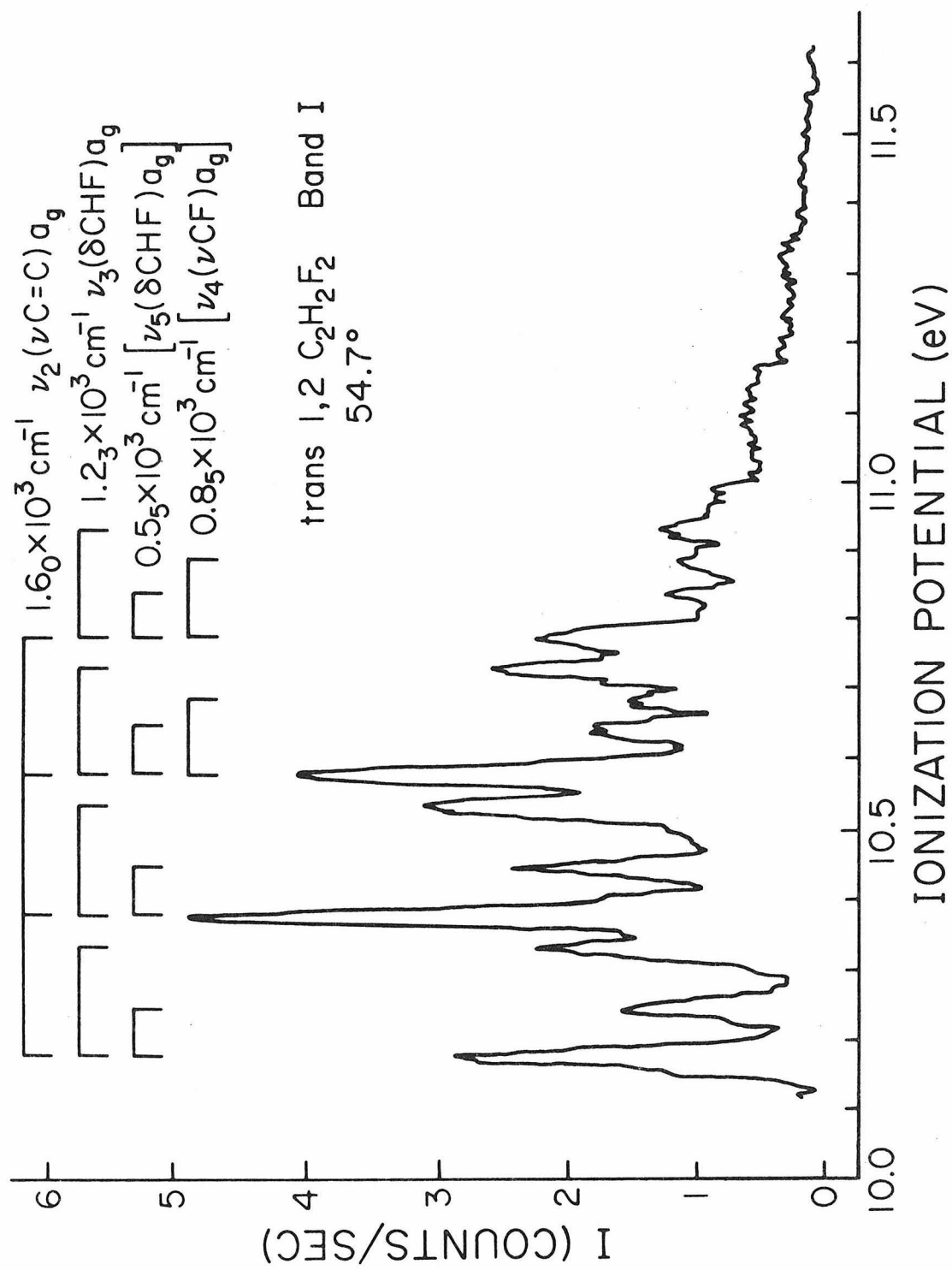


Figure 15.

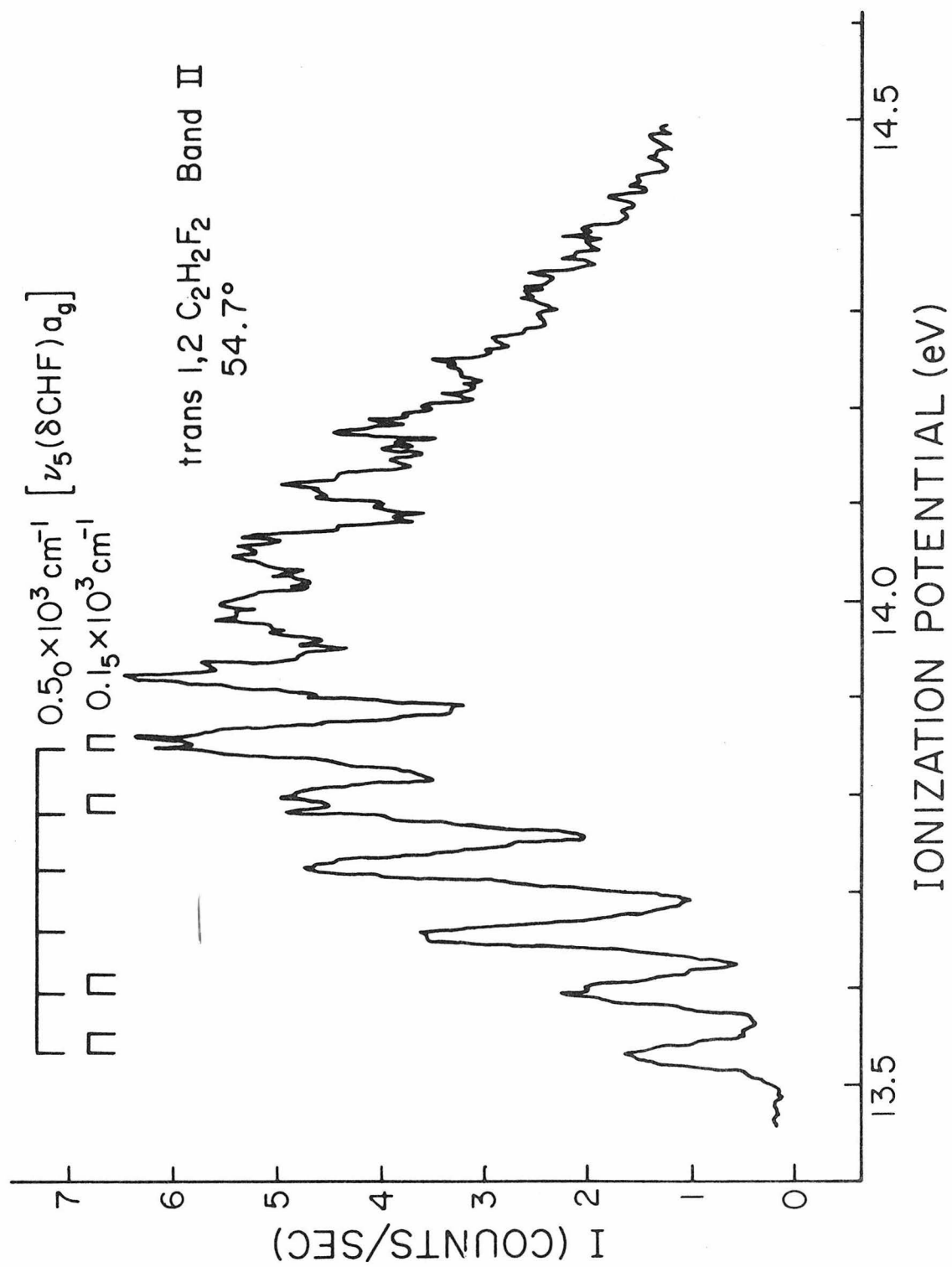


Figure 16.

