PHOTOELECTRON SPECTROSCOPY OF MOLECULAR BEAMS

by J. Berkowitz

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I. INTRODUCTION AND CHEMICAL STUDIES

The history of physical science in this century is replete with examples of phenomena initially discovered and investigated by physicists, which have subsequently become tools of the chemists. Visible and infrared spectroscopy, mass spectroscopy, nuclear magnetic resonance and Mössbauer experiments are but a few examples of this trend. I shall try to demonstrate in this paper that the field of photoelectron spectroscopy may develop in a reverse fashion.

Somewhat more than a decade ago, Vilesov, Kurbatov and Terenin (1) reported on the kinetic energy spectrum of electrons observed when monochromatized electromagnetic radiation with energy between 6 and 11.7 eV was incident upon aromatic amines and methyl derivatives of benzene. This early study was limited in its upper energy by the absorption cutoff of LiF windows. About a year later, Turner and Al-Joboury (2) presented the first in a series of papers in which the resonance line of helium (21.217 eV) was used as incident radiation, and analysis of photoelectrons was performed with a concentric cylindrical retarding field.

The introduction of the He(I) line turned out to be highly advantageous, not only because it can be generated as a sharp line with high intensity, but also because the photoionization cross sections of many common gases are near their maximum (3) at this wavelength. In addition, with 21.2 eV one has sufficient energy to eject electrons from the valence orbitals of most compounds. This fortuitous confluence of circumstances strongly influenced the development of molecular photoelectron spectroscopy in the

succeeding decade. The energy analyzers have improved during this period, but most studies still emphasize the measurement of ionization potentials with the He(I) line, and interpret their results in terms of the bonding (or antibonding) nature of the orbitals from which the corresponding electrons have been removed. A convenient summary of such data is the handbook by Turner, Baker, Baker and Brundle (4). Other laboratories (5) that have contributed prominently to the measurement of 584 Å photoelectron spectra of volatile molecules include those of Price, Orchard, Heilbronner, Schweig and Schaefer, Bock, Beck, Carlson, Frost and McDowell, Lindholm and others. Today the apparatus for such studies is commercially available and more exotic and complex molecules are continually being added to our store of 534 Å photoelectron spectra.

Some molecules cannot readily be prepared as ambient gases in the steady state, and must be prepared as molecular beams. This class of systems includes free radicals, excited states of molecules, atoms (besides the rare gases and mercury) and in general, materials of low volatility.

The study of free radicals in beams has been pursued in the past few years at Southampton by Jonathan (6) and co-workers, who have detected O, N, H, $O_2^1\Delta_g$, CS; at Vancouver by Frost, McDowell (7) and collaborators, who have reported on NF_2 , ClO_2 , S_2O , O_3 and also CS; and recently at Sussex by Kroto (8) and co-workers.

Relatively involatile systems had been investigated at Argonne by Dr. J. L. Dehmer and the author (9). For this purpose, an apparatus of high collection efficiency was constructed. In initial studies on the thallium halides, it was found that electrons localized on the halogen, which acted as nonbonding lone pairs in the case of the relatively covalent hydrogen halides and methyl halides, were the bonding electrons in the ionic thallium halides. Thus, if the thallium halide in its ground state is closely approximated by the representation Tl^+X^- , then

occurs when the electron is removed from the halogen-like orbital. If the initial bonding had strong contribution from the coulombic e^2/r potential, which is of the order of -5 eV, this is drastically reduced in the ion to $-ae^2/2r^4$, which is of order 0.2 eV. By contrast, an electron removed from a metal-like orbital can be represented by

resulting in an ionic state more strongly bound than the neutral ground state. This behavior has since been verified in the indium halides, and by extensive ab initio calculations as well as

semiempirical calculations on the aluminum and gallium halides. Hence, the extension of photoelectron spectroscopy to the study of high temperature species has proved rewarding by providing a dramatic illustration of the different bonding characteristics of ionic molecules (which tend to be involatile) and covalent molecules (which tend to be volatile).

