

## Rotational intensities in photodetachment and photoionization

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In this Brief Report we extend the work on the frame-transformation method to give an analytic form for the relative intensities of rotational transitions in photodetachment and photoionization. The specific case of photoabsorption by a  $^1\Sigma$  species, resulting in a  $^2\Pi$  species and an  $s$  electron, is treated analytically. The results are in good agreement with both threshold photodetachment cross sections and photoelectron spectra.

The observation of resolved<sup>1</sup> or partially resolved<sup>2-4</sup> rotational structure in photodetachment of diatomic negative ions is a new development in the high-resolution spectroscopy of bound-free processes. Data from these experiments have been fitted using the frame-transformation method with some success. The purposes of this Brief Report are to explicitly state the assumptions used, give an expression for the relative intensities of the rotational structure in the case of  $XH^- ^1\Sigma$  photodetachment to produce  $XH ^2\Pi$  and an  $s$  electron, and to apply these results to the  $OH^-$  photoelectron spectrum obtained by Breyer *et al.*<sup>2</sup>

Several thresholds appear in photodetachment<sup>5</sup> of  $S^-$ , caused by fine structure in the ion and neutral. The frame-transformation method, which involves a recoupling of the angular momenta, was first applied to negative-ion photodetachment by Rau and Fano<sup>6</sup> to explain the relative intensities of these thresholds. This method and its extensions<sup>7,8</sup> have been successful in predicting atomic negative-ion photodetachment threshold strengths.<sup>5,9,10</sup> It has also successfully predicted the relative intensities and line shapes observed in atomic negative-ion photoelectron spectroscopy,<sup>8,11,12</sup> where the photon energy is well above the threshold photodetachment range.

In the case of molecular photodetachment, many additional transitions occur as a result of rotational structure in both the negative ion and the neutral. The problem of calculating the relative intensities for the rotational structure was posed for the case of HF ionization by Walker and co-workers.<sup>13</sup> Using the frame-transformation method, Walker<sup>14</sup> also predicted the photoelectron spectra for the group-VI hydrides,  $XH^-$ . While the method appeared to require numerical diagonalization of a matrix, we present here the analytic result. Hotop *et al.*<sup>4</sup> fitted their  $OH^-$  and  $OD^-$  threshold photodetachment spectra using the frame-transformation approach in the limit where the fine structure is small compared with the rotational spacing [Hund's case (b)]. Their analysis gave better values for the electron affinities than

could be obtained otherwise, but the limited resolution precluded a quantitative evaluation of the model. Janousek and Brauman<sup>3</sup> achieved a good fit of their  $SH^-$  threshold photodetachment spectra by assuming the cross section above threshold rose as  $(E - E_{thr})^{1/2}$  (i.e., the Wigner threshold law) and that the relative intensity of each rotational transition was given by the frame-transformation method. Their fit allowed an accurate determination of the electron affinity and an estimate of the temperature of the ions, but again a quantitative test of the model was not possible. Breyer *et al.*<sup>2</sup> obtained a good fit to their photoelectron spectra of  $OH^-$ ,  $SH^-$ , and  $SD^-$  by a procedure, where, instead of calculating the projection factors in the frame transformation, these factors (assumed independent of rotational quantum number) were varied to fit the data. Recently, individual rotational transitions have been observed<sup>1</sup> in  $OH^-$  threshold photodetachment. The relative intensities observed for the individual rotational transitions were in good agreement with those predicted using the frame-transformation method and were found to depend upon rotational quantum number. In order to unravel these differences, we derive an analytic form for the intensities of rotational transitions in photodetachment of a  $^1\Sigma$  molecule. While discussed in the context of photodetachment of  $OH^-$ , the results are equally valid for other negative ions and for photoionization.

The model describes the absorption of a photon by a  $^1\Sigma$  negative ion to produce an excited complex in a  $^1\Pi$  state. This complex subsequently dissociates into its  $j-j$ -coupled electron and neutral constituents. This model is a good description for an absorber described in the molecular-orbital picture as a  $\pi^4$  ground state which absorbs a photon to a  $\pi^3\sigma$  complex. The electron in the  $\sigma$  orbital can detach into any angular momentum wave, although near threshold the  $s$  wave will dominate.<sup>1,2</sup> The resulting fragment is in a  $^2\Pi$  state. The relative intensity for a negative ion with angular momentum  $J''$  photodetaching to produce a neutral  $^2\Pi_n$  molecule with angu-

lar momentum  $J'$  and an  $s$  electron can be written as a sum over intermediate states,

$$I(J', \Omega, J'') \sim \left| \sum_{J_i} \langle {}^2\Pi_{\Omega}, J'; ks, \frac{1}{2} | {}^1\Pi, J_i \rangle \langle {}^1\Pi, J_i | z | {}^1\Sigma, J'' \rangle \right|^2. \quad (1)$$