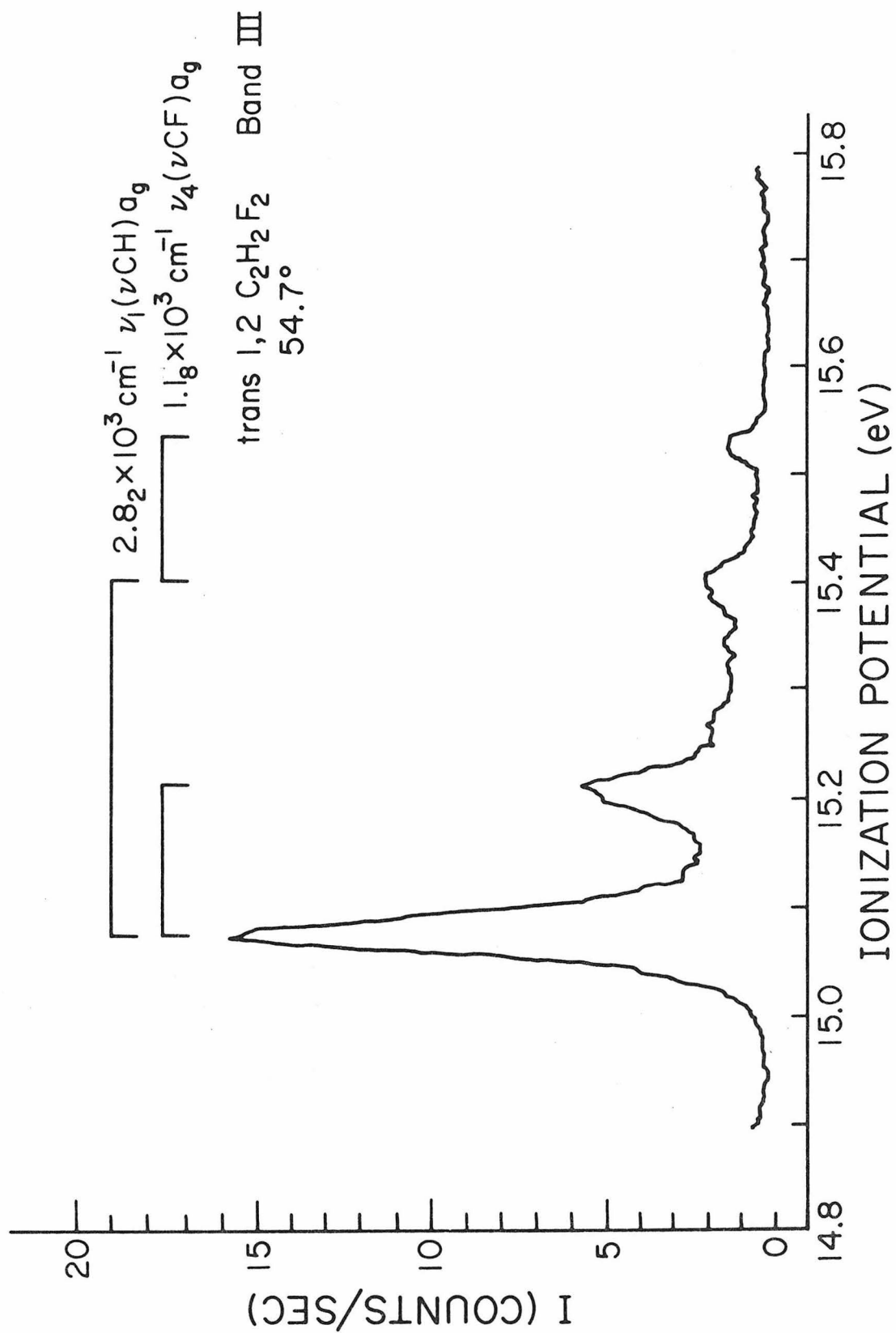


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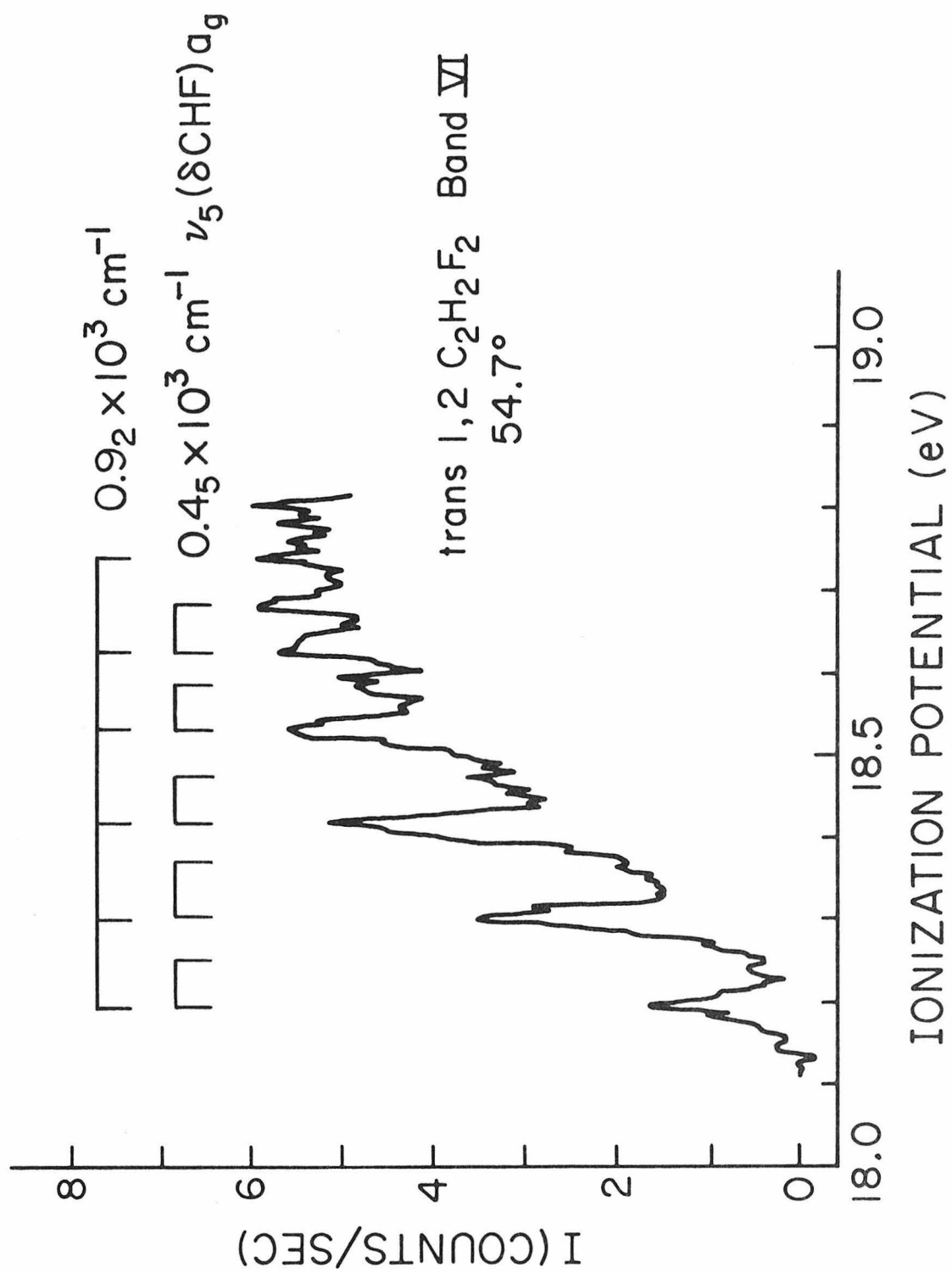


