

# Product angular distributions in dissociative recombination

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The dependence of the dissociative recombination cross section upon the angle between the incoming electron beam and the ion internuclear axis is determined for diatomic molecules. Product angular distributions are derived for the component partial waves of the Coulomb wave function. In agreement with earlier results for dissociative attachment, it is shown that in the slow rotation approximation, if electron capture is dominated by a single partial wave, the product angular distribution is given by the square of the absolute value of the partial wave spherical harmonic describing the incoming electron. © 2004 American Institute of Physics.

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## I. INTRODUCTION

A remarkable amount of progress has been reported recently<sup>1</sup> in both theoretical and experimental studies of dissociative recombination (DR) reactions,



where  $AB^+$  is a molecular ion and  $A$  and  $B$  are neutral fragments, i.e., atoms if the ion is a diatomic and atoms and/or molecules if the ion is a polyatomic. These studies have reported cross sections as a function of electron energy, rate coefficients as a function of electron temperature, and quantum yields. An aspect of DR that has received little attention is the dependence of the quantum yields, cross sections and rate coefficients upon the angle between the ion internuclear axis and the direction of the incoming electron. This angle does not appear in most DR analyses where the cross sections, rate coefficients, and quantum yields are averaged over all directions for the incoming electron. However, in the derivation of DR product quantum yields from storage ring data, knowledge of the angular product distribution is needed.<sup>2-8</sup> In these experiments, the ions circulating in the ring are merged in a straight section with a collinear electron beam guided by a magnetic field. The neutral DR products impinge upon a phosphor screen located several meters downstream from the capture position. The shape of the projected image on the phosphor screen is dependent upon the angle between the electron and the ion internuclear axis, the kinetic energy release of the neutral products, the distance from capture to the imaging screen, and the velocity of the ion beam. For more details, the reader is referred to the original papers.<sup>2-8</sup> The quantum yields are determined by fitting predicted model projections to the image shape displayed on the phosphor screen. Each model projection is for DR from a single ion vibrational level along a single route that generates atoms with a known kinetic energy release. In deriving these model projections, the appropriate angular distributions must be used or the model projections and the deduced quantum yields will be incorrect. The neutral particle distribution can be anisotropic and the assumption of an isotropic distribution can lead to the incorrect interpretation of experimental data.

An accurate fitting procedure can also lead to the experimental prediction of the symmetries of the dissociative states. For some molecules, the fitting can be difficult if DR involves many dissociation routes, often of different molecular symmetries, giving rise to a variety of angular distributions from a single ion vibrational level. Clearly, the determination of quantum yields requires both theoretical and experimental contributions.

Although there has been no prior work on the angular distribution of products in DR, pioneering theoretical work on the distribution has been reported for dissociative attachment<sup>9</sup> (DA) in which a neutral molecule captures an electron followed by dissociation to a neutral atom and a negatively charged atom. DA shares some features with DR and the derivation of angular distributions in this paper follows the important earlier work of O'Malley and Taylor.<sup>9</sup> Much of the work reported here also closely follows the pioneering scattering theory treatment of DR developed by Bardsley<sup>10</sup> and Giusti-Suzor, Bardsley, and Derkits.<sup>11</sup> Bardsley<sup>10</sup> derived an expression for the direct DR cross section and accounted for the nonlocal nature of the potential. (The nonlocal character of the potential was not treated in DA.<sup>9</sup>) Giusti-Suzor and co-workers<sup>11</sup> revised the Bardsley<sup>10</sup> procedure and included Rydberg states within the scattering theory framework. However, the product angular distributions were not addressed in either of these papers. An additional pioneering contribution is that of Dunn,<sup>12</sup> who reported selection rules, derived solely from symmetry considerations, for orientation of the internuclear axis at 0° and 90° relative to the electron beam. These rules were discussed in the context of electron impact excitation, capture, and dissociative ionization of neutrals. Angular distributions were not considered and the role of different electron partial wave symmetries was not described.