We have recently extended these studies to the very ionic alkali halides. There is, of course, a large transfer of charge occurring in the formation of M^+X^- from M^0 and X^0 . The consequence is a filled halogen p-like molecular orbital, while the first metal-like orbital is the next inner p shell (for all cases except lithium). Each of these p-type orbitals can be expected to be split by the cylindrical molecular field into a p_π and p_σ orbital, the p_π being the less bound one on the halogen end, the p_σ on the metal end since the splitting is caused by potentials of opposite sign. The ionization potential of the halogen-like orbital should be roughly the sum of the electron affinity of the halogen negative ion and its binding energy in the field of the positive ion, or ca. 3 eV + 5 eV $\approx$ 8 eV. As in the thallium, indium and gallium monohalides, we anticipate that removal of an electron from an orbital localized around the halogen will severely disrupt the ionic molecular bond.

The ionization of the metal p-like orbital should occur roughly at the same energy as it does in the free atom, modified by a chemical shift due to charge transfer of the valence s-electron, not unlike the chemical shift observed in ESCA studies. This metal p ionization energy is -38 eV for sodium, -25 eV for potassium, -20-22 eV for rubidium and -17-19 eV for cesium. Hence, with an ionizing photon energy of 21.2 eV, the only metal p-type orbitals likely to be observed would be in the cesium halides.

The 584 Å photoelectron spectrum of cesium iodide is shown in Fig. 1. We note the two regions of ionic states, the one around 8 eV corresponding to ionization from the iodide 5 p-like orbital, the other around 19 eV corresponding to ionization from the cesium 5p-like orbital. Walker (10), Lehmer and I have examined the splitting of each of these orbitals in some detail. In addition to the aforementioned π - σ splitting, which seems to scale inversely with the ionicity of the molecule, there exists a spin-orbit splitting which has very nearly the same spin-orbit coupling parameter as the corresponding atom. That is, the iodide 5p-like orbital has a spin-orbit coupling parameter close to that of atomic iodine 5p. From ab initio calculations available for 9 of the 20 alkali halides and extrapolations of these results, we have been able to construct a table of π - σ splittings for the outermost, halogen-like orbitals of all of the alkali halides, and also of their spin-orbit splittings. These two types of splitting are of

Fig. 1. The He(I) photoelectron spectrum of CsI.

comparable magnitude, and ultimately it is necessary to construct and solve a 2×2 secular equation to deduce the resulting states. For example, the iodide $5p$ -like orbital of cesium iodide has a π - σ splitting of -0.12 eV and a spin orbit splitting of 0.63 eV. The initial splitting diagram is shown in Fig. 2. The $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ state, having the same Ω value, then interact, and the magnitude of

Fig. 2. Partial splitting diagram of the CsI (iodide orbital) ionization, including π - σ and spin-orbit effects.

their repulsion can be obtained from the solution to the secular equation. The details of this calculation can be found in the original manuscript (10). The resulting juxtaposition of states is shown in Fig. 3. The $2\Pi_{3/2}$ and $2\Sigma^+_{1/2}$ states are separated by only -0.08 eV, while $2\Pi_{1/2}$ is separated from the mean of the other states by -0.95 eV. The experimental data (Fig. 1) reveal two peaks, the lower one more intense, and separated from the upper one by about 0.92 eV. This splitting is very nearly that of the iodine atom, not 2/3 of this value as in HI. This is because the iodine in CsI is almost spherically symmetric (i.e. the π - σ splitting is small compared to the spin-orbit splitting). The more ionic alkali halides, which have the smallest π - σ splittings, have resultant splittings characteristic of individual, spherically symmetric ions only slightly perturbed by the neighboring ion.

Taking into account the peak widths, the corresponding calculation for CsBr predicts a partial splitting into two peaks, with a separation of -0.4 eV, and for CsCl and CsF a single peak, in good agreement with the experimental results (10). Predictions regarding this fine structure for the other alkali halides can be found in the original article (10).

A rewarding aspect of photoelectron spectroscopic investigations is that a spectrum of a single molecular system, when finally understood, enables one to predict the behavior of the entire homologous series. This is, of course, a consequence of the molecular orbital structure of matter. One can observe this in the

Fig. 3. Final splitting diagram of CsI, including Ω - Ω interaction.