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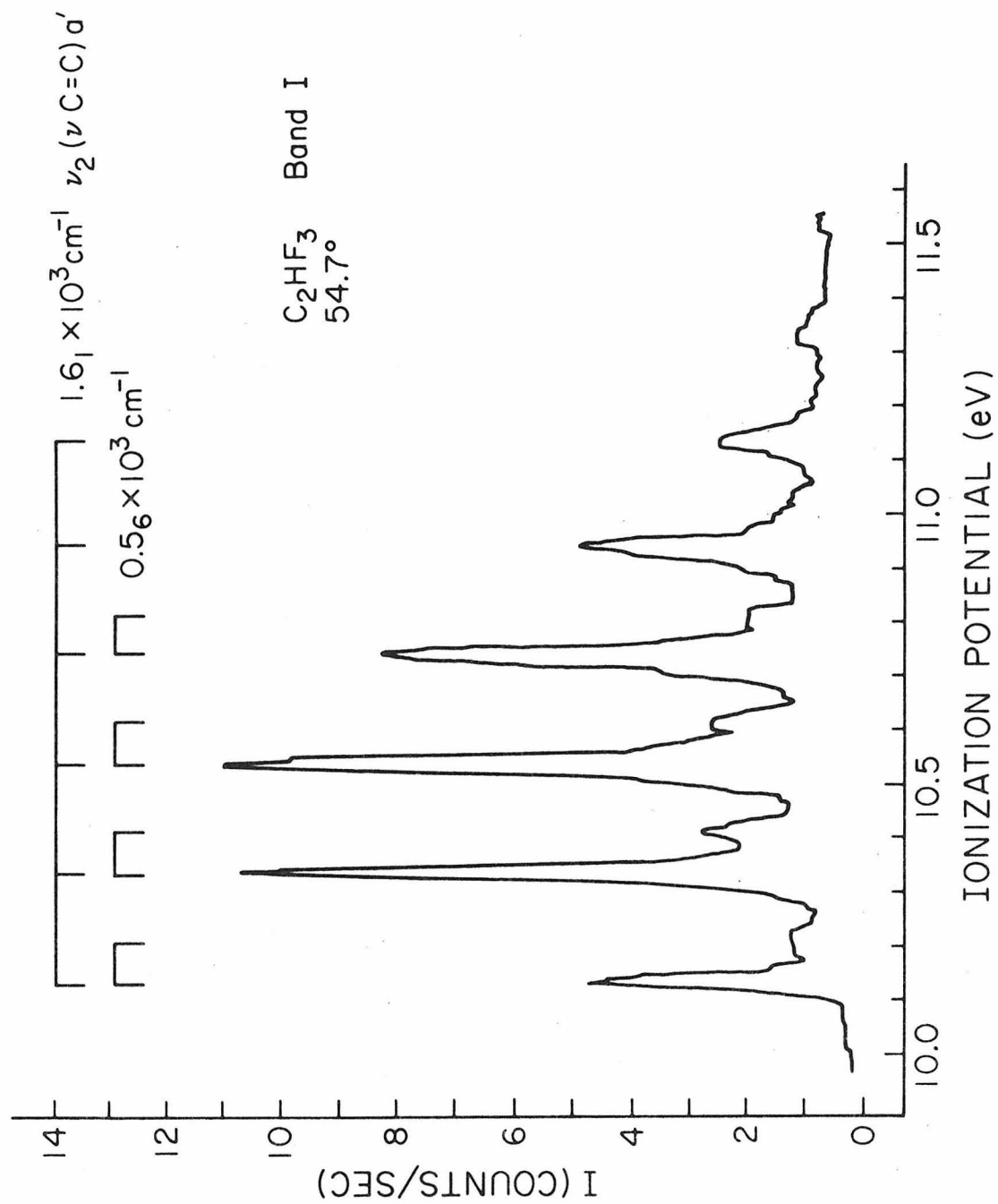


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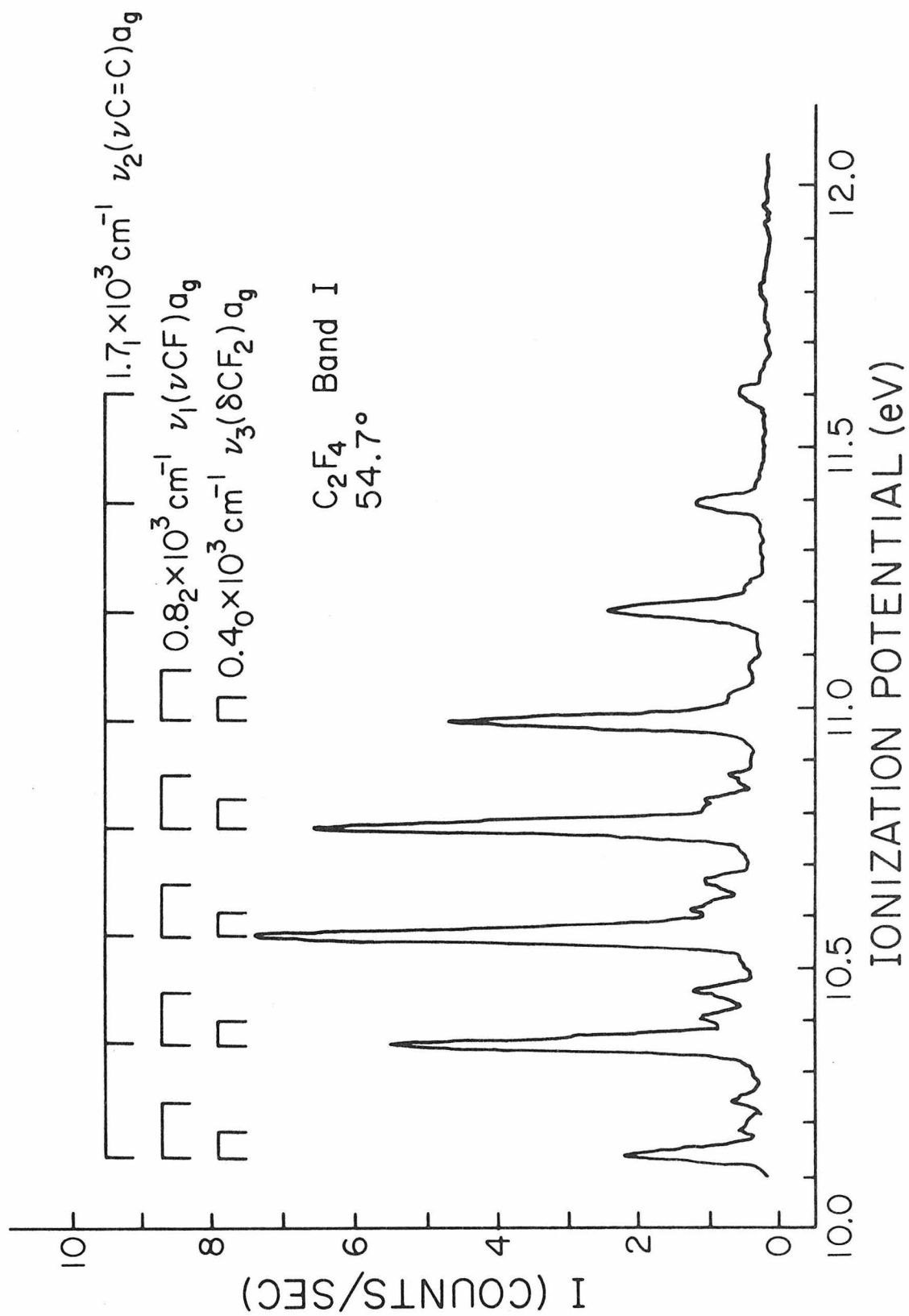


Figure 20.