The direct DR cross section is approximately proportional to the square of the electronic capture width. Before deriving the angular dependence of the cross section, the angular dependence of the electronic width is derived in the next section. In Sec. III, the DR cross section angular distribution is derived. Section IV has the discussion and conclusions.

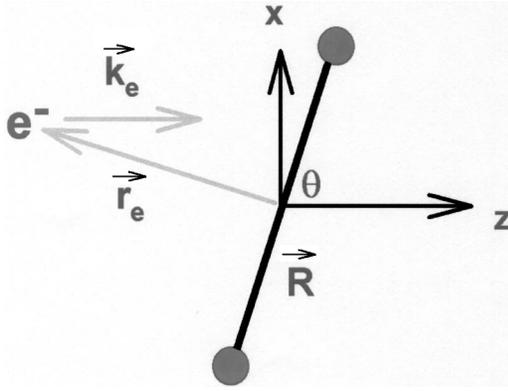


FIG. 1. Coordinates for electron ( $e^-$ ) capture by a diatomic ion. The internuclear axis,  $\vec{R}$ , is oriented at an angle  $\vartheta$  from the  $z$  axis and lies in the  $xz$  plane. The incoming electron at position  $\vec{r}_e$ , relative to the center of charge of the ion, has wave vector  $\vec{k}_e$  and is moving parallel to the  $z$  axis.

## II. ANGULAR DEPENDENCE OF THE ELECTRONIC WIDTH MATRIX ELEMENT

The nomenclature used here is similar to that used previously.<sup>9</sup> The angular distribution of the DR atomic products is a function of the polar coordinate angle  $\theta$  between the momentum vector  $\vec{k}_e$  of the incoming electron and the molecular axis  $\vec{R}$  (see Fig. 1).  $\vec{k}_e$  is taken to be parallel to the space fixed  $z$  axis and has  $\vec{R}$  as its polar axis.  $\vec{r}_e$  is the position vector of the incoming electron relative to the molecule fixed coordinate origin at the center of charge. The incoming Coulomb wave is taken to be cylindrically symmetrical about the  $z$  axis and is independent of the polar coordinate azimuthal angle,  $\varphi$ .

In the treatment used here, it is assumed that dissociation occurs much more rapidly than rotation. For most diatomics, dissociation proceeds in the time needed for a vibration, i.e., about  $10^{-14}$ – $10^{-15}$  s and for the low rotational levels, the rotational time is usually about  $10^{-12}$  s.

The electronic wave function of the reactants on the left side of Eq. (1) is an antisymmetrized product of a target ion wave function and a continuum Coulomb orbital,

$$\psi_{\nu E}(q, \vec{k}_e, R) = \{ \phi_{\text{ion}}(q^T, R) \phi_{\vec{k}_e}^-(\vec{r}_e) \}, \quad (2)$$

where  $q$  and  $q^T$  represent the coordinates of all the electrons and of the target electrons, respectively, in the body fixed frame.  $E$  is the total energy and  $\nu$  is the ion vibrational level.  $\nu$  is included as an index because  $E = k_e^2/2m + E_\nu$ . The braces  $\{ \}$  denote the antisymmetrization of the target and Coulomb electrons. The implicit  $R$  dependence of the electronic target wave function is denoted by including  $R$  in the parentheses. The coulomb wave can be expanded in partial waves,<sup>13</sup>

$$\phi_{\vec{k}_e}^-(\vec{r}_e) = \sum_{\ell=0}^{\infty} (2\ell+1) i^\ell e^{i\sigma_\ell} \frac{1}{k_e r_e} F_\ell(k_e r_e) P_\ell(\hat{r}_e \cdot \hat{k}_e), \quad (3)$$

where  $\sigma_\ell$  is the Coulomb partial wave phase shift,  $F_\ell$  is a confluent hypergeometric function, and  $P_\ell$  is a Legendre

polynomial. The Legendre polynomial in Eq. (3) is expressed in terms of spherical harmonics,  $Y_{\ell m}$ , by using the addition theorem:<sup>14</sup>

$$P_\ell(\hat{r}_e \cdot \hat{k}_e) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{r}_e) Y_{\ell m}^*(\hat{k}_e), \quad (4)$$

where  $m$  is the projection of the electron angular momentum  $\ell$  onto the internuclear axis. Substituting Eq. (4) into Eq. (3) leads to

$$\begin{aligned} \phi_{\vec{k}_e}^-(\vec{r}_e) &= 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell e^{i\sigma_\ell} \frac{1}{k_e r_e} \\ &\times F_\ell(k_e r_e) Y_{\ell m}(\hat{r}_e) Y_{\ell m}^*(\hat{k}_e). \end{aligned} \quad (5)$$