existing spectra of HF, HCl, HBr and HI; the corresponding diatomic halogens; the Group III monohalides of Tl, In, Ga, Al and B; the Group II dihalides, and also the alkali halides. As our knowledge of the ionic states of small molecules increases, it becomes attractive to predict their mass spectra. Table 1 is a composite of parent to fragment (MX^+/M^+) ratios of the diatomic alkali halides, primarily obtained from electron impact data. One can see a strong correlation with the ionicity of the molecule, the most ionic (CsF) having an undetectable parent ion, whereas the least ionic (LiI) has almost an order of magnitude more parent than fragment. We can rationalize these observations from the photoelectron spectroscopic analysis by first noting that 70 eV electron impact ionization will be dominated by ionization from the lower lying halogen-like orbitals. To first order, the magnitude of the π - σ splitting will determine whether at least one of the fine structure states of this p-like orbital is bound. When the π - σ splitting is small, both the $^2\Pi$ and $^2\Sigma$ ionic states tend to be repulsive, and hence strongly favor the formation of fragment ions. When the π - σ splitting is relatively large, as in the cases of LiCl, LiBr and LiI, the $^2\Pi$ state becomes significantly bound, and provides a

TABLE 1

Parent to fragment ratio (MX^+/M^+) in the ionization of alkali halides

	F	Cl	Br	I	Refs.
Li	0.11-0.31	3.39	2.18	7.46	(a)
Na	0.026	0.59	0.71	1.17	(b)
K	0.002	0.17	0.29	0.56	(b)
Rb		0.07			(b)
		0.06	0.155	0.24	(c)
Cs		0.012			(b)
	0.00	0.014	0.07	0.26	(d)
	<.005	0.015	0.028	0.14	(c)

(a) (Electron impact), J. Berkowitz, H. A. Tasman and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962).

(b) (Electron impact), J. Berkowitz and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).

(c) (Photon impact), J. Berkowitz, J. Chem. Phys. 50, 3503 (1969); J. Berkowitz, Adv. High Temp. Chem. 3, 123 (1971).

(d) (Electron impact), P. A. Akishin, L. N. Gorokhov and L. N. Sidorov, Dokl. Akad. Nauk SSSR 135, 113 (1960).

source of parent ion. By including the effects of spin-orbit splitting, it is even possible to rationalize the nonmonotonicity in the fragmentation behavior of LiCl, LiBr and LiI.

So far, we have given examples of other types of molecules which can be examined by 584 Å photoelectron spectroscopy. The information obtained is still primarily of a chemical nature. We have not yet given any evidence to support our thesis that future studies will prove rewarding to atomic and chemical physicists. We shall postpone this demonstration a bit longer to consider briefly the parallel development of photoelectron spectroscopy in the x-ray region that has been pioneered by Prof. Siegbahn and his colleagues at Uppsala (11).

The photoionization cross sections of molecules, which are near their maximum at 584 Å, are typically two orders of magnitude smaller in the 8-10 Å region (MgK α , AlK α). Hence, the corresponding photoelectron spectroscopic measurements on free molecules are considerably more difficult at this photon energy. The partial cross sections for ionization from the valence shells decrease even more drastically, and represent a small fraction of the total ionization in the x-ray region. By comparison with the wealth of data accumulated at 584 Å, relatively fewer molecular systems have been studied at 9.9 Å, and most of these studies have been confined to the larger partial cross sections of the inner shells. These inner shells are localized strongly in the vicinity of the atoms that make up a particular molecule. The photoelectron spectra of these inner shells are, to zeroth order, atomic photoelectron spectra. However, these atomic lines are shifted from their free atom energy values by the chemical environment in which they reside. This chemical shift, typically a few volts, can be measured accurately and has been extensively correlated with the charge distribution within the molecule, and the valence state of particular atoms in the molecule. The only point we wish to make here is that this branch of the photoelectron spectroscopy of molecules has also been strongly oriented toward the determination of chemical information. Indeed, the acronym ESCA (Electron Spectroscopy for Chemical Analysis) is an indication of the primary thrust of this research. X-ray photoelectron spectroscopy has also been extended recently to the study of high temperature species (12), where the combined requirements of working with molecular beams and with low photoionization cross sections makes the experiment very difficult.

II. PHYSICAL STUDIES

The properties that I wish to characterize here as physical ones are intensities and angular distributions, from which one can infer transition probabilities and phase shifts. These quantities

are determined by the nature of the continuum wave function, as well as that of the neutral ground state, whereas by and large, chemical properties are discussed in terms of the initial state's molecular orbitals.