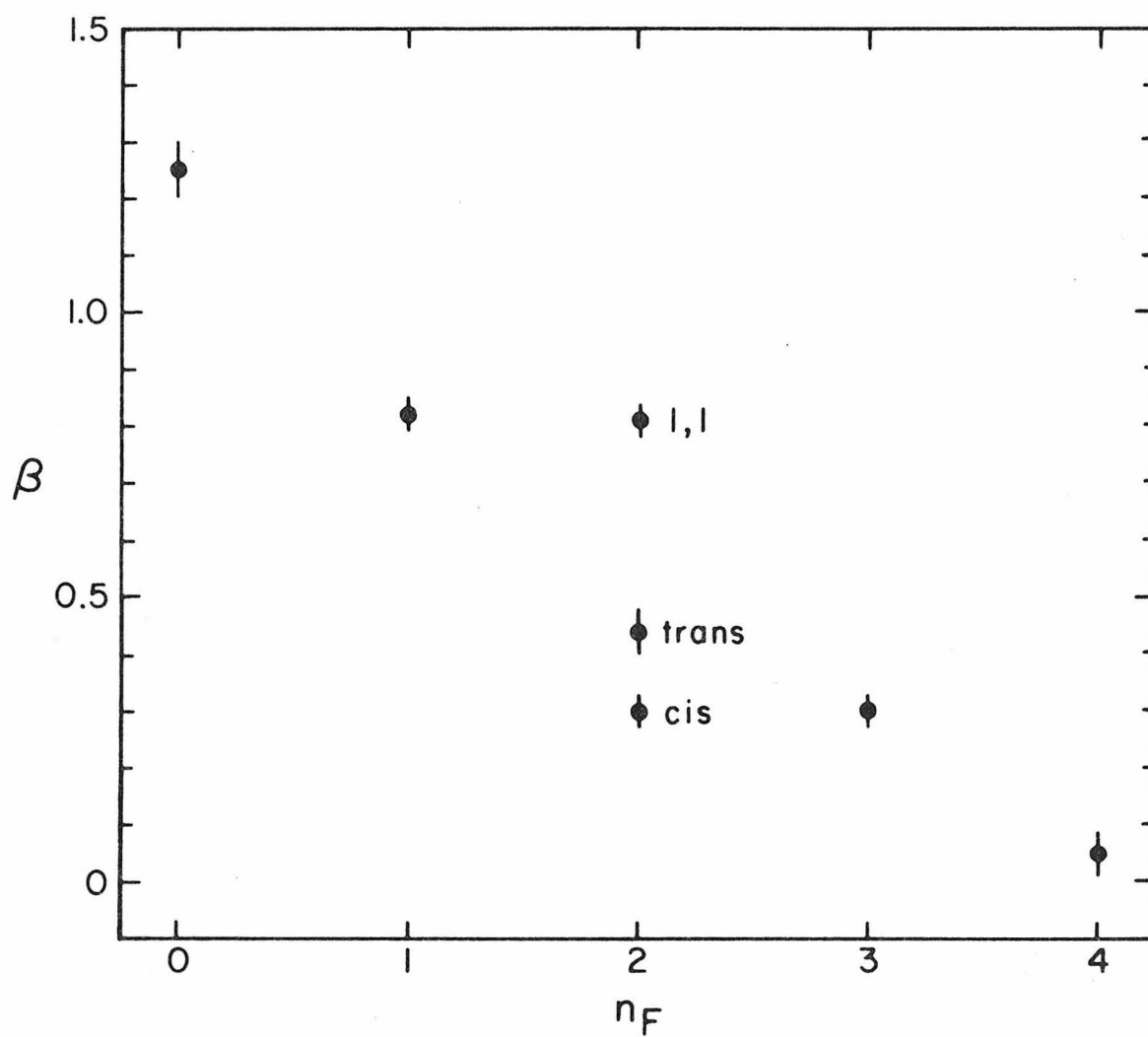


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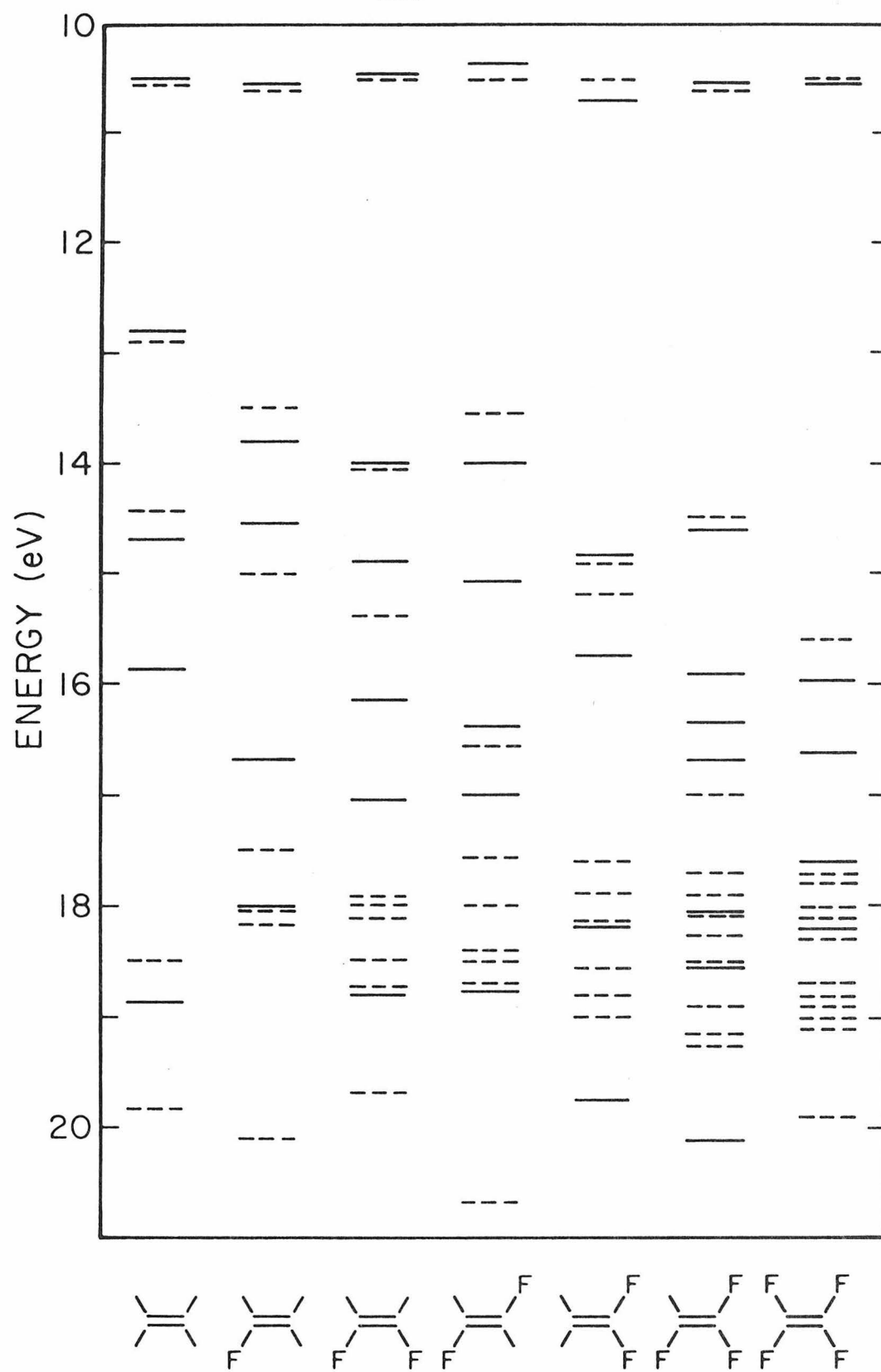


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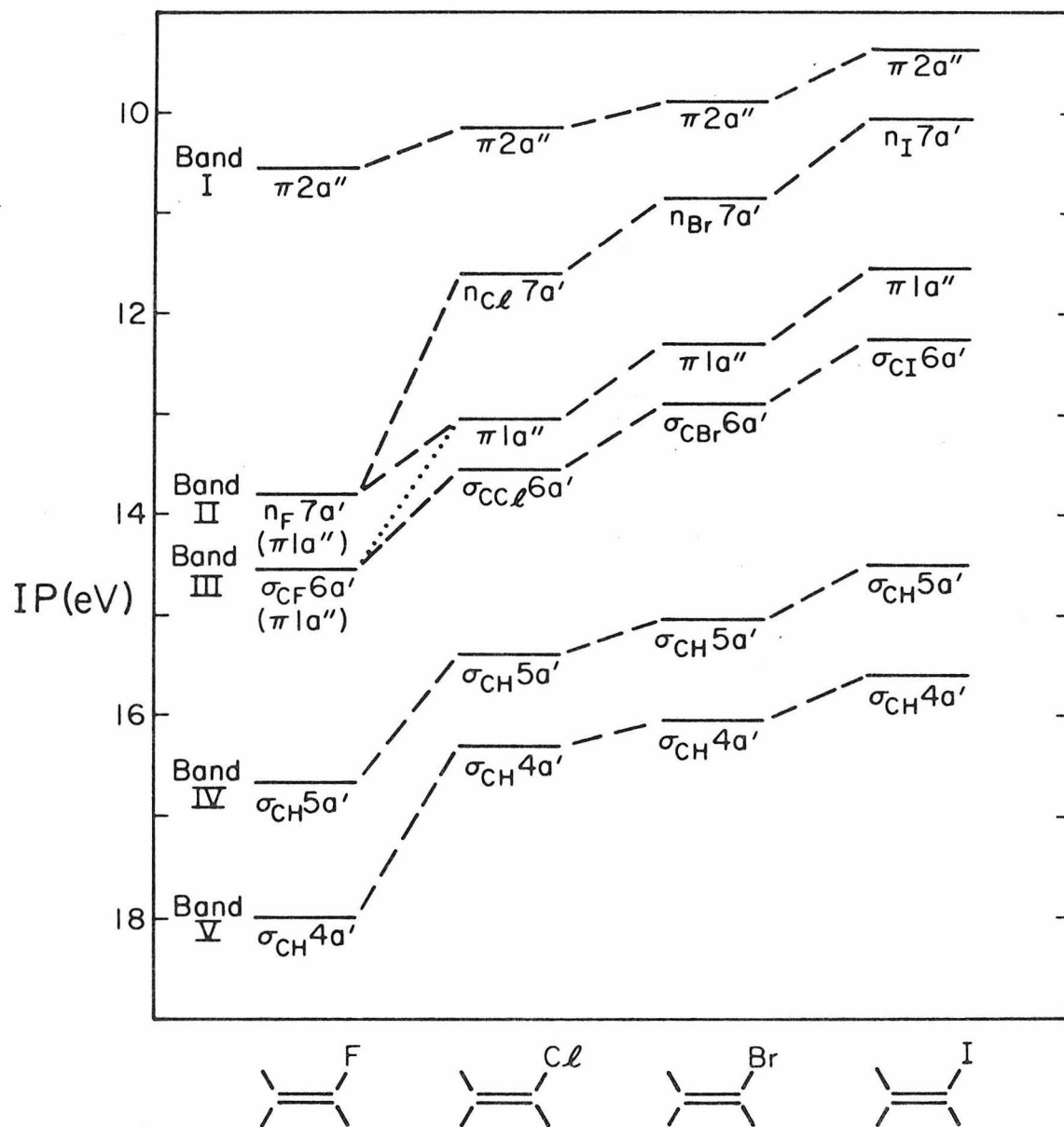