The coupling that drives DR is a matrix element of the electronic Hamiltonian,  $H(q, R)$ , between the dissociative state,  $\psi_d$ , and  $\psi_{\nu E}$ ,

$$V_{\text{el}}(\vec{k}_e, R) = \langle \psi_d(q, R) | H(q, R) | \psi_{\nu E}(q, \vec{k}_e, R) \rangle, \quad (6)$$

where the integration is over  $q$ .  $V_{\text{el}}(\vec{k}_e, R)$  is related to the electronic capture width  $\Gamma$  by  $\Gamma(R) = \frac{1}{2} \int V_{\text{el}}^2(\vec{k}_e, R) d\Omega$ . From Eqs. (2), (5), and (6) we have

$$\begin{aligned} V_{\text{el}}(\vec{k}_e, R) &= 4\pi \left\langle \psi_d(q, R) \left| H(q, R) \right| \left\{ \phi_{\text{ion}}(q^T, R) \right. \right. \\ &\times \left. \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell e^{i\sigma_\ell} \frac{1}{k_e r_e} F_\ell(k_e r_e) Y_{\ell m}(\hat{r}_e) \right\} \left. \right\rangle \\ &\times Y_{\ell m}^*(\hat{k}_e), \end{aligned} \quad (7)$$

where both  $Y_{\ell m}(\hat{r}_e)$  and  $Y_{\ell m}^*(\hat{k}_e)$  have  $\vec{R}$  as the polar axis. The integration is over the electron coordinates in the molecular frame so that Eq. (7) can be rewritten as

$$V_{\text{el}}(\vec{k}_e, R) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V_{\ell m}(k_e, R) Y_{\ell m}^*(\hat{k}_e). \quad (8)$$

The angular dependence of  $V_{\text{el}}(\vec{k}_e, R)$  is expressed by the spherical harmonic on the right side of Eq. (8). A spherical harmonic with  $\vec{R}$  as the polar axis and with coordinates  $\vartheta_R$  and  $\phi_R$ ,  $Y_{\ell m}^*(\hat{k}_e)$ , is equivalent to a spherical harmonic with  $\hat{k}_e$  or  $z$  as the polar axis and with coordinates  $\vartheta_{k_e}$  and  $\phi_{k_e}$ ,  $Y_{\ell m}^*(\hat{R})$ . O'Malley and Taylor have pointed out that in this case,  $\vartheta_R = \vartheta_{k_e}$  and  $\phi_R = -\phi_{k_e}$ . Therefore, we have

$$\begin{aligned} Y_{\ell m}^*(\hat{k}_e) &= Y_{\ell m}^*(\vartheta_R, \phi_R) \\ &= Y_{\ell m}^*(\vartheta_{k_e}, -\phi_{k_e}) = Y_{\ell m}(\vartheta_{k_e}, \phi_{k_e}) = Y_{\ell m}(\hat{R}). \end{aligned} \quad (9)$$

Equation (8) can now be replaced with

$$V_{\text{el}}(k_e, \vec{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V_{\ell m}(k_e, R) Y_{\ell m}(\hat{R}). \quad (10)$$