In the dipole approximation, which is excellent for low-energy photons, the differential photoionization cross section for unpolarized incident radiation is

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

where ϵ is the energy of the ejected photoelectron, $\sigma_t(\epsilon)$ is the total photoionization cross section, θ is the angle between the incoming photon direction and the outgoing electron direction, $P_2(\cos \theta) = 1/2(3 \cos^2 \theta - 1)$, and $\beta(\epsilon)$ is an asymmetry parameter which, in the approximation of Russell-Saunders coupling and one-electron wave functions can be shown to take the form

$$\beta(\epsilon) = \frac{l(l-1) R_{l-1}^2(\epsilon) + (l+1)(l+2) R_{l+1}^2(\epsilon) - 6l(l+1) R_{l-1} R_{l+1} \cos \left[\delta_{l+1}^{(t)} - \delta_{l-1}^{(t)} \right]}{(2l+1) \left[l R_{l-1}^2(\epsilon) + (l+1) R_{l+1}^2(\epsilon) \right]} \quad (2)$$

In this latter expression, $R_{l\pm 1}(\epsilon)$ is the dipole matrix element, defined by

$$R_{l\pm 1}(\epsilon) = \int_0^\infty P_{nl}(r) r P_{\epsilon, l\pm 1}(r) dr,$$

and $\delta_{l\pm 1}^{(t)}(\epsilon)$ are the phase shifts of the continuum $l \pm 1$ partial waves with respect to free waves.

Even without detailed calculations, these expressions can teach us something about experimental design and the nature of the photoionization process. From eq. (1) we note that when $P_2(\cos \theta) = 0$, the differential cross section will be independent of β . This occurs for $\theta = 54^\circ 44'$. From the wealth of photoelectron spectra currently in the literature, extremely few measurements have been made at this angle. Hence, in general, the relative intensities of the various bands, which have been primarily measured at $\theta = 90^\circ$, are not meaningful unless one has an independent measurement of β at that energy. However, if one can perform measurements at the $54^\circ 44'$ angle, relative intensities can be directly related to calculated intensities without requiring a knowledge of β .

The electron energy analyzer which was previously mentioned as a high transmission device for studies of molecular beams, can

conveniently be constructed with θ near the $54^{\circ}44'$ value. The design parameters of the particular analyzer constructed at Argonne (9) happen to optimize at $\theta = 60^{\circ}$. In addition, it has no retarding, accelerating or focusing lenses. Taking into account the $\Delta E/E$ effect (13), this analyzer appears to have a flat transmission function for electrons with kinetic energy greater than ~ 1.5 eV, falling off to lower energy.

I shall describe below three separate experiments which involved accurate relative intensity measurements with this instrument, and show how an interpretation of the results by appropriate theory has given us new insight into the photoionization process.

A. Comparison of photoelectron intensities and Franck-Condon factors in the photoionization of H_2 , HD and D_2 .

The relevant transitions in the $584 \text{ \AA}$ photoelectron spectrum of H_2 are

$$H_2(X^1\Sigma_g^+, v'' = 0) + h\nu \rightarrow H_2(X^2\Sigma_g^+, v' = 0, 1, 2, \dots) + e^-$$

Designating the initial state as a , and the final state as b , we may formally write the cross section for this process as

$$\sigma(a \rightarrow b) = \frac{8\pi^3 e^2 \nu}{c} \sum_b \sum_{\alpha} |\langle b | M_{\alpha} | a \rangle|^2 \quad (3)$$

where ν is the frequency of incident radiation, e and c have their usual meaning and α is the index for electron coordinates x , y and z . The first summation is over the degenerate final states.

In the Born-Oppenheimer approximation, both initial and final states are written as products of electronic functions ψ , vibrational functions P and rotational functions Y , i.e.

$$|a\rangle = \psi_a(R, \underline{r}_1, \underline{r}_2) R^{-1} P_a(v_a, R) Y(J_a, m_a) \quad (4)$$

$$\langle b | = \psi_b^*(R, \underline{r}_1, \underline{r}_2, E_e) R^{-1} P_b(v_b, R) Y^*(J_b, m_b) \quad (5)$$

where R is the internuclear distance, $\underline{r}_1$ and $\underline{r}_2$ are the coordinates of the two electrons with respect to axes fixed in the molecule, v is the vibrational quantum number and J and M are the rotational quantum number and its projection, and E_e is the electron kinetic energy. If for the moment we assume the rotational functions to be uncoupled and integrate over the rotational coordinates, we can write the transition matrix element as follows:

$$\langle b | M_{\alpha} | a \rangle = \int_0^{\infty} P_b^* M_{\alpha} P_a dr \quad (6)$$

where

$$M_{\alpha} = \iiint \psi_b^* (r_{1\alpha} + r_{2\alpha}) \psi_a dr_1 dr_2 \quad (7)$$