Figure 23.

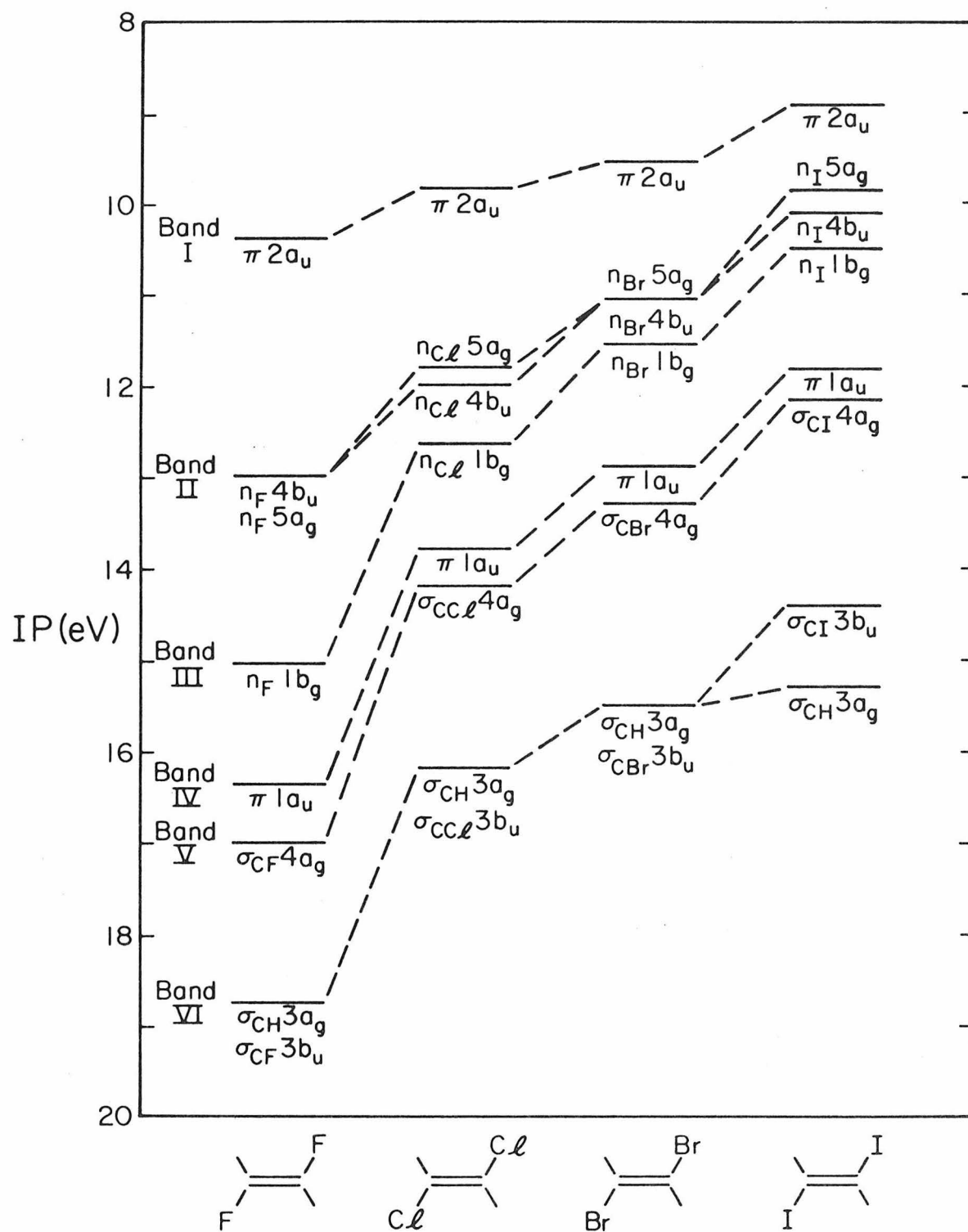


Figure 24.

CHAPTER 10

SUMMARY AND CONCLUSIONS

This thesis has described the measurements of the angular distributions in the photoelectron spectroscopy of several diatomic and polyatomic molecules. The results indicate that a significant amount of chemical information can be obtained by these measurements that is not available in the fixed angle spectra alone.

In the H_2 and D_2 study, the value of β was very high (roughly 1.75) since the molecular orbitals involved are mostly composed of atomic 1s orbitals. In addition, it was found that β did not vary by more than about 10% across the vibrational levels in agreement with theoretical predictions.

In the carbon monoxide study, β was measured carefully among several vibrational levels of three electronic bands and found to vary rapidly and nonmonotonically among them. Consideration of these data and other experimental and theoretical data led to the conclusion that autoionization is occurring in CO at 584 Å and that β is very sensitive to the presence of such a process. The fixed angle spectra furnish Franck-Condon factors which deviate from the calculated ones by a small but non-negligible amount. Such rapid and nonmonotonic variation of β among vibrational levels of an electronic band may turn out to be, in general, a more sensitive indicator of autoionization than the deviation of experimental Franck-Condon factors from the theoretical ones.

The angular distributions in the photoelectron spectra of benzene and its monohalogenated derivatives were measured. In benzene the assignments of the photoelectron bands to the corresponding orbitals are well known. By using the trends in β and in the shapes and positions of the bands across this series of molecules it was possible to extend some of the assignments to the bands in the monohalogenated derivatives. This "chemical scanning", where the same type of measurement is performed on a series of related compounds, is a valuable way of gaining insight into the electronic structure of molecules.

The photoelectron angular distributions of SF_6 were measured. For other molecules it was previously found that the values of β for two components of a band split by Jahn-Teller interactions are about equal. This empirical fact was then used in conjunction with theoretical data in making the orbital assignments to the photoelectron bands of SF_6 . The results for SF_6 indicate that it would be worthwhile to study the photoelectron angular distributions of other inorganic hexafluorides, such as UF_6 and WF_6 , in order to clarify their electronic structure.

Next, the photoelectron angular distributions of the five member heterocyclics furan, thiophene, and pyrrole were measured. In other molecules it was previously found that the value of β for photoionization of π orbitals is higher by 0.2 to 1.0 than for σ orbitals. This empirical rule was used in the heterocyclics to assign the photoelectron bands to the corresponding π orbitals.

