Theory of Threshold Energy Dependence of Photodetachment of Diatomic Molecular Negative Ions

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The energy dependence near zero energy of the continuum wave function of an electron in a molecular potential field is found by an iterative solution of the wave equation. This leads to shapes for the photodetachment cross section near threshold which are found to depend on whether the molecular ion is heteronuclear or homonuclear and on the u, g symmetry (for homonuclear case) of the outer molecular orbital. The predicted energy dependences are found to be consistent with the available experimental data.

I. INTRODUCTION AND MOLECULAR APPROXIMATIONS

THE threshold behavior of the cross section for photodetachment of an electron from an atomic negative ion is well understood.[1] It is the case of a reaction with two final products (electron and atom) interacting with one another through a short-range spherically symmetric potential. The general treatment of such two-particle reactions has been given by Wigner,[2] who found that the energy dependence near threshold was a function of the relative orbital angular momentum of the product particles. In the case of electron photodetachment from atomic negative ions, the final l is obtainable from the initial l of the bound state via the selection rules for dipole radiation. In the diatomic molecular case the potential between the product particles is no longer spherically symmetric but axially symmetric, making the expansion of the final-state wave functions in spherical harmonics inappropriate. In the present work we derive the threshold shape of the molecular photodetachment curve in a general way which makes no assumptions about the molecular potential other than its basic symmetry properties and the fact that it is short-ranged.

In the Born-Oppenheimer approximation the total molecular wave function may be written as a product of a function of the nuclear coordinates alone and a function of the electron coordinates in which the nuclear coordinates are contained as parameters. For any given nuclear coordinates the electronic functions form a complete orthonormal set. The total electronic eigenfunctions may be constructed from a configuration of molecular orbitals obtained from a self-consistent-field calculation. The energy dependence of the differential cross section for photodetachment[3] is entirely contained in

$$d\sigma \sim \nu k \left| \int u_k{}^* \mathbf{r} u_0 d\mathbf{r} \right|^2 d\Omega, \qquad (1)$$

where ν is the photon frequency, $\mathbf{k}$ is the electron wave vector, and u_0 and u_k are bound and continuum orbitals corresponding to the initial and final states of the photodetachment process. As these two orbitals are orthogonal, the effect of the inner electrons is to introduce energy-independent overlap integrals into the expression for the cross section. Simultaneous nuclear dipole transitions are forbidden in the Born-Oppenheimer approximation as terms containing the nuclear dipole operators will vanish by the orthogonality of the electronic states. If the molecules initially are in a distribution of vibration-rotation states, then the resultant photodetachment cross section is a superposition of curves having the form of (1), each setting in at slightly displaced thresholds.

II. FINAL-STATE CONTINUUM WAVE FUNCTION

The initial and final outer orbitals are eigenfunctions of the Schrödinger equation

$$[\nabla^2 + k^2 - V]u = 0, \qquad (2)$$

where $V = V(\rho, z)$ is the axially symmetric effective molecular potential. The molecular axis is taken to be the z axis, and the cylindrical coordinates ρ, z, and φ are used. In a negative ion there are usually one, or perhaps a few, bound-state solutions for (2) and the continuum of positive-energy solutions, u_k. The initial bound-state solution is independent of the energy of the photon or of the detached electron and may be written as

$$u_0 = \chi_0(\rho, z) e^{i\lambda_0 \varphi}, \qquad (3)$$

where $\lambda_0 \hbar$ is the angular momentum component along the molecular axis.

The normalization of the continuum function in (1) is such that as $V \rightarrow 0$, $u_k \rightarrow e^{i\mathbf{k} \cdot \mathbf{r}}$. Hence, we seek a solution of (2) of the form $u_k = e^{i\mathbf{k} \cdot \mathbf{r}} + v$, which leads to the nonhomogeneous partial differential equation for v,

$$[\nabla^2 + k^2]v = V(e^{i\mathbf{k} \cdot \mathbf{r}} + v). \qquad (4)$$

Since V is a short-range potential we expect a solution

[1] Branscomb, Burch, Smith, and Geltman, Phys. Rev. 111, 504 (1958).
[2] E. P. Wigner, Phys. Rev. 73, 1002 (1948).
[3] H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. 35, p. 381.