In this expression the sum over magnetic quantum numbers is implied, but not explicitly written. The first bra represents the state of the final OH +  $e^-$  system, where the OH is described as a Hund's case (a) molecule in a  ${}^2\Pi_{\Omega}$  state with total angular momentum  $J'$  and angular momentum projection on the internuclear axis  $\Omega$ . The electron leaves in an  $s$  wave with momentum  $k$  and angular momentum (spin) of  $J_e = S_e = \frac{1}{2}$ . The ket  $|{}^1\Pi, J_i\rangle$  describes the intermediate (virtual) state of the (OH +  $e^-$ ) complex with angular momentum  $J_i$ . The  $\langle z \rangle$  matrix element gives the amplitude for absorption from the initial  ${}^1\Sigma$  state of OH $^-$  to the intermediate state. We neglect absorption to  ${}^3\Pi$  intermediate states, as the spin-orbit interaction responsible for such absorption is weak for most light molecules. Note that Eq. (1) indicates the amplitudes are to be summed before being squared. The previous molecular treatments<sup>2,3,13</sup> have

$$I(J', J'', \alpha) \sim \left| \sum_{J_i = J' \pm 1/2} \sum_{\Omega = 1/2, 3/2} \langle u_{\alpha}, J' | {}^2\Pi_{\Omega}, J', ks, \frac{1}{2} \rangle \langle {}^2\Pi_{\Omega}, J', ks, \frac{1}{2} | {}^1\Pi, J_i \rangle \langle {}^1\Pi, J_i | r | {}^1\Sigma, J'' \rangle \right|^2, \quad (2)$$

where  $u_{\alpha}$  is the intermediate-case OH wave function, having an admixture of  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  character. The first term in Eq. (2) projects the true intermediate-case wave function for OH onto the Hund's case (a) basis set. The second term in Eq. (2) [given in Eqs. (4) and (5) of Ref. 13] projects the final  $j$ - $j$ -coupled  $e$ -OH system in a Hund's case (a) basis set onto the  $L$ - $S$ -coupled OH $^-$  intermediate complex. The frame transformation must project the angular momenta  $J_e = S_e$  and  $J'$  of the  $j$ - $j$ -coupled system onto  $J_i$  and  $S = 0$  of the  $L$ - $S$ -coupled complex. The third term is an electronic matrix element times the square root of the Hönl-London factor. Assuming the electronic matrix element does not vary with rotational quantum number the relative intensities of the rotational photodetachment transitions can be calculated.

To project the intermediate-case wave functions  $u_{\alpha}$  onto the Hund's case (a) basis set, we solve for the eigenfunctions

$$\hat{H}u_{\alpha} = E_{\alpha}u_{\alpha}, \quad \hat{H} = B(\vec{J}' - \vec{L}' - \vec{S}')^2 + A\vec{L}' \cdot \vec{S}', \quad (3)$$

where  $\hat{H}$  is the Hamiltonian for the  $e^-$  + OH system with the  $e^-$  far away from the OH such that even the long-range forces are negligible.  $B$  is the rotational constant,  $A$  is the spin-orbit coupling constant, and  $\vec{J}'$ ,  $\vec{L}'$ , and  $\vec{S}'$  are angular momenta of the XH molecule with their usual meaning.<sup>15</sup> This Hamiltonian can be found in many places and in several

summed the squares of the reduced matrix elements. Both methods are correct, as can be verified either by performing the sum over magnetic quantum numbers in Eq. (1) or by using the Wigner-Eckart theorem to show that summing over the magnetic quantum numbers causes the interference terms to cancel [see Eq. (22), Ref. 6]. This equality is a direct consequence of the orthonormality of the Clebsch-Gordan coefficients.

In many instances (including OH in its higher rotational levels) Hund's case (a) is a poor description of the  ${}^2\Pi$  fragment. To apply the model to cases intermediate between (a) and (b), the intermediate-case wave function is projected onto a case (a) basis set. The analysis then proceeds as it would for a true case (a) molecule. Inserting this intermediate-case transformation into Eq. (1) and summing over magnetic quantum numbers, we obtain

different forms (see the form on p. 306 of Ref. 15 versus that of Ref. 13). The intermediate-case wave function  $u_{\alpha}$  can be expressed as a linear combination of case (a) wave functions:

$$|u_{\alpha}, J'\rangle = c_1 |{}^2\Pi_{1/2}, J', ks, \frac{1}{2}\rangle + c_2 |{}^2\Pi_{3/2}, J', ks, \frac{1}{2}\rangle. \quad (4)$$