The asymmetry parameter β was measured for the lowest IP carbon-carbon π orbital of ethylene, benzene, and some of their fluorinated derivatives. In the fluoroethylene series, β decreased monotonically and substantially from the value for ethylene upon increasing fluorine substitution. In the fluorobenzene series, the decrease in β upon fluorine substitution was less pronounced and nonmonotonic. These results were interpreted in terms of the resonant mixing of fluorine π lone pair orbitals with the carbon-carbon π orbitals. The importance of this study is that it indicates the sensitivity of β to the atomic composition of the molecular orbitals. Similar studies of other related compounds such as the chloroethylene and chlorobenzene series would probably lead to further understanding of the factors that affect β and of the electronic structure of these compounds.

Finally, the photoelectron angular distributions of the higher IP bands in all of the fluoroethylenes were measured. These data, as well as other experimental data, were used to assign some of the photoelectron bands to the corresponding orbitals.

Thus, in conclusion, it has been shown how photoelectron angular distributions can enhance the understanding of the electronic structure of molecules. The asymmetry parameter β seems to be related to characteristics of molecular orbitals, such as their symmetry and atomic composition, the presence of autoionization processes, resonance mixing, σ - π hybridization, Jahn-Teller splittings, and spin-orbit splittings. It is anticipated that further studies of the present kind would reveal other factors

that affect β . In addition, it would be very worthwhile to measure β as a function of photoelectron kinetic energy for molecules using an excitation source that has a variable wavelength. Finally, it is expected that even more information would be available if β values for molecules could be calculated quickly and accurately. The data presented in this thesis may be used in the future to assess the accuracy of calculated β values.

Proposition 1: Study of the Energy Dependence of the Anisotropy
Parameter for Electrons Photodetached from Atomic and Molecular
Negative Ions

Abstract: It is proposed that the energy dependence of the anisotropy parameter β for electrons photodetached from species such as NO^- , O_2^- , CH^- , CH_2^- , Si^- , and the alkali negative ions be measured using a tunable cw dye laser which is crossed with a beam of these negative ions. This energy dependence would help enable the photoelectron band assignments to be made and clarify the physics of the ionization process.

In the past few years it has been shown that photodetachment of electrons from atomic and molecular ions can yield important information on the physical and chemical properties of small systems.

Previously, electron affinities [1-14] and singlet-triplet splitting [1, 2, 13] in neutrals have been measured accurately and molecular geometries and potential energy curves [1-4, 11-14] have been determined. Briefly, in this experiment an electron is ejected from the negative ion, usually by an incident laser beam,



and the intensity of the photoelectrons are monitored as a function of their kinetic energy. It has also been shown [6, 11, 12, 15] that by rotating the polarization vector of the light using a half wave plate in the laser cavity, the angular distributions of the photodetached electrons can be measured. The differential photoionization cross section $\frac{d\sigma}{d\Omega}$ was found [15, 16] to take the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta)] \quad (2)$$

where σ is the integral photoionization cross section, P_2 is the second Legendre polynomial, θ is the angle between the polarization vector of the light and the momentum vector of the electron, and β is the asymmetry or anisotropy parameter which ranges from -1 to +2. Angular distributions have been measured for only a few systems [6, 11, 12, 15], using a fixed frequency light source (ArII laser) in all cases.

It is proposed that a tunable dye laser be used to study the angular distributions of photodetached electrons and the energy dependence of the asymmetry parameter be measured by varying the excitation frequency. These data would be very valuable since it is believed that knowledge of the energy dependence of β would further the understanding of the dynamics of the photoejection process [17,18]. The most interesting species to study by this technique are NO^- [11], O_2^- [12], CH^- [3], CH_2^- [13], Si^- [4], and the alkali negative ions [5,6]. In molecular systems it would be possible to study β as a function of various initial and final vibrational states to see if the variation of β with vibrational state is equivalent to the variation with photoelectron energy, as has been assumed for neutral species [19]. The values of β and their energy dependence would be helpful in making the assignments of the photoelectron peaks to the corresponding orbitals in cases such as CH^- [3] where there is some question. In the alkali negative ions, it would be informative to measure β as a function of excitation wavelength in the region of the autodetaching states to see if it exhibits resonance behavior as expected [20,21]. In addition, the accurate calculation of β for some of these systems should be possible and the comparison between experimental and theoretical results would be mutually rewarding.

The main experimental problem would be in obtaining a reasonably high signal to noise ratio due to the lower power of the CW dye laser. However, it is estimated that the count rate would be sufficient to accurately

measure β as a function of energy. Of course, the negative ion beam current and the laser power as a function of the half wave plate angle would have to be monitored.

In summary, it seems that the measurement of the energy dependence of the anisotropy parameter for photodetached electrons would yield a wealth of information on the physics of photoejection and on photoelectron band assignments.

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Proposition 2: Detection of Air Pollutants with a Tunable Diode Laser
and a Resonant, Multipass Acoustic Detector

Abstract: It is proposed that ambient air and automobile exhaust be analyzed for NO and NO₂ using a tunable diode laser and a resonant, multipass acoustic detector. This technique would be more sensitive than other methods and would enable detection of these species even in the presence of constituents which have overlapping absorption bands, such as H₂O.

Over 90 years ago, Alexander Graham Bell [1] described the results of an experiment where undispersed sunlight passed through slots in a rotating disk and was focussed on a solid, liquid, or gas, in a sample tube. The observer witnessed emitted sound at the same frequency of the light chopper. Bell showed remarkable insight when he stated..."I anticipate that it (the spectraphone) has a wide and independent field of usefulness in the investigation of absorption spectra in the ultra-red." Only recently, Bell's predictions have come true as it has been shown [2-13] that optoacoustic spectroscopy can yield chemical information which is complementary to data provided by other spectroscopic techniques.

In the gas phase experiments, radiation is incident on a sample gas whose partial pressure may be very low, in a cell where the total pressure is typically around 1 atm. If the radiation has the proper frequency it is absorbed and some of it is eventually transferred to the translational energy of the gas. This translational energy is equivalent to a pressure rise in the cell which manifests itself as an acoustic wave that can be detected by a sensitive microphone. The electrical signal is processed by phase sensitive techniques. Kreuzer et al., [2] have shown that infrared optoacoustic spectroscopy can be used as a sensitive detector of air pollutants. Aoki and Katayama [7] have used the technique to study vibrational-translational energy transfer. Robin and Kuebler [13] have studied radiationless decay in aromatic ketones.

It is proposed that an acoustic detector be used on conjunction with a tunable diode laser for detection of air pollutants using infrared

spectroscopy. Previously, laser acoustic infrared spectroscopy has been done with a CO₂ or CO laser [2] and only rarely with a diode laser [14]. However, diode lasers have several important characteristics that make them suitable for this experiment. First of all, they are tunable over about 40 cm⁻¹ by merely varying the power supply current and can be constructed to emit wavelengths from 3 to 30 μm by changing the chemical composition of the semiconductor [15]. They also have extremely narrow linewidths, typically 10⁻⁵ cm⁻¹, which makes them suitable for studying linewidths of IR transitions [10]. In particular, one could examine statistical models of vibrational to translational energy transfer [16]. The resolution is also important since there are so many molecules that have overlapping IR absorption bands and it is therefore possible to avoid the interfering lines and tune into the desired band [10,17,18]. In addition, the laser power is now typically 5 × 10⁻³ watt which is much higher than thermal IR sources [15].

The main advantage in using the acoustic detector is the high sensitivity. In conventional IR absorption experiments, the absorption is measured as the difference between two large quantities, the incident and transmitted intensity. In the acoustic technique, the absorption leads directly to a measurable quantity, the pressure rise. By using a multipass cell and chopping at one of the acoustical resonance frequencies it is estimated that this technique would have a ppb sensitivity which is better than commercial IR instruments [10]. In addition, the technique is applicable over a wide dynamic range of concentrations [9].