of (4) by iteration to be convergent. The nth iteration gives

$$v^{(n)} = \int d\mathbf{r}_n \frac{e^{ikR_n}}{R_n} V(\mathbf{r}_n)[e^{i\mathbf{k}\cdot\mathbf{r}_n} + v^{(n-1)}(\mathbf{r}_n)], \quad (5)$$

with $R_n = |\mathbf{r}_n - \mathbf{r}|$ and $v^{(0)} = 0$. To take advantage of the molecular symmetry, we make use of the following expansions for the plane wave[4] and the three-dimensional Green's function for the Helmholtz equation[5]:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikz\cos\alpha} \sum_{\lambda=-\infty}^{\infty} i^\lambda e^{-i\lambda\beta} J_\lambda(k\rho\sin\alpha) e^{i\lambda\varphi}, \quad (6a)$$

$$\frac{e^{ikR_n}}{R_n} = i \sum_{\lambda=-\infty}^{\infty} e^{i\lambda(\varphi-\varphi_n)} \int_0^\infty t\,dt$$
$$\times J_\lambda(t\rho) J_\lambda(t\rho_n) \frac{\exp[i(k^2-t^2)^{\frac{1}{2}}|z-z_n|]}{(k^2-t^2)^{\frac{1}{2}}}, \quad (6b)$$

in which α is the angle between $\mathbf{k}$ and the z axis and β is the azimuthal angle of $\mathbf{k}$. Also, expanding

$$v^{(n)} = \sum_{\lambda=-\infty}^{\infty} i^\lambda e^{-i\lambda\beta} F_\lambda^{(n)}(\rho,z) e^{i\lambda\varphi},$$

we have, after substituting (6a, b) into (5) and integrating over the φ-like variable,

$$F_\lambda^{(n)} = 2\pi i \int_0^\infty \rho_1 d\rho_1 \int_{-\infty}^\infty dz_1 \int_0^\infty t_1 dt_1\, J_\lambda(t_1\rho) J_\lambda(t_1\rho_1) V(\rho_1,z_1) \frac{\exp[i(k^2-t_1^2)^{\frac{1}{2}}|z-z_1|]}{(k^2-t_1^2)^{\frac{1}{2}}} e^{ikz_1\cos\alpha} J_\lambda(k\rho_1\sin\alpha)$$

$$+ (2\pi i)^n \int_0^\infty \rho_n d\rho_n \int_{-\infty}^\infty dz_n \int_0^\infty t_n dt_n\, J_\lambda(t_n\rho) J_\lambda(t_n\rho_n) V(\rho_n,z_n) \frac{\exp[i(k^2-t_n^2)^{\frac{1}{2}}|z-z_n|]}{(k^2-t_n^2)^{\frac{1}{2}}}$$

$$\times \int_0^\infty \rho_{n-1} d\rho_{n-1} \int_{-\infty}^\infty dz_{n-1} \int_0^\infty t_{n-1} dt_{n-1}\, J_\lambda(t_{n-1}\rho) J_\lambda(t_{n-1}\rho_{n-1}) V(\rho_{n-1}, z_{n-1}) \frac{\exp[i(k^2-t_{n-1}^2)^{\frac{1}{2}}|z-z_{n-1}|]}{(k^2-t_{n-1}^2)^{\frac{1}{2}}}$$

$$\times \cdots \int_0^\infty \rho_1 d\rho_1 \int_{-\infty}^\infty dz_1 \int_0^\infty t_1 dt_1\, J_\lambda(t_1\rho) J_\lambda(t_1\rho_1) V(\rho_1,z_1) \frac{\exp[i(k^2-t_1^2)^{\frac{1}{2}}|z-z_1|]}{(k^2-t_1^2)^{\frac{1}{2}}} e^{ikz_1\cos\alpha} J_\lambda(k\rho_1\sin\alpha). \quad (7)$$

In the case of a homonuclear molecule, V is an even function of z about the center of symmetry. Also $\exp[i(k^2-t_1^2)^{\frac{1}{2}}|z-z_1|]$ is an even function of z about z_1. The exponential $e^{ikz_1\cos\alpha}$ is the sum of an even and odd part about the center of symmetry, $\cos(kz_1\cos\alpha) + i\sin(kz_1\cos\alpha)$. Hence, the integral with respect to z_1 contains an even and an odd part in z. This evenness or oddness is propagated through all the iterative integrations in (7) over the z-like variable. For heteronuclear molecules, V has no symmetry with respect to z and consequently $F_\lambda^{(n)}$ will not be divisible into an even and an odd part.