The coefficients  $c$  are the coefficients in the eigenvectors of the XH Hamiltonian,<sup>13</sup> given by<sup>16</sup>

$$c_{1a} = \left( \frac{X - 2 + \lambda}{2X} \right)^{1/2}, \quad c_{2a} = \mp \left( \frac{X + 2 - \lambda}{2X} \right)^{1/2}, \quad (5)$$

$$c_{1b} = \left( \frac{X + 2 - \lambda}{2X} \right)^{1/2}, \quad c_{2b} = \pm \left( \frac{X - 2 + \lambda}{2X} \right)^{1/2},$$

where

$$X = +[4(J' + \frac{1}{2})^2 + \lambda(\lambda - 4)]^{1/2}, \quad \lambda = A/B. \quad (6)$$

The upper signs of Eq. (5) refer to regular  ${}^2\Pi$  states (those with  $\lambda$  positive), while the lower signs apply for inverted  ${}^2\Pi$  states (those with  $\lambda$  negative, which is the case for group-VI hydrides). For negative values of  $\lambda$ , use of the coefficients subscripted with  $a$  gives a state of predominantly  ${}^2\Pi_{3/2}$  character, while the coefficients subscripted with  $b$  give states of  ${}^2\Pi_{1/2}$  character. These constants  $c$  are the values for the first bracket in Eq. (2).

The frame transformation embodied in the second term of Eq. (2) must project the angular momenta

$J_e = S_e$  and  $J'$  of the  $j$ - $j$ -coupled system onto  $J_i$  and  $S = 0$  of the  $L$ - $S$ -coupled complex. This transformation can be viewed as switching which two of three angular momenta are coupled together first. The three angular momenta are the spin of the outgoing electron ( $S_e = \frac{1}{2}$ ), the spin of the molecule ( $S' = \frac{1}{2}$ ), and the orbital plus rotational angular momentum of the molecule ( $N'$ ). Here,  $\vec{J}' = \vec{N}' + \vec{S}'$  and  $\vec{S}_i = \vec{S}_e + \vec{S}'$ . This frame transformation  $T_{J',S_i=0}$  is given by [see Eq. (108.5), Ref. 15]

$$|N', S_i = 0; J_i\rangle = \sum_{J'} T_{J', S_i=0} |S_e, J'; J_i\rangle, \quad (7)$$

and is evaluated to give [see Eq. (108.6), Ref. 15]

$$\begin{aligned} T_{J', S_i=0} &= -(2J' + 1)^{1/2} \begin{pmatrix} J_i & \frac{1}{2} & J' \\ \frac{1}{2} & J_i & 0 \end{pmatrix} \\ &= (-1)^{J' + J_i - 1/2} \left( \frac{2J' + 1}{2(2J_i + 1)} \right)^{1/2}. \end{aligned} \quad (8)$$

The orbital angular momentum of an  $s$ -wave electron is zero, so it is not considered here. Its inclusion is necessary for electrons with orbital angular momentum different from zero. This makes the calculation algebraically more tedious, though conceptually no more difficult.

To complete the calculation of the second term in Eq. (2), the angular momentum of the neutral molecule must be projected onto the internuclear axis to obtain the relative components of  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  character. These components are just the Clebsch-Gordan coefficients,  $\langle \frac{1}{2} J' 1 - \Omega | J_i 1 \rangle$ , for  $\Omega = \frac{1}{2}$  or  $\frac{3}{2}$ . The second term in Eq. (2) is thus

$$(-1)^{2J'} \left( \frac{2J' + 1}{2(2J_i + 1)} \right)^{1/2} \langle J' \frac{1}{2} \Omega 1 - \Omega | J_i 1 \rangle, \quad (9)$$

which is equivalent to the expressions given in Eq. (5) of Ref. 13. The numbers given in Table I of the work by Janousek and Brauman<sup>3</sup> are the squares of the product of the first two terms in Eq. (2) summed over values of  $\Omega$ , and so are given by the expression

$$\left( \frac{2J' + 1}{2(2J_i + 1)} \right) [c_1 \langle J' \frac{1}{2} \frac{1}{2} \frac{1}{2} | J_i 1 \rangle + c_2 \langle J' \frac{1}{2} \frac{3}{2} \frac{1}{2} | J_i 1 \rangle]^2. \quad (10)$$

Taking the Honl-London factors,<sup>2,13</sup> and using Eqs. (2), (5), and (10), the relative intensities of rotational photodetachment transitions can be calculated.