Tunable diode laser optoacoustic spectroscopy should be applicable for the study of many species over the range of diode laser wavelengths (3 to 30 μm). However, for the purpose of this report a specific application is indicated. It is proposed that both ambient air and automobile exhaust be analyzed for NO and NO₂. These species are difficult to detect because of interference from H₂O absorption lines [19]. The NO absorption band is centered at 5.3 μm and that of NO₂ is 6.2 μm . Typical uncontrolled automobile exhaust contains NO and NO₂ in concentrations of 100 to 1000 ppm whereas the concentrations in ambient air are typically 0.01 ppm [19]. Thus the concentrations expected are within the estimated concentration range of this technique. The narrow linewidth of the diode laser essentially eliminates the problem of H₂O interference since the laser can be tuned to avoid the H₂O absorption. The experiments could be done using Pb S_{1-x} Se_x diode lasers where $x \cong 0.33$ for the NO experiment and $x \cong 0.41$ for the NO₂ case [15]. The laser is chopped at a frequency which is equal to a resonance acoustic wave, typically 1 kHz depending on the size of the cell [3,11]. Finally, background signal can be substantially reduced by placing the end mirrors outside the active acoustic cell [3].

In summary, it appears that tunable diode laser optoacoustic infrared spectroscopy would be a very worthwhile analytical technique. It would enable analysis of a variety of small molecules over a wide concentration range, even in the presence of species which interfere with the analysis using conventional techniques. It could also be used to examine collisional and Doppler broadening of IR spectral lines.

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Proposition 3: Multiphoton Ionization and Thermal Lensing
Spectroscopy of Some Polyenes

Abstract: It is proposed that the gas phase multiphoton ionization and thermal lensing and liquid phase thermal lensing spectra be obtained for 1-trans-3-pentadiene, 1,3-hexadiene, cis-2-trans-4-hexadiene, and trans-hexatriene using a nitrogen pumped dye laser. The object is to characterize excited states of these molecules which are inaccessible by single photon studies.

In the past few years, the importance of multiphoton spectroscopy for the identification of excited molecular states has been realized. One such technique is to excite a molecule with two or more laser photons and look at the fluorescence emitted from excited states [1]. The main problem with this method is that there are many molecules that decay non-radiatively. Most recently, the techniques of multiphoton ionization (MPI) [2-8] and thermal lensing (TL) [8-14] have been employed for the detection of excited molecular states. In the former, three or more photons are absorbed by the molecule which will eject an electron if the energy absorbed is greater than the ionization potential. Thus the ejected electron current is monitored as a function of the laser wavelength; resonances occur when the energy corresponding to the excitation wavelength times a positive integer coincides with the energy of a molecular state. In the thermal lensing experiment, photons are absorbed by the collection of molecules which then heat up due to this absorbed energy. The heating effect causes a small change in the index of refraction of the substance which acts like a divergent lens, spreading the laser beam diameter. The laser wavelength is varied while the intensity of the transmitted laser beam is recorded, a decrease in intensity signifying a resonance. Both of these experiments are rather new and not well characterized but it has already been shown [2-14] that they permit the identification of states which are inaccessible by one photon spectroscopy.

It is proposed that the multiphoton ionization and thermal lensing techniques be applied to the study of excited states of the polyenes 1-trans-3-pentadiene, 1,3-hexadiene, cis-2-trans-4-hexa-

diene, and trans-hexatriene. The characterization of the excited states of these molecules is important for the understanding of the photochemistry of the visual process. These techniques allow the detection of states which cannot be excited directly by a single photon. The gas phase multiphoton ionization and thermal lensing excitation spectra could be obtained for all of these molecules to look for the 2-photon excited "gerade" symmetry Rydberg and valence states. A similar study was previously performed on trans-butadiene [8] where the MPI and TL spectra were found to be essentially identical. In addition, a Rydberg state of symmetry 1B_g was found which was probably buried beneath another band in the electron impact spectrum [15]. By studying the multiphoton spectra of the above series of molecules it is hoped that several one-photon forbidden electronic states would be observed and their vibrational frequencies measured. It would also be interesting to see if structure appears in the spectra which is due to the resonance of a single laser photon with the lowest triplet states of these molecules which occur in the energy range of 2.6 to 3.2 eV [16-17]. It was previously found that the MPI spectra of pyrazine [6] shows a peak which is due to a one-photon resonance with the lowest triplet state.

By studying the liquid phase or high-pressure gas phase thermal lensing spectra of these molecules it should be possible to characterize the states seen in the gas phase as Rydberg or valence by using the known behavior of Rydberg states upon going to the liquid phase [18]. For example, the MPI spectrum of trans-hexatriene has been obtained [2] but it is not known whether the observed state is the 1A_g valence

or a g-Rydberg state. The liquid phase thermal lensing technique should help determine this in the same way that was done for trans-butadiene [8, 9].

The experiment could be performed using equipment similar to that of Johnson [3-5,7], Turner et al. [6], and Vaida et al. [8]. Basically, the excitation source is a nitrogen pumped dye laser. For the ionization experiments, the sample cell contains the vapor (at about 50 mTorr) and also an electrode through which the electrons are collected. The electron current can be measured by either an electrometer or a high-speed sensitive pulse amplifier. In the thermal lensing experiments the dye laser excited the sample which is contained in a quartz cell. The beam from a He-Ne laser also passes through the cell in the interaction region. The intensity of the He-Ne laser is monitored after it passes through a 0.5 mm pinhole located about 50 cm from the interaction region. In both experiments, the energy of the dye laser beam is measured and the resulting signal is corrected for its variation. The dye laser can be operated from 360 to 740 nm using several different dyes. This permits the energy range of 3.3 eV to 6.8 eV to be studied for a two-photon absorption.

In summary, it appears that the excited states of some polyenes could be characterized by multiphoton ionization and thermal lensing spectroscopy.

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Proposition 4: Study of the Electronic Structure of B_2H_6 Using Low Energy, Variable Angle Electron Scattering and Variable Angle Photoelectron Spectroscopy

Abstract: It is proposed that the energies and symmetries of the filled and unfilled orbitals of diborane be characterized using variable angle photoelectron spectroscopy and low energy, variable angle electron impact spectroscopy. This molecule is important because of its use in chemical synthesis and its inherently interesting polycenter bonding. Therefore the electronic structure of B_2H_6 needs to be well understood.

Low energy, variable angle electron impact spectroscopy has been shown¹⁻³ to be a very important technique for the identification of atomic and molecular excited states. In this experiment, a beam of low energy monochromatic electrons is used to excite atoms or molecules. By measuring the kinetic energy lost by the electrons upon inelastic collisions with the sample, it is possible to map out a spectrum analogous to an optical absorption spectrum. In electron impact spectroscopy, however, the selection rules applicable in optical spectroscopy are more relaxed. In particular, singlet-triplet transitions are observable.¹⁻³ These transitions can be distinguished from singlet-singlet transitions by their different angular distributions. The differential cross section (DCS) for a singlet-singlet transition is usually sharply forward peaked whereas that for a singlet-triplet transition is more isotropic.⁴ The reason for this is that a singlet-triplet transition involves exchange between the incident electron and the molecular electrons; the mixing necessary for this exchange to occur results in an almost isotropic angular distribution. In addition, certain singlet-singlet transitions which are symmetry forbidden in optical spectroscopy can be observed in electron impact spectroscopy and are identified by a DCS which is not quite so forward peaked as an allowed singlet-singlet transition. The dependence of the DCS on incident electron energy can be used to identify the type of transition.¹⁻⁴ The main disadvantage of this technique is its low resolution, typically 0.1 eV.

A complementary technique that is used for studying atomic and molecular electronic structure is variable angle photoelectron

spectroscopy.⁵⁻⁷ In this experiment, a beam of ultraviolet light of energy $E_{h\nu}$ is incident on a sample and causes electrons to be ejected from the occupied orbitals. The photoelectrons have a kinetic energy (KE) which is easily related to the ionization potentials (IP) of the sample:

$$E_{h\nu} = KE + IP .$$

Also, the photoelectron intensity has an angular dependence

$$I \propto a + b \cos^2 \theta$$

where θ is the angle between the unpolarized light beam and the momentum vector of the electron and a and b are related to the asymmetry parameter β which ranges from -1 to $+2$. This parameter is sensitive to the symmetry of the orbital from which the electrons are ejected. For example, the value of β for ionization from the $b_{3u} \pi$ orbital in ethylene is roughly 1.25 whereas it is less than 0.75 for the σ orbitals.⁸ Measurements of β therefore can lead to the assignments of the photoelectron bands to the corresponding orbitals.

