A prediction of anomalous behavior in experimental photoionization cross sections

Jack Simons*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112
(Received 13 March 1975)

In this note we address our attention to processes in which the photoejection of an electron from a molecule gives rise to major changes in the electron density of the remaining electrons. It has been long recognized that a reorganization of electron density accompanies the photoejection of an electron. However, because ionization events are commonly interpreted in terms of an orbital energy level picture of the *parent* species, it is important to understand the limitations of such an approach as well as to know how to extend this model. The principal conclusion of the present work is that the magnitude and angular dependence of the experimentally observed photoelectron cross section are sensitive to the orbital reorganization and correlation energy change which accompany ionization. Unusually small cross sections and/or cross sections whose angular distribution is characteristic of excited orbital(s) of the parent can result from these effects.

The differential cross section for the ejection of an electron having momentum $\mathbf{k}_f\hbar$ from the state $|\psi_i^N\rangle$ of an N-electron atom, molecule, or ion is given by[1]

$$\sigma_{i\to f}(\theta,\phi)=\frac{e^2}{2\Pi mc}\frac{|k_f|}{\omega}\left|\langle U_{\mathbf{k}_f}\psi_f^{N-1}\sum_{j=1}^{N}e^{i\mathbf{k}\cdot\mathbf{r}_j}\hat{A}\cdot\nabla_j|\psi_i^N\rangle\right|^2 . \tag{1}$$

In Eq. (1), ω is the frequency of the photon, $\mathbf{k}$ is its propagation vector ($|k|=\omega/c$), $\hat{A}$ is a unit vector in the direction of the vector potential of the photon, $U_{\mathbf{k}_f}$ is the continuum orbital describing the ejected electron, and $|\psi_f^{N-1}\rangle$ is the resultant state of the $(N-1)$ electron daughter.

In this note, attention will be concentrated on the conditions under which the matrix element in Eq. (1) can give rise to anomalously small ionization cross sections and angular distributions which are not consistent with a Koopmans' theorem-level[2] description. To simplify the mathematical description of the parent and daughter wavefunctions, we assume that the parent is a closed-shell species; the extension of our analysis to open-shell systems is straightforward. This allows us to write a reasonable approximation to the ground state wavefunction $|\psi_0^N\rangle$ as[3]

$$|\psi_0^N\rangle=K_0^{-1/2}\left[|0\rangle+\sum_{\substack{\alpha<\beta\\ m<n}}C_{\alpha\beta}^{mn}|{}_{\alpha\beta}^{mn}\rangle\right] , \tag{2}$$

where $|0\rangle$ represents the single-determinant SCF[4] wavefunction $|\phi_1\cdots\phi_{N-1}\phi_N|$, $|{}_{\alpha\beta}^{mn}\rangle$ is a determinant in which spin orbitals ϕ_α and ϕ_β ($\alpha,\beta\leq N$) have been replaced by ϕ_m and ϕ_n ($m,n>N$). The double-excitation expansion coefficients $C_{\alpha\beta}^{mn}$ are assumed to be known from a variational calculation on the parent, and K_0 is a normalization constant. The ground-state wavefunction of the daughter $|\psi_0^{N-1}\rangle$ can be reasonably well approximated as follows[5]:

$$|\psi_0^{N-1}\rangle=K^{-1/2}\left[X_N|{}_N\rangle+\sum_{\alpha=1}^{N-1}\sum_{m=N+1}^{2M}X_\alpha^m|{}_{N\,\alpha}^{\,m}\rangle\right] , \tag{3}$$

In Eq. (3) K is the normalization constant, the X's are expansion coefficients which we assume to have been variationally determined, $|{}_N\rangle$ is a Slater determinant in which ϕ_N has been removed from $|0\rangle$, and $|{}_{N\,\alpha}^{\,m}\rangle$ is a determinant in which ϕ_N has been removed and ϕ_α has been replaced by ϕ_m. In photoionization events where charge reorganization is large the amplitude X_N may be quite small and one or more of the amplitudes X_α^m (e.g., X_{N-1}^{N+1}) may be quite large. This is precisely the situation which gives rise to anomalous photoionization cross sections.

The result of substituting Eqs. (2) and (3) into Eq. (1) is

$$\langle U_{\mathbf{k}_f}\psi_0^{N-1}|V|\psi_0^N\rangle=K_0^{-1/2}F_{fi}\left[X_N\langle U_{\mathbf{k}_f}|v|\phi_N\rangle+\sum_{\alpha=1}^{N-1}\sum_{m<n=N+1}^{2M}X_\alpha^m C_{\alpha N}^{mn}\langle U_{\mathbf{k}_f}|v|\phi_n\rangle\right] , \tag{4}$$

where the one-photon perturbation has been represented by v, and F_{fi} is the Franck–Condon factor.[6] Let us recall that we are interested in cases in which the charge reorganization accompanying ionization is so large that the amplitude X_N is significantly less than unity whereas one or more of the amplitudes X_α^m are significantly greater than zero.

