Angular distribution of the fragments produced from collisionally dissociated HeH$^+$ ion using Slater type orbitals

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The angular distribution of the fragments produced from the electron impact dissociation of HeH$^+$ molecular ion has been studied in the energy range from 30 ev to 1000 ev by applying the Born approximation. For this purpose the electronic excitation $X^1\Sigma \rightarrow A^1\Sigma$ coupled with rotational-vibrational transition has been considered. The electronic wave functions have been constructed from Slater type orbitals using two configurations for the $A^1\Sigma$ state and a single configuration for the $X^1\Sigma$ state of HeH$^+$ ion. It is found that there is no significant effect on the angular distribution of fragments due to the heteronuclearity of the molecular ion.

1. Introduction

The collision induced dissociation of HeH$^+$ ion has been the subject of several recent experiments (Stearns *et al* 1971, Schopman *et al* 1971). The most interesting feature of these studies is the observed asymmetry in the intensities of the dissociation fragments in the forward and backward directions for zero-angle scattering (Schopman *et al* 1971). Such asymmetry has also been observed in the case of the heteronuclear HD$^+$ ion (Dong & Durup 1970). Attempts have been made to interpret the asymmetry by including the electron-dipole interaction term in the Hamiltonian for HD$^+$+e system (Barua *et al* 1971, Saha *et al* 1972). It has further been suggested that the asymmetry may be due to the effect of electric field of the ion source on the dipole moment of the heteronuclear molecular ion.

Important details of the processes involved in the collision induced dissociation of molecular ions can be obtained by a detailed study of the angular distribution of the dissociation fragments. Such studies have been extensively done for H$_2$$^+$ ion both experimentally and theoretically. For HeH$^+$ ion experimental studies of the angular distribution of the dissociation fragments by collision with inert gas atoms have been performed (Schopman *et al* 1971). Theoretically, however, an attempt has been made to study in detail the angular distribution

of the dissociation fragments. Here, another approach has been made to study the angular distribution of the fragments produced from the electron impact dissociation of HeH⁺ ion by the $X^1\Sigma \rightarrow A^1\Sigma$ transition. The calculations have been performed by using the Born approximation and Slater type orbitals to construct the molecular orbitals.

2. FORMULATION AND RESULTS

In the collision of an electron with HeH⁺ molecular ion, the electronic and nuclear coordinates are specified as follows. The nuclei He and H of HeH⁺ are denoted by a and b respectively, the internuclear distance by R, the coordinates of bound electrons 1 and 2 by r_1 and r_2 and the coordinate of the impinging electron 3 by r_3 (figure 1). k_i and k_f are the wave vectors of the incoming and outgoing electron respectively. Then $k_i^2 = k_f^2 + 2\mu\Delta E$, where ΔE is the energy required to raise the molecular ion at the equilibrium internuclear separation of the ground $X^1\Sigma$ state to the first excited $A^1\Sigma$ state and μ is the reduced mass of the system.
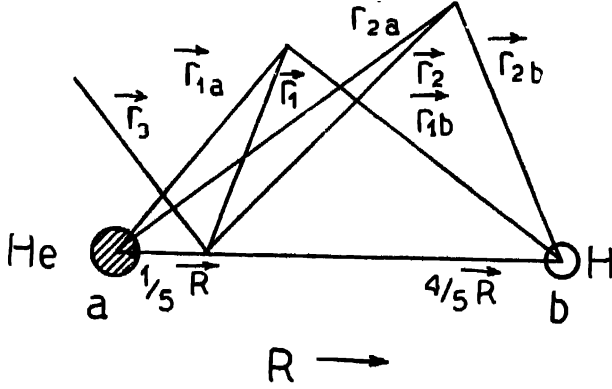

Fig. 1. Coordinate system describing the collision of an electron with HeH⁺ ion. O is the centre of mass of the ion and R is the internuclear distance.

The wave function for the $X^1\Sigma$ state has been chosen as

$$\Psi_0(r_1,\ r_2;\ R) = \phi_a^{1s}(1)\phi_b^{1s}(2) + \phi_a^{1s}(2)\phi_b^{1s}(1), \tag{1}$$

and that for the $A^1\Sigma$ state as

$$\Psi_s(r_1,\ r_2;\ R) = c_1\psi_1(r_1,\ r_2;\ R) + c_2\psi_2(r_1,\ r_2;\ R)$$

$$= \left(\frac{c_1}{\sqrt{2}}\right)[\phi_a^{1s}(1)\phi_b^{1s}(2) + \phi_a^{1s}(2)\phi_b^{1s}(1)]$$

$$+ \left(\frac{c_2}{\sqrt{2}}\right)[\phi_a^{1s}(1)\phi_b^{2s}(2) + \phi_a^{1s}(2)\phi_b^{2s}(1)]. \tag{2}$$

In eqs. (1) and (2) ϕ's are Slater type atomic orbitals and c's are the coefficients for the different configurations. The Slater type orbitals used may be written as

$$\phi_i{}^{1s}(r) = \left(\frac{z_i}{\pi}\right)^{\frac{1}{2}} \exp{(-z_i r)} \qquad \ldots \text{ (3a)}$$

$$\phi_i{}^{2s}(r) = \left(\frac{z_i{}^{b}}{96\pi}\right)^{\frac{1}{2}} r \exp{(-z_i r/2)}, \qquad \ldots \text{ (3b)}$$

z_i is the nuclear charge for ith nucleus. c_1 and c_2 can be obtained by normalizing $\psi_s(r_1, r_2; R)$ to unity and making Ψ_s and Ψ_0 orthogonal to each other.