In Eq. (10), the angular dependence of the dissociating products is given by  $Y_{\ell m}^*(\hat{R})$  with polar angles  $\vartheta_{k_e}$  and  $\phi_{k_e}$  of the

internuclear axis relative to the polar axis  $z$  or  $\hat{k}_e$ . In addition, the value of  $m$  is restricted by  $\Lambda_d = \Lambda_i + m$  where  $\Lambda_i$  and  $\Lambda_d$  are the ion and dissociative state angular momentum projections on  $\vec{R}$ , respectively. Each of these projections can be positive or negative depending upon the direction of precession of the angular momentum vectors about  $\vec{R}$ . The value of  $m$  is fixed once the values of  $\Lambda_d$  and  $\Lambda_i$  are specified. Since  $V_{\ell m}$  and  $V_{\ell - m}$  are identical (as long as the appropriate signed values of  $\Lambda_d$  and  $\Lambda_i$  are used in each case) we have

$$V_{\text{el}}^m(k_e, \vec{R}) = \sum_{\ell=|m|}^{\infty} V_{\ell|m|}(k_e, R) Y_{\ell m}(\hat{R}), \quad (11)$$

which is equivalent to the expression found by O'Malley and Taylor for electron attachment. (Note that a factor of 2 is now included in  $V_{\ell|m|}$  to account for both  $m = \ell$  and  $m = -\ell$ .) For some diatomics, the summation in Eq. (11) is given by a single term because of the small value of  $V_{\ell|m|}$  for  $\ell > |m|$ . For this case, the angular distribution is given by

$$\begin{aligned} V_{\text{el}}^{\ell, m}(k_e, \vec{R}) &= V_{\ell|m|}(k_e, R) Y_{\ell m}(\hat{R}) \\ &= V_{|m||m|}(k_e, R) Y_{|m|m}(\hat{R}). \end{aligned} \quad (12)$$

### III. ANGULAR DEPENDENCE OF THE DR CROSS SECTION

The reader is referred to the earlier papers<sup>10,11</sup> for the details of the derivation of the angle-independent cross-section expression. Here, a slightly revised final cross-section expression is used in order to show the product angular distributions. The total wave function is<sup>11</sup>

$$\begin{aligned} \Psi(q, \vec{k}_e, R) &= \sum_{\nu} \int dE' b_{\nu}(E') \psi_{\nu E'}(q, \vec{k}_e, R) \chi_{\nu}(R) \\ &+ \psi_d(q, R) s_d(R) + \sum_{p, \nu} a_{p\nu} \psi_p(q, R) \chi_{\nu}(R), \end{aligned} \quad (13)$$

where the index  $p$  is for an electronic Rydberg state and  $a_{p\nu}$  is the coefficient of the  $\nu$  vibrational level in Rydberg state  $p$ .  $s_d$  is the dissociative nuclear wave function and the  $\chi_{\nu}(R)$  are the bound ion or Rydberg state vibrational levels. The final cross-section expression derived in Ref. 11 accounts for only a single Rydberg vibrational level but can be easily generalized to multiple Rydberg levels:

$$\begin{aligned} \sigma_{\text{DR}}(\varepsilon, \hat{R}) &= \frac{\pi^2}{\varepsilon} \frac{\omega}{2} \frac{\hbar K}{M} \left| \frac{1}{C} \left( -V_{\nu_i}(E, \hat{R}) \right. \right. \\ &+ i\pi \sum_{\nu} d_{\nu} V_{\nu}(E, \hat{R}) - \sum_{p\nu} V_{\nu}(E, \hat{R}) \rho_p a_{p\nu} \\ &\left. \left. + i\pi \sum_{p\nu} \sum_{\nu'} V_{\nu'}(E, \hat{R}) \rho_p a_{p\nu} W_{\nu\nu'} \right) \right|^2, \end{aligned} \quad (14)$$

where  $\varepsilon$  is the electron energy,  $\omega$  is the statistical weight of the dissociative state divided by that for the ion,  $K$  is the relative momentum of the dissociating atoms,  $M$  is the total

reduced mass,  $C$  is a Wronskian (see Ref. 11), and  $\rho_{n^*} = (n^*)^{-1.5}$  where  $n^*$  is the effective principal quantum number. The vibronic coupling between the ion level and the Rydberg levels is given by<sup>15</sup>  $W_{\nu\nu'} = (\nu'/2M\omega_e)^{1/2} d\mu/dR$ , where  $\nu' = \nu + 1$ ,  $\omega_e$  is the vibrational frequency of the ion and  $\mu$  is the quantum defect of the Rydberg series, i.e.,  $\mu = n - n^*$ .  $d_{\nu}$  is given by