For  $J' = J'' - \frac{3}{2}$ ,

$$I \sim \frac{J'' - 1}{2(2J'' - 1)} [c_1 (J'')^{1/2} + c_2 (J'' - 2)^{1/2}]^2,$$

and for  $J' = J'' - \frac{1}{2}$ ,

$$\begin{aligned} I \sim \frac{J'' - 1}{2(2J'' - 1)} [-c_1 (J'' - 1)^{1/2} + c_2 (J'' + 1)^{1/2}]^2 \\ + \frac{1}{2} [c_1 (J'' + 1)^{1/2} + c_2 (J'' - 1)^{1/2}]^2. \end{aligned} \quad (11)$$

Similarly, for  $J' = J'' + \frac{1}{2}$ ,

$$\begin{aligned} I \sim \frac{1}{2} [-c_1 (J'')^{1/2} + c_2 (J'' + 2)^{1/2}]^2 \\ + \frac{J'' + 2}{2(2J'' + 3)} [c_1 (J'' + 2)^{1/2} + c_2 (J'')^{1/2}]^2, \end{aligned}$$

and for  $J' = J'' + \frac{3}{2}$ ,

$$I \sim \frac{J'' + 2}{2J'' + 3} [-c_1 (J'' + 1)^{1/2} + c_2 (J'' + 3)^{1/2}]^2.$$

In the cases where  $\lambda < 0$ , using the coefficients of Eq. (5) with subscript  $a$  gives intensities for the state with more  ${}^2\Pi_{3/2}$  character. The coefficients with  $b$  subscripts yield intensities for the  ${}^2\Pi_{1/2}$  states.

Breyer *et al.*<sup>2</sup> justifiably concluded the Walker model<sup>14</sup> was incorrect, since their results were dramatically different from Walker's theoretical spectrum.<sup>14</sup> No explicit equations for the intensities were given by Walker, so there was no way to directly

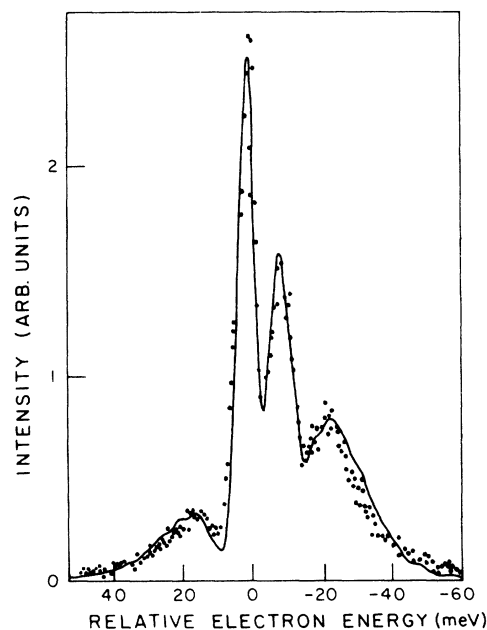


FIG. 1. The  $\text{OH}^-$  488-nm photoelectron spectrum of Breyer *et al.* (Ref. 2) (dots) compared with the results of the calculations described here. The resolution of the experiment, 5 meV, has been folded into the theoretical prediction. The rotational temperature of the negative ion used in the fit is 600 K. Two parameters for the energy offset and the intensity have been fitted using the model described in the text to give good agreement with the experiment.

compare theory with experiment. However, the results of Walker's theory as given by Eq. (11) have since been applied to experiment<sup>1,3</sup> with success. It appears the difference between the experimental spectrum of Breyer *et al.*<sup>2</sup> and the work of Walker<sup>14</sup> arises because of a numerical error in plotting Fig. 1 in Ref. 14. Therefore we have made another attempt to fit the OH<sup>-</sup> photoelectron spectrum using the known<sup>1</sup> rotational constants of OH<sup>-</sup> and OH and with only three free parameters—an intensity normalization, an energy offset (since the experiment did not measure the absolute electron energies), and the rotational temperature of the negative ions. The rotational temperature of the negative ions is needed for the fit in order to know the relative population in each of the states with angular momentum  $J''$ . This relative population must be multiplied by the photodetachment intensity given above to compare the theoretical with the experimental photoelectron spectrum. The results of this new calculation are compared with the data of Breyer *et al.*<sup>2</sup> in Fig. 1 and indicate that the frame-transformation method accurately predicts the relative intensities of rotational photodetachment transitions. Deviations from the theoretical spectrum may arise from the significant  $d$ -wave contribution to the photodetachment and from a non-Boltzmann distribution of OH<sup>-</sup> rotational

states. This treatment is valid for threshold photodetachment spectra as well as the photoelectron spectra<sup>2,3</sup> of OH<sup>-</sup> and SH<sup>-</sup>.

Extension of this method to other photodetachment transitions is straightforward, although it may necessitate using numerical methods to diagonalize the final-state Hamiltonian. If we wish to consider the OH<sup>-</sup> photodetachment allowing the electron to appear as a  $d$  wave, the treatment [specifically, Eq. (8)] would involve use of a  $9-j$  symbol, but is straightforward. Although the fundamental ideas presented here are not new, the results are presented in an analytic form not available previously, and they correct a misconception based upon an incorrect figure in the earlier work of Walker.<sup>14</sup>

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