Since ψ_b and ψ_a are functions not only of the electron coordinates but also of the internuclear distance R , it follows that M_{α} will also be a function of R . In addition, ψ_b is a function of E_e , and hence M_{α} must also be dependent on E_e . In calculating Franck-Condon factors and identifying them with vibrational intensities, one is explicitly ignoring this dependence, and is writing eq. 6 in the form

$$\langle b | M_{\alpha} | a \rangle = M_{\alpha}^{(0)} \int_0^{\infty} P_b^* P_a dR \quad (8)$$

where the integral corresponds to the Franck-Condon factor, and $M_{\alpha}^{(0)}$ is the value of M_{α} at a typical R - customarily chosen to be the equilibrium distance in the electronic ground state a . Flannery and Öpik (14) have shown how M_{α} varies with R and E_e in the ionization of H_2 , choosing one reasonable model for ψ_b and ψ_a . Itikawa (15) has expanded both upon this model and upon a more sophisticated one for ψ_b . In each case, he has expressed the resulting M_{α} function as a power series

$$M_{\alpha} = \gamma + \delta (R - R_e) + \epsilon (R - R_e)^2$$

(in which γ , δ and ϵ are constant), inserted it into eq. 6, and calculated the vibrational intensities.

Experimentally, we (16) have carefully integrated the areas under the vibrational bands obtained in the 584 Å photoelectron spectrum for H_2 , HD and D_2 . The experiments were performed with a resolution width of 20 meV, where rotational structure was beginning to influence the peak shape. The relative intensity was taken as the area divided by the corresponding electron energy. They were plotted as ratios of the corresponding Franck-Condon factors vs. vibrational number, where the Franck-Condon factors are very precise calculations by Peek (17). The results for D_2 are shown in Fig. 4, together with data by Frost et al. (18) and Itikawa's calculations. If the approximations involved in eq. (8) were valid, we would expect perfect agreement with Franck-Condon factors, in which case the data points should describe a straight horizontal line. Clearly, the data points have a positive slope, indicating a substantial deviation from purely Franck-Condon behavior. The agreement with Itikawa's case (C) is particularly

Fig. 4. The ratio of the experimental (or calculated) vibrational intensity to the Franck-Condon factor for D_2 , plotted as a function of the vibrational quantum number v' .
 ○○ Frost, McDowell and Vroom; □□ Itikawa, case (B);
 △△ Itikawa, case (C); and ●● Berkowitz and Spohr.

good, indicating that this particular choice of continuum function is a reasonable one, and also providing support for the view that the essence of the physics has been included in the calculations, despite several approximations in Itikawa's calculations.

B. Rotational band shapes in the photoelectron spectra of HF and DF

It has long been realized that the peak shapes observed in photoelectron spectroscopy contain useful information. When individual vibrational levels are not resolved, it is assumed that a broad peak corresponds to a considerable change of geometry on ionization, while a narrow peak suggests that the ion has a similar geometry to that of the neutral molecule. However, much less work has been concerned with the effects of rotational broadening which may be investigated when individual vibrational levels of the ion are resolved.

The photoionization process in HF corresponding to

is of particular interest in this context, because the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states are incompletely resolved, and the shape of an individual vibrational band is determined not only by the nature of the rotational transitions, but also by the spin-orbit coupling. By considering the hamiltonian of the entire system, calculating the rotational line strength of each rotational transition and using an experimental line width derived from a nearby atomic line obtained in the same experiment, a theoretical band contour can be constructed. In this instance, the theoretical band contour was calculated for several assumed values of the spin-orbit coupling constant. The best fit enabled us to extract a rather accurate value of the spin-orbit coupling constant from the band contour.

We shall only sketch the outlines of the calculation here. For details see ref. (19).