$$d_{\nu} = \langle \chi(R) | V_{\ell|m|}(k_e, R) | s_d(R) \rangle. \quad (15)$$

In Eq. (14),  $V_{\nu_i}$  and  $V_{\nu}$  are given by

$$V_{\nu_i}(E, \hat{R}) = \int \chi_{\nu_i} V_{\text{el}}^{\ell, m}(k_e, \vec{R}) F_{1E}(R) dR, \quad (16)$$

$$V_{\nu}(E, \hat{R}) = \int \chi_{\nu} V_{\text{el}}^{\ell, m}(k_e, \vec{R}) F_{1E}(R) dR,$$

where  $\chi_{\nu_i}$  is the initial ion vibrational level and  $\chi_{\nu}$  is ion vibrational level  $\nu$ .  $F_{1E}(R)$  is a solution of the homogeneous equation:

$$\left( -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + E_d(R) - E \right) F_{1E}(R) = 0. \quad (17)$$

If only a single partial wave is dominant for the incoming electron, Eq. (12) can be used to rewrite Eqs. (16) as

$$V_{\nu_i}(E, \hat{R}) = Y_{\ell m}(\hat{R}) \int \chi_{\nu_i} V_{\ell|m|}(k_e, R) F_{1E}(R) dR, \quad (18)$$

$$V_{\nu}(E, \hat{R}) = Y_{\ell m}(\hat{R}) \int \chi_{\nu} V_{\ell|m|}(k_e, R) F_{1E}(R) dR.$$

With Eqs. (18), Eq. (14) becomes

$$\begin{aligned} \sigma_{\text{DR}}(\varepsilon, \hat{R}) &= \frac{\pi^2}{\varepsilon} \frac{\omega}{2} \frac{\hbar K}{M} |Y_{\ell m}^*(\hat{R})|^2 \left| \frac{1}{C} \left( -V_{\nu_i}(E) \right. \right. \\ &+ i\pi \sum_{\nu} d_{\nu} V_{\nu}(E) - \sum_{p\nu} V_{\nu}(E) \rho_p a_{p\nu} \\ &\left. \left. + i\pi \sum_{p\nu} \sum_{\nu'} V_{\nu'}(E) \rho_p a_{p\nu} W_{\nu\nu'} \right) \right|^2, \end{aligned} \quad (19)$$

where

$$V_{\nu_i}(E) = \int \chi_{\nu_i} V_{\ell|m|}(k_e, R) F_{1E}(R) dR,$$

$$V_{\nu}(E) = \int \chi_{\nu} V_{\ell|m|}(k_e, R) F_{1E}(R) dR.$$

For a single dominant electron partial wave, the angular dependence of the DR cross section reduces to  $|Y_{\ell m}^*(\hat{R})|^2$ . The angular dependence of the dissociation products, in this case, is the same as that for dissociative attachment. The dissociation products have the same angular dependence as the dominant partial wave of the incoming electron. Table I lists the Legendre polynomials for the electron partial waves up to  $\ell = 3$ . Tables II–III have all possible product distributions for molecular symmetries formed by capture of an electron partial wave (up to  $\ell = 3$ ) by a diatomic ion in the  $\Sigma_g^+$ ,  $\Sigma_u^+$ ,  $\Pi_g$ ,  $\Pi_u$ ,  $\Sigma^+$ , and  $\Pi$  states.

TABLE I. Angular distributions for the DR of diatomic ions. The distributions in column 4 are from the spherical harmonics of the waves in column 1. The distributions are normalized so that  $\int_0^{2\pi} d\varphi \int_0^\pi f_0^2(\text{distribution}) \sin \vartheta d\vartheta = 1$ . For heteronuclear molecules, simply drop the  $g$  and  $u$  subscripts in column 1.