The k dependence in the limit of $k \rightarrow 0$ is obtained by making the power series expansions of $e^{ikz\cos\alpha}$ and $J_\lambda(k\rho\sin\alpha)$ in (6a) and (7). This leads to

$$u_k = e^{i\mathbf{k}\cdot\mathbf{r}} + \lim_{n\to\infty} v^{(n)} = \sum_{\lambda=-\infty}^{\infty} i^\lambda e^{-i\lambda\beta} G_\lambda(\rho,z) e^{i\lambda\varphi}, \quad (8)$$

where, in the heteronuclear case,

$$G_\lambda = (k\sin\alpha)^\lambda \sum_{\mu,\nu=0}^{\infty} A_{\mu\nu}^{(\lambda)}(z,\rho)(k\sin\alpha)^{2\mu}(k\cos\alpha)^\nu, \quad (9a)$$

and in the homonuclear case,

$$G_\lambda = G_\lambda\ (\text{even}) + G_\lambda\ (\text{odd}),$$

with

$$G_\lambda(\text{even}) = (k\sin\alpha)^\lambda \sum_{\mu,\nu=0}^{\infty} B_{\mu\nu}^{(\lambda)}(\rho,z)(k\sin\alpha)^{2\mu}(k\cos\alpha)^{2\nu},$$

and

$$G_\lambda(\text{odd}) = (k\sin\alpha)^\lambda (k\cos\alpha)$$
$$\times \sum_{\mu,\nu=0}^{\infty} C_{\mu\nu}^{(\lambda)}(\rho,z)(k\sin\alpha)^{2\mu}(k\cos\alpha)^{2\nu}. \quad (9b)$$

The k dependence in the A, B, and C coefficients can be written as a power series in k^2 starting with the constant term, since $\exp[i(k^2-t_1^2)^{\frac{1}{2}}|z-z_1|]/(k^2-t_1^2)^{\frac{1}{2}} \rightarrow$ a function independent of k as $k \rightarrow 0$. The limiting k dependence is thus explicitly exhibited in the factors multiplying the above infinite series. Note that the limiting k dependence in G_λ is the same as would be obtained in the first Born approximation, i.e., with $u_k = e^{i\mathbf{k}\cdot\mathbf{r}}$. Hence, at least in this case, the first Born approximation would give the correct threshold energy dependence.

III. DIPOLE MATRIX ELEMENT AND CROSS SECTION

The dipole matrix element in (1) becomes, after the φ integration,

[4] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), p. 372.

[5] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 888; G. Breit and H. A. Bethe, Phys. Rev. **93**, 888 (1954). The threshold shape will not depend on whether the ingoing or outgoing modification is used for the "scattered wave."

TABLE I. Values of threshold exponent m.

$\|\lambda_0\|$		Heteronuclear	Homonuclear	
			g	u
	0	1	3	1
$\|\lambda_0\| \geqslant 1$	$\|\lambda_0\|$ even	$2\|\lambda_0\|-1$	$2\|\lambda_0\|-1$	$2\|\lambda_0\|+1$
	$\|\lambda_0\|$ odd	$2\|\lambda_0\|-1$	$2\|\lambda_0\|+1$	$2\|\lambda_0\|-1$

$$\mathbf{M} = \int u_k^* \mathbf{r} u_0 d\mathbf{r}$$

$$= 2\pi \sum_{\lambda=-\infty}^{\infty} (-i)^\lambda e^{i\lambda\beta} \int_0^\infty \rho d\rho \int_{-\infty}^\infty dz\, \chi_0(\rho,z) G_\lambda^*(\rho,z)$$

$$\times [(\mathbf{e}_x - i\mathbf{e}_y)\tfrac{1}{2}\rho\delta_{\lambda,\lambda_0+1}$$

$$+ (\mathbf{e}_x + i\mathbf{e}_y)\tfrac{1}{2}\rho\delta_{\lambda,\lambda_0-1} + \mathbf{e}_z z\delta_{\lambda,\lambda_0}],$$

and as $d\Omega = \sin\alpha \, d\alpha \, d\beta$,

$$\int_0^{2\pi} |\mathbf{M}|^2 d\beta = (2\pi)^3 \left\{ \frac{1}{2} \left| \int\int \rho d\rho \, dz \, \chi_0 \rho G_{\lambda_0+1}^* \right|^2 \right.$$

$$+ \frac{1}{2} \left| \int\int \rho d\rho \, dz \, \chi_0 \rho G_{\lambda_0-1}^* \right|^2$$

$$\left. + \left| \int\int \rho d\rho \, dz \, \chi_0 z G_{\lambda_0}^* \right|^2 \right\}. \quad (10)$$

For a given λ_0 the threshold energy dependences are found by substituting the expansions (9a, b) into (10). The integration over α causes the odd powers of $k \cos\alpha$ which enter through the sum in (9a) to vanish.