If we only consider ionization of the outermost $(\pi)^4$ system of HF into the s partial wave, the final state of the system ion plus electron has the configuration $\pi^3\sigma$, which gives rise to $^3\Pi$ and $^1\Pi$ states. These two states are degenerate, i.e. the triplet and singlet Rydberg series approach the same ionic limit. The $^3\Pi$ state consists of three components with $\Omega = 2, 1$ and 0 . The $^1\Pi$ state has $\Omega = 1$. In the nonrotating molecule, electric dipole transitions from the ground state of the neutral molecule ($^1\Sigma^+$) are only allowed to the $^1\Pi_1$ state. However, spin-orbit coupling mixes the $^1\Pi_1$ and $^3\Pi_1$ states, and the rotation of the molecule couples the three components of the $^3\Pi$ state by means of spin-uncoupling (20). Hence, transitions become allowed to all four final states. The hamiltonian describing the interactions is of the form

$$H = B[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2] + H^{SO} = H^R + H^{SO} \quad (9)$$

where J is the total angular momentum, L and S are the electronic orbital and spin angular momenta, and H^{SO} is the spin-orbit contribution. This is written in matrix form in Table 2.

This matrix is then diagonalized, and the rotational line strengths are calculated by using the Hönl-London factors for a $^1\Sigma \rightarrow ^1\Pi$ transition (21), which are

$$R \text{ branch intensity} \propto (J + 2)$$

$$Q \text{ branch intensity} \propto (2J + 1)$$

$$P \text{ branch intensity} \propto (J - 1)$$

TABLE 2

Matrix elements of $H = H^R + H^{SO}$ for $^3\Pi$ and $^1\Pi$ states in Hund's case (a)¹

	$^3\Pi_2$	$^3\Pi_1$	$^3\Pi_0$	$^1\Pi_1$
$^3\Pi_2$	$A/2 + B[J^2+J-4]$	$B\sqrt{2(J+2)(J-1)}$	0	0
$^3\Pi_1$	$B\sqrt{2(J+2)(J-1)}$	$BJ(J+1)$	$B\sqrt{2J(J+1)}$	$A/2$
$^3\Pi_0$	0	$B\sqrt{2J(J+1)}$	$-A/2 + BJ(J+1)$	0
$^1\Pi_1$	0	$A/2$	0	$B[J^2+J-2]$

¹A is the spin-orbit coupling for the ion $^2\Pi$ state.

The vibrational band contour is then constructed from the sum of rotational lines, each one broadened by an experimental line width and weighted with the appropriate intensity and Boltzmann factor. The only variable parameters in this approach are the spin-orbit coupling constant and the ionization potential, which we define as the difference in energy between the $J = 0$ rotational level of the molecule and the $J = 3/2$ rotational level of the $^2\Pi_{3/2}$ state of the ion. Only the spin-orbit coupling constant affects the band shape.

Figure 5 shows the experimental results for DF^+ , $v' = 0$, together with the $Ar^+ 2p_{1/2}$ line and the calculated contour that gives the best fit. From this fitting procedure, we have deduced a spin-orbit coupling constant of $290 \pm 10 \text{ cm}^{-1}$. This is significantly different from the value 240 cm^{-1} that had been deduced by measuring the partially resolved splitting in the photoelectron spectrum. It is also in line with the ratio of doublet splittings in HX^+ and the corresponding X, given in Table 3. For the determination of ionization potentials, rapid scans are preferable since they minimize the likelihood of any change of surface potential occurring between the argon peaks (used for calibration) and the HF^+ or DF^+ peaks. The values of the ionization potentials obtained from the best fit between calculation and experiment are

$$HF: 16.044 \pm 0.003 \text{ eV}$$

$$DF: 16.058 \pm 0.003 \text{ eV}$$

These errors are an order of magnitude smaller than the experimental line width. After correcting for molecular and ionic zero point energies, there is a residual discrepancy which may be due to an electronic isotope effect (19, 22).

The ionization potentials given above are slightly different from those obtained previously by photoionization mass spectrometry (23). This is due to the difficulty of choosing a proper

Fig. 5. Slow scan spectrum of DF^+ , $X^2\Pi_{3/2,1/2}$, $v' = 0$. Solid line: calculated contour based on $A = 290 \text{ cm}^{-1}$. $\bullet$ experimental points.

TABLE 3

Ratio of molecular to atomic spin-orbit splitting

Ion	$^2\Pi_{1/2} - ^2\Pi_{3/2}$	$^2P_{1/2} - ^2P_{3/2}$	Ratio
	cm^{-1}	cm^{-1}	
HI^+	5650	7603	0.743
HBr^+	2653	3685	0.720
HCl^+	643	881	0.730
HF^+	290	404	0.72

threshold function for the mass spectrometric determination, as well as the less detailed treatment of rotation. The results given here must be considered more precise.