Electron partial wave	$\ell$	$m$	Product angular distribution
$s\sigma_g$	0	0	1 (isotropic)
$p\sigma_u$	1	0	$3 \cos^2 \vartheta$
$p\pi_u$	1	1	$\frac{3}{2} \sin^2 \vartheta$
$d\sigma_g$	2	0	$\frac{5}{4}(3 \cos^2 \vartheta - 1)^2$
$d\pi_g$	2	1	$\frac{15}{2} \sin^2 \vartheta \cos^2 \vartheta$
$d\delta g$	2	2	$\frac{15}{8} \sin^4 \vartheta$
$f\sigma_u$	3	0	$\frac{7}{4}(5 \cos^3 \vartheta - 3 \cos \vartheta)^2$
$f\pi_u$	3	1	$\frac{21}{16} \sin^2 \vartheta (5 \cos^2 \vartheta - 1)^2$
$f\delta u$	3	2	$\frac{105}{8} \sin^4 \vartheta \cos^2 \vartheta$
$f\varphi u$	3	3	$\frac{35}{16} \sin^6 \vartheta$

#### IV. DISCUSSION AND CONCLUSIONS

It is instructive to examine the expected angular distributions for a specific molecular ion.  $O_2^+$  has been the subject of many DR experiments over the years because of its importance in planetary atmospheres. From the low vibrational levels of the  $X^2\Pi_g$  ground state of  $O_2^+$ , six diabatic states provide routes for DR:<sup>16,17</sup>  $^3\Pi_u$  ( $^3P+^3P, 6.96$  eV),  $^1\Pi_u$  ( $^3P+^3P, 6.96$  eV),  $A^3\Sigma_u^+$  ( $^3P+^3P, 6.96$  eV),  $B^3\Sigma_u^-$  ( $^3P+^1D, 4.99$  eV),  $f^1\Sigma_u^+$  ( $^1S+^1D, 0.80$  eV), and  $^1\Delta_u$  ( $^1D+^1D, 3.02$  eV). The states of the product atoms and the total kinetic energy released upon dissociation (for capture of a zero energy electron by  $v=0$ ) are shown in paren-

TABLE II. Final neutral states formed by the capture of an electron by a homonuclear ion.

Electron partial wave	Ion state			
	$\Sigma_g^+$	$\Sigma_u^+$	$\Pi_g$	$\Pi_u$
	Neutral dissociative state			
$s\sigma_g$	$\Sigma_g^+$	$\Sigma_u^+$	$\Pi_g$	$\Pi_u$
$p\sigma_u$	$\Sigma_u^+$	$\Sigma_g^+$	$\Pi_u$	$\Pi_g$
$p\pi_u$	$\Pi_u$	$\Pi_g$	$\left\{ \begin{array}{l} \Sigma_u^+ \\ \Sigma_u^- \\ \Delta_u \end{array} \right.$	$\left\{ \begin{array}{l} \Sigma_g^+ \\ \Sigma_g^- \\ \Delta_g \end{array} \right.$
$d\sigma_g$	$\Sigma_g^+$	$\Sigma_u^+$	$\Pi_g$	$\Pi_u$
$d\pi_g$	$\Pi_g$	$\Pi_u$	$\left\{ \begin{array}{l} \Sigma_g^+ \\ \Sigma_g^- \\ \Delta_g \end{array} \right.$	$\left\{ \begin{array}{l} \Sigma_u^+ \\ \Sigma_u^- \\ \Delta_u \end{array} \right.$
$d\delta g$	$\Delta_g$	$\Delta_u$	$\left\{ \begin{array}{l} \Pi_g \\ \Phi_g \end{array} \right.$	$\left\{ \begin{array}{l} \Pi_u \\ \Phi_u \end{array} \right.$
$f\sigma_u$	$\Sigma_u^+$	$\Sigma_g^+$	$\Pi_u$	$\Pi_g$
$f\pi_u$	$\Pi_u$	$\Pi_g$	$\left\{ \begin{array}{l} \Sigma_u^+ \\ \Sigma_u^- \\ \Delta_u \end{array} \right.$	$\left\{ \begin{array}{l} \Sigma_g^+ \\ \Sigma_g^- \\ \Delta_g \end{array} \right.$
$f\delta u$	$\Delta_u$	$\Delta_g$	$\left\{ \begin{array}{l} \Pi_u \\ \Phi_u \end{array} \right.$	$\left\{ \begin{array}{l} \Pi_g \\ \Phi_g \end{array} \right.$
$f\varphi u$	$\Phi_u$	$\Phi_g$	$\left\{ \begin{array}{l} \Pi_u \\ \Phi_u \end{array} \right.$	$\left\{ \begin{array}{l} \Pi_g \\ \Phi_g \end{array} \right.$