In the homonuclear case, the bound orbital must have either g or u symmetry, that is, remain unchanged or change in sign when the electron coordinates are inverted through the center of symmetry of the molecule. This requires the following behavior of χ_0:

$$g \text{ orbital: } \chi_0(\rho,z) = (-1)^{\lambda_0} \chi_0(\rho, -z),$$
$$u \text{ orbital: } \chi_0(\rho,z) = (-1)^{\lambda_0+1} \chi_0(\rho, -z), \quad (11)$$

or χ_0 will be even or odd with respect to z depending on λ_0 and whether the orbital is g or u. In the first two terms of (10) both χ_0 and $G_{\lambda_0\pm1}^*$ must have the same parity to keep the integration over z from vanishing, while in the last term χ_0 and $G_{\lambda_0}^*$ must have opposite parity. For $\lambda_0 < 0$, one uses $J_{-n} = (-1)^n J_n$, showing that the limiting energy dependence is a function of $|\lambda_0|$ only.

Writing the threshold form of the photodetachment cross section as

$$\sigma \sim \nu k^m (1 + a_1 k^2 + a_2 k^4 + \cdots), \quad (12)$$

we find from (1), (9a, b), (10), and (11) the set of values of the exponent m for the various cases given in Table I.

IV. COMPARISON WITH EXPERIMENT

Photodetachment measurements have been made for only two molecular negative ions, OH^- and O_2^-. With OH^-,[6] a photodetachment curve which rises very sharply (on energy scale) from threshold has been observed. A detailed analysis has not yet been made of the data but it seems to fit (12) most closely with $m=1$. This would be consistent with our theoretical result for a σ or π orbital in a heteronuclear molecule. It is reasonable to expect OH^- to have the same electron configuration, π^4, as the isoelectronic molecule HF.[7]

The detailed behavior of the O_2^- photodetachment curve is presented in the accompanying paper.[8] An actual threshold energy was not found, but the shape of the curve down to the lowest photon energies used closely followed (12) with $m=3$. If this is indeed the threshold form, it is theoretically obtainable in a detachment from a σ_g, π_g, or δ_g orbital in O_2^-. This is consistent with a π_g^3 configuration,[9] which is believed to be the lowest lying. A more detailed discussion of other possible interpretations of the O_2^- results is contained in the companion paper.[8]

It should be emphasized that the foregoing results apply only in cases where the Born-Oppenheimer separation of electronic and nuclear motion is valid. Right at threshold the magnitude of the outgoing electron's velocity is less than or the same order as that of the nuclear velocities, implying a breakdown of the Born-Oppenheimer approximation. However, at 0.1 ev above threshold the electron velocity is already much greater than that of the nuclei. Also we make no attempt to evaluate the coefficients in (12) which would tell how far above threshold the limiting shape is valid. This would require a detailed knowledge of the molecular potential.

It is of interest for the sake of completeness to note that the similar process of photoionization (single) of neutral molecules will have a threshold energy dependence of the form $\nu(1 - e^{-2\pi/k})^{-1}(1 + a_1 k^2 + \cdots)$, independent of the initial molecular orbital or the type of molecule. This is brought about by the predominance of the long-range attractive Coulomb field between electron and positive ion at large separations.[2]

ACKNOWLEDGMENTS

[6] S. J. Smith and L. M. Branscomb, Phys. Rev. 99, 1657(A) (1955); L. M. Branscomb, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1957), Vol. 9, p. 43 and Fig. 12.
[7] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), second edition, p. 341.
[8] Burch, Smith, and Branscomb, Bull. Am. Phys. Soc. Ser. II, 2, 301 (1957), and Phys. Rev. 112, 171 (1958), preceding paper.
[9] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) A239, 269 (1946).