Although only the s wave has been considered in the theory given here, we have reason to believe (19) that the inclusion of the dominant d wave will not seriously affect our conclusions. The d wave will allow larger angular momentum transfers to take place

than for an s wave and transitions become allowed from HF (J) to HF⁺ (J ± 1/2, J ± 3/2, J ± 5/2). The effect of these extra transitions will be to broaden the overall peaks with respect to that calculated for s waves only, and to reduce any dip between the two halves of the doublet.

It should be noted that this analysis has presupposed an experiment conducted at θ = 54°44'. If the experiment were conducted at a very different θ, such as 90°, the angular distribution of each rotational transition at the energy of the experiment would have to be known.

C. Spin-orbit coupling and the ratio of photoionization cross sections in some atoms.

One of the earliest experiments reported in photoelectron spectroscopy corresponded to the reaction

When measurements become a bit more refined, it was found that the ratios of intensities of the ²P_{3/2} to ²P_{1/2} were less than 2:1 (their ratio of statistical weights) in every instance. In 1968, Samson and Cairns (24) reported this ratio to be 1.98, 1.79 and 1.60 for Ar, Kr and Xe, respectively. We have recently remeasured these ratios with our cylindrical analyzer, and find fair agreement.

In addition, we (25) have measured the ratio of spin-orbit split states formed in the ionization of the set Zn, Cd and Hg.

Thus

The ratio of statistical weights in this case should be 1.50. For Zn⁺ it appears to be close to this value, but for Cd⁺ it is 1.79, and for Hg, 2.18, i.e. larger than statistical.

In an attempt to rationalize these observations, Dr. Walker (25) has recently performed some calculations using Dirac-Slater relativistic wave functions for both the bound and continuum states. From these calculations has emerged a general

understanding of branching ratios and their departure from statistical weight predictions, which is a generalization of Cooper's calculations (26). Cooper had previously noted that, although the dipole selection rules permitted $\Delta l = \pm 1$, the $l + 1$ channel usually dominates the cross section.

At very low photoelectron energies, the first major maximum of the continuum orbital of the $l + 1$ channel will lie outside the region of space occupied by the bound orbital. As the photoelectron energy increases, this maximum moves nearer the nucleus, and the dipole matrix element increases. When the photoelectron energy increases still further, the first major maximum of the continuum orbital begins to overlap the nodes of the bound orbital (if any) and the dipole matrix element decreases and finally changes sign, giving rise to the Cooper minimum in the partial cross section.

Now consider what happens when spin-orbit coupling is introduced. This causes the $j = l - 1/2$ component of the bound orbital, for which the spin-orbit potential is attractive, to be drawn slightly closer to the nucleus than the $j = l + 1/2$. As a result, when the photoelectron energy increases from zero, the continuum orbital will have a greater overlap with the $j = l + 1/2$ component of the bound state, and the ratio $\sigma(l+1/2)/\sigma(l-1/2)$ will be greater than the statistical value of $(l+1)/l$. Similarly, the continuum orbital will overlap the first node of the $j = l + 1/2$ before that of the $j = l - 1/2$, and in this part of the spectrum $\sigma(l+1/2)/\sigma(l-1/2) < (l+1)/l$. Figure 6 illustrates this. The same considerations hold after the Cooper minimum is passed. Thus we can make the generalization that if the partial cross section is rising, the ratio of cross sections is greater than statistical, while if the partial cross section is falling, the ratio will be less than statistical. For the rare gases Ar, Kr and Xe, the cross section is falling at 21.2 eV, while for Zn, Cd and Hg it is rising.

III. SUMMARY AND CONCLUSIONS

There are other physical aspects of photoelectron spectroscopy, such as the measurement of the angular distribution asymmetry parameter β as a function of photoelectron energy, and the determination of branching ratios and β 's across autoionizing peaks for which there is neither time nor space at this conference. However, I hope that I have given enough examples to support the view that the branching ratio of photoelectron spectroscopy between chemistry and physics will move more strongly to the latter in the next few years.

Fig. 6. Cross section per electron for photoionization of the $5d_{5/2,3/2}$ orbital of mercury as a function of incident photon energy. $5d_{3/2}$ - open circles and $5d_{5/2}$ - closed circles. The topmost curve shows $\sigma_{5/2}/\sigma_{3/2}$ as a function of incident photon energy.

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