TABLE III. Final neutral states formed by the capture of an electron by a heteronuclear ion.

Electron partial wave	Ion state	
	$\Sigma^+$	$\Pi$
	Neutral dissociative state	
$s\sigma$	$\Sigma^+$	$\Pi$
$p\sigma$	$\Sigma^+$	$\Pi$
$p\pi$	$\Pi$	$\Sigma^+ \Sigma^- \Delta$
$d\sigma$	$\Sigma^+$	$\Pi$
$d\pi$	$\Pi$	$\Sigma^+ \Sigma^- \Delta$
$d\delta$	$\Delta$	$\Pi \Phi$
$f\sigma$	$\Sigma^+$	$\Pi$
$f\pi$	$\Pi$	$\Sigma^+ \Sigma^- \Delta$
$f\delta$	$\Delta$	$\Pi \Phi$
$f\varphi$	$\Phi$	$\Delta \Gamma$

theses. Note that there are four values of the kinetic energy release. In order to form the  $\Pi_u$  states, symmetry considerations require that the free electron must be captured into a  $3\sigma_u$  orbital. The  $\sigma_u$  free-electron orbital has  $\ell=1$  and  $m=0$  and the ground-state atoms will have a  $\cos^2 \theta$  distribution (Table I). However, the remaining four states are all formed by attachment of a  $\pi_u$  free electron, i.e.,  $\ell=1$  and  $m=1$ , and have a  $\sin^2 \theta$  product distribution. The contribution of  $A^3\Sigma_u^+$  to  $v=0$  DR at low electron energies is small compared to that due to the  $\Pi_u$  states. The four peaks due to each kinetic energy release are easily distinguishable in the experimental projected distributions (see Fig. 5 of Ref. 2) although there is some overlap between the 6.96 and 4.99 eV peaks. The results reported here predict that the atoms contributing to the 6.96 eV peak will have mostly a  $\cos^2 \theta$  angular distribution but atoms giving rise to each of the other peaks will have mostly a  $\sin^2 \theta$  angular distribution.

Note that these predictions assume that the product angular distribution is determined by the symmetry of the initial capture state and that there are no interactions between dissociative states that could change the distribution. However, one well-known interaction is between  $f^1\Sigma_u^+$  and  $B^3\Sigma_u^-$ .<sup>17</sup> Indeed, most of the dissociative flux along  $f^1\Sigma_u^+$ , for DR of  $v=0$ , arises from initial capture into  $B^3\Sigma_u^-$ . The flux transfer is due to spin-orbit coupling between the Rydberg states of these symmetries.<sup>17</sup> The coupling affects the kinetic energy release and the projected distribution but has no effect upon the angular distributions since both  $B^3\Sigma_u^-$  and  $f^1\Sigma_u^+$  have the same angular distributions.

A detailed comparison of these predictions to the experimental results requires the calculation of projected distributions from the theoretical angular distributions. An analysis of the experimental results for both  $O_2^+$  and other ions will be the subject of a separate paper.<sup>18</sup>

The angular distributions reported here for DR are the same as those reported earlier<sup>9</sup> for DA. The nonlocal potential, which is important for DR but not included in the prior treatment of DA, does not affect the product distributions. The results reported here are also consistent with the predictions of Dunn for dissociation at zero and  $90^\circ$  from the direction of the electron beam.

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<sup>1</sup>See, e.g., *Dissociative Recombination of Molecular Ions with Electrons*, edited by S. L. Guberman (Kluwer/Plenum Academic, New York, 2003).

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