It is proposed that these two techniques be applied to study the electronic structure of diborane, B_2H_6 . The electronic structure of this molecule has been a subject of interest for several years, especially because of its polycenter bonding. Unfortunately, it is not yet well understood. There have been numerous calculations⁹⁻¹⁶ on the electronic structure of B_2H_6 , the best of which is probably the CI calculation by Elbert et al.¹⁶ Experimentally, the fixed angle photoelectron spectrum has been obtained¹³ and the optical absorption

spectrum has been measured out to about 11.4 eV.¹⁷ Brundle et al.¹³ have compared its photoelectron spectrum to that of ethylene and argued that the band at 14.7 eV in the diborane spectrum corresponds to the $b_{3u} \pi$ orbital. It is anticipated that this band should have a relatively high value of β , similar to that of ethylene,⁸ and it should therefore be easy to verify this assignment. The measurement of β for the σ bands may permit their assignment on the basis of comparison with the corresponding values for ethylene.

Next, the electron energy loss spectrum should be obtained from threshold to about 15 eV in order to clarify the excited states of B_2H_6 . In particular, the CI calculation predicts¹⁶ several triplet states to exist between 7 and 10 eV that should be possible to find using this technique. As far as singlet-singlet transitions are concerned, Brundle et al.¹³ have assigned the band at 6.8 eV in the optical absorption spectrum to a $\sigma \rightarrow \pi^*$ ($^1A_g \rightarrow ^1B_{3g}$) transition and that at 8.3 eV to a $\sigma \rightarrow \pi^*$ ($^1A_g \rightarrow ^1B_{3g}$) transition on the basis of SCF calculations. These assignments are supported by the CI calculation of Elbert et al.¹⁶ On the other hand, the assignments for the strong transitions at 9.3 eV and 10.7 eV are not clear. It is hoped that the angular and energy dependence of the electron scattering DCS's for these bands would enable one to determine whether these bands correspond to a superposition of several symmetry forbidden transitions or one or two symmetry allowed ones. Finally, it should be possible to observe and characterize the states above 11.4 eV which have not been seen before.

In conclusion, it appears that the understanding of the electronic structure of B_2H_6 could be enhanced by the measurement of the photoelectron angular distributions and the electron impact energy loss spectra. These data would fill the present gap in the experimental work on its electronic structure and would complement the theoretical work.

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Proposition 5: Study of Molecules Adsorbed on Electrodes Using
Resonance Raman Spectroelectrochemistry

Abstract: It is proposed to use resonant Raman spectroscopy to study the orientation and bonding of four different molecules adsorbed on electrode surfaces using a tunable dye laser. By obtaining these spectra as well as Raman excitation spectra as a function of applied electrode potential, pH, bulk concentration, and supporting electrolyte concentration it should be possible to learn about the interactions between molecules and electrodes in the liquid phase.

The field of spectroelectrochemistry combines two different techniques, spectroscopy and electrochemistry, to study the redox chemistry of molecules.¹ Spectroscopy is used to probe the nature of the molecular species at or near the electrode. The electrodes are used to generate different oxidation states of the molecules, or can be used merely as a metal surface to which molecules in bulk solution adsorb. One such spectroscopic technique recently applied to electrochemical problems is normal Raman (NR) spectroscopy. Perhaps the most interesting aspect of Raman scattering from molecules adsorbed to an electrode is that the scattered light is 5 to 6 orders of magnitude more intense than expected on the basis of comparison with Raman scattering from a corresponding solution.² The reason for this large signal enhancement is not yet clear but may be that the Raman scattering cross section is increased due to the presence of high electric field gradients in the vicinity of the electrode.³

Raman spectroscopy of molecules adsorbed to an electrode apparently can be used to explore the nature of the adsorbed molecule and its bond to the surface. The molecular system most frequently studied so far is pyridine adsorbed on a silver electrode.³⁻⁵ By examining the Raman scattering intensity from pyridine as a function of applied electrode potential, pH, bulk pyridine concentration, and supporting electrolyte (KCl) concentration, it was postulated³ that the neutral pyridine molecules are axially bonded to the silver surface through the nitrogen lone pair orbitals and that two chloride ions are involved in the bond in an unknown way. Some other systems studied by NR spectroscopy are pyridine adsorbed on copper electrodes,⁶

tetracyanoethylene radical anion (TCNE^-) adsorbed on a platinum electrode,⁷ I_2 adsorbed on a platinum electrode,⁸ para-nitrosodimethylaniline (pNDMA) adsorbed on a silver electrode,² and other amines adsorbed on silver electrodes.³ In all cases the electrodes have to be carefully prepared by mechanical polishing and electrolytic pretreatment. The studies are done in an aqueous solution since water is a poor Raman scatterer.

One spectroscopic technique that has not been utilized to an appreciable extent in spectroelectrochemistry is resonant Raman scattering.^{9,10} A laser is used to excite a molecule into its absorption band and the result is a large enhancement of Raman cross sections. Of particular interest is the Raman excitation spectrum where one monitors the intensity of a Raman band as a function of the exciting laser frequency. A spectrum that resembles the absorption band is obtained but it sometimes gives additional information.¹⁰ In some cases it is possible to do this for several different Raman bands and consequently deconvolute the absorption spectrum.¹⁰

It is proposed that resonant Raman spectroscopy be utilized to explore the bonding of molecules to electrode surfaces. This technique should be applied to several different systems to try to determine whether it furnishes the desired information. The simplest system is, of course, a diatomic molecule. It has been found⁸ that iodine adsorbs on a platinum electrode in a solution of KI at an applied potential of about 0.5 volts vs. SCE. It also exhibits a normal Raman spectral band at 174 cm^{-1} using excitation from an argon ion laser.⁸ It is

proposed to use instead a tunable dye laser pumped with the visible and uv lines of the argon laser to record the Raman excitation spectrum of this 174 cm^{-1} band in the region 4400 to 6900 Å. It has a gas phase absorption band in the region 4350 - 6700 Å and should exhibit the resonance Raman effect.¹¹ By comparing this spectrum to the gas phase absorption spectrum¹¹ and the gas phase resonance Raman excitation spectrum¹² it should be possible to make deductions about the nature of the bond of the I_2 molecules to the silver surface. The desired information is the orientation of the I_2 molecule and the orbitals involved in the bonding.

Next it would be interesting to obtain the resonance Raman spectrum of an intermediate size molecule such as the tetracyanoethylene radical anion (TCNE^-). It has been found⁷ that TCNE^- is adsorbed on a platinum electrode. The "preresonance" Raman spectra were obtained⁷ at an applied potential of -0.2 V vs. SCE. Preresonance means that spectra were obtained at some of the wavelengths of the argon ion laser and there was an imperfect match between these wavelengths and the absorption band of TCNE^- . It is anticipated that a great deal more could be learned about this system by obtaining the resonance Raman excitation spectra of several of its Raman bands using a tunable dye laser excited by the uv lines of the argon ion laser.

For similar reasons, it should be interesting to measure the resonance Raman spectra of larger molecules such as methyl orange and crystal yellow adsorbed on silver electrodes.³ These molecules have electronic absorption bands in the visible region and should show resonance Raman scattering when excited at the proper frequency.

The resonance Raman excitation spectra should help deconvolute the absorption bands of these molecules. Also, studying the Raman intensities and frequencies as a function of the applied potential, the pH, and the solution concentrations should lead to further understanding of the interaction of the molecules with the surface.³

Some of the experimental problems anticipated in these studies are the following. First, the electrode surfaces would have to be carefully prepared in the manner described previously.¹⁻¹⁰ Next, the problem of intense local heating of the bulk solution due to the absorption of the focussed laser beam would have to be solved. The best approach would be either circulation of the solution or the removal of the absorbing solution by flushing with supporting electrolyte.³ The exciting dye laser beam should be passed through a premonochromator to remove broadband dye fluorescence. The Raman signal would have to be corrected for the incident laser power and the analyzing monochromator sensitivity should be calibrated as a function of frequency. Finally, fluorescence of the samples adsorbed to the electrode could interfere with the detection of the Raman scattering. If this turns out to be a problem, it may be necessary to modulate the excitation beam and use the different temporal response of the two signals to distinguish between them. It is believed that all of the above problems could be overcome and resonant Raman spectra could be obtained.

In conclusion, it seems that resonant Raman spectroscopy would be a feasible way to study the interactions of molecules with electrode surfaces.

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