Under the above conditions on the magnitudes of X_N and X_α^n, one easily sees from Eq. (4) that the transition matrix element will be dominated by contributions from the terms $C_{\alpha N}^{mn}X_\alpha^m\langle U_{\mathbf{k}_f}|v|\phi_n\rangle$ if X_α^m is sufficiently large and one or more of the parent's double-excitation expansion coefficients $C_{\alpha N}^{mn}$ is large. This conclusion is, of course, further enhanced in the event that the integral $\langle U_{\mathbf{k}_f}|v|\phi_N\rangle$ is small. Thus, if the parent's ground state is highly correlated with respect to spin orbital ϕ_N ($C_{\alpha N}^{mn}$ large) and if there is major orbital reorganization ($X_\alpha^m > X_N$), one expects $\sigma(\theta,\phi)$ to be small in magnitude with angular dependence characteristic of one or more of the parent's virtual orbitals ($\langle U_{\mathbf{k}_f}|v|\phi_N\rangle$). On the other hand, if the parent's ground state is not strongly correlated ($C_{\alpha N}^{mn}$ small), then $\sigma(\theta,\phi)$ will be dominated by the term $X_N\langle U_{\mathbf{k}_f}|v|\phi_N\rangle$, which would give rise to a small magnitude cross section ($|X_N|^2$ small) whose angular dependence is characteristic of ϕ_N.

The above observations regarding the behavior of $\sigma(\theta,\phi)$ under conditions of large orbital reorganization

are not valid for two-photon processes, since if $|X_{N-1}^{N+1}|^2 \sim 1$, the dominant contribution to $\sigma(\theta, \phi)$ is $\sum_{\alpha,n} K_0^{-1/2} K^{-1/2} F_{fi} X_\alpha^n \langle {}_N^k f_\alpha^n | v_2 | 0 \rangle$ which would not be small. One is thus led to speculate that two-photon ionization spectroscopy may be a valuable tool for determining whether large orbital relaxation effects are present.

In the event that experimental data are obtained which indicate an unusually small photoionization cross section which is not merely a result of unfavorable Franck–Condon factors,[6] the possibility of significant orbital relaxation should be further investigated. By carrying out two-photon experiments, one may be able to confirm or negate this possibility. If the occurence of an anomalously small $\sigma(\theta, \phi)$ is accompanied by an angular distribution which is not characteristic of the expected Koopmans' orbital, one may be able to conclude that the ground state of the parent is highly correlated.

It is our feeling that such "anomalous" cases will become much more common and familiar in connection with studies of the photodetachment of negative molecular ions, although the phenomenon is by no means restricted to these species. In gas-phase molecular anions, there is a delicate balance between electron–nuclear attractions and electron–electron repulsions. Thus, treatment of electron correlations is essential to understanding the stability and charge density of these negative ions. Moreover, it is known that the formation of a negative molecular ion can give rise to a major change in electron density, i.e., to a more diffuse and/or significantly altered orbital structure. This kind of behavior is discussed in an article[7] in which we studied the change in electron density accompanying the ionization of BeH^-. In such situations, a combination of one- and two-photon detachment studies of negative molecular ions offers attractive possibilities for better understanding the electronic structures of these very interesting species.

*Alfred P. Sloan Foundation Fellow.

[1]H. A. Bethe, *Intermediate Quantum Mechanics* (Benjamin, New York, 1964), Chap. 14.

[2]T. Koopmans, Physica 1, 104 (1934).

[3]It is well known that a superposition of the SCF determinant and doubly excited determinants gives a reasonably accurate description of the electron correlation in closed-shell systems. For a discussion of such configuration interaction wavefunctions, see H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, (1972).

[4]See, for example, C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[5]The effects of electron correlation in the daughter could be treated by including configurations which are doubly excited relative to $|_N\rangle$, e.g., $|_{N\alpha\beta}^{m n}\rangle$. Such terms, although certainly present, will not be included in our approximation to $|\psi_0^{N-1}\rangle$ because they are not essential to a discussion of the anomalous behavior of $\sigma(\theta, \phi)$ which is the topic of this work, and they do not affect the principal conclusions which we shall draw.

[6]These factors can have important effects on the magnitude and (photon) energy dependence of $\sigma(\theta, \phi)$. However, we shall not further discuss their role in this paper because our principal goal is to elucidate the effects of electronic structure differences.

[7]J. Kenney and J. Simons, J. Chem. Phys. 62, 592 (1975).