Since we are interested in calculating only the direct scattering amplitude by using Born approximation, the electron-dipole interaction term and electron-nuclei interaction terms in the interaction potential

$$V(r_1, r_2, r_3, R) =$$

$$-\frac{2}{|r_3 + 1/5R|} - \frac{1}{|r_3 - 4/5R|} + \frac{1}{|r_3 - r_2|} + \frac{1}{|r_3 - r_1|} - \frac{DP_1(\hat{r_3}.\hat{R})}{r_3{}^2}$$

$$\ldots \text{ (4)}$$

will not contribute. The scattering amplitude for $X^1\Sigma \rightarrow A^1\Sigma$ transition under these conditions may be written as

$$f_s(K, \Theta, \Phi) = -\frac{2}{K^2} \int \int \int \{\exp{(iK.r_1)} + \exp{(iK.r_2)}\}$$

$$\times \Psi_s{}^*(r_1, r_2; R)\Psi_0(r_1, r_2; R)\chi_s{}^*(R)\chi_0(R)dr_1\,dr_3\,dR$$

$$= -\frac{2}{K^2}(f_{s1} + f_{s2}), \qquad \ldots \text{ (5)}.$$

where

$$f_{s1} = \int \int \int \exp{(iK.r_1)}\Psi_s{}^*(r_1, r_2; R)\psi_0(r_1, r_2; R)$$

$$\chi_s{}^*(R)\chi_0(R)dr_1\,dr_2\,dR$$

$$= \int [c_1(R_1 + R_2 + R_3) + c_2(R_4 + R_5 + R_6 + R_7)]$$

$$\times \chi_s{}^*(R)\chi_0(R)dR, \qquad \ldots \text{ (6)}$$

where the R's are given below. A similar expression for f_{s2} can be obtained by replacing r_1 by r_2.

In eqs. (5) and (6) $K = k_i - k_f$, the momentum transfer vector is taken along the z-axis of the system, $\chi_0(R)$ and $\chi_s(R)$ are the nuclear wavefunctions for the initial rotation-vibration state $(v = 0, J = 0)$ and continuum respectively.

The nuclear wavefunctions used are similar to those for H$_2^+$ ion used by Zare (1967) which are given as

$$\chi_0(\boldsymbol{R}) = F_{vJ}{}^0(\boldsymbol{R})Y_{JM}(\theta,\phi) \qquad \qquad \dots \;(7)$$

and

$$\chi_s(\boldsymbol{R}) = \sum_{J'} (2J'+1)(-i)^{J'}\exp(i\delta_{J'})F^s{}_{J'}\,P_{J'}(\hat{\kappa}.\hat{R}), \qquad \dots \;(8)$$

where $F_{vJ}{}^0(R)$ and $F^s{}_{J'}(R)$ are the radial wave-functions; the latter has the form of a sine-wave with phase-shift $\delta_{J'}$ at large separations. The propagation vector $\boldsymbol{k}$ is along the asymptote of the recoiling atoms and $\boldsymbol{R}$ is the position vector which also coincides with the molecular axis. The polar angles for $\hat{\kappa}$ and $\hat{R}$ are (θ,ϕ) and (Θ,Φ) respectively and $P_{J'}(\hat{\kappa},\hat{R})$ can be written as

$$P_{J'}(\hat{\kappa}.\hat{R}) = \frac{4\pi}{2J'+1}\sum_{M'=-J'}^{J'} Y^*_{J'M'}(\theta,\phi)Y_{J'M'}(\Theta,\Phi),$$

and hence

$$\chi_s{}^*(\boldsymbol{R}) = 4\pi \sum_{J'}\sum_{M'=-J'} \exp(i\delta_{J'})F^s{}_{J'}(R)Y_{J'M'}(\theta,\phi)Y_{J'M'}(\Theta,\Phi). \qquad (9)$$

Putting

$$\boldsymbol{r}_1 = \boldsymbol{r}_{1a}-\tfrac{1}{5}\boldsymbol{R}$$
$$= \boldsymbol{r}_{1b}+\tfrac{4}{5}\boldsymbol{R}, \qquad (10)$$

the R_i's in eq. (6) are given as

$$R_1 = \frac{16z_a{}^4}{(4z_a{}^2+K^2)^2}\exp(-i\boldsymbol{K}.\tfrac{1}{5}\boldsymbol{R})$$
$$= L_1\sum(2n+1)(-i)^n j_n(\tfrac{1}{5}KR)P_n(\cos \qquad (11)$$

$$R_2 = \frac{16}{(4+K^2)^2}\exp(i\boldsymbol{K}.\tfrac{4}{5}\boldsymbol{R})$$
$$= L_2\sum_n(2n+1)i^n j_n(\tfrac{4}{5}KR)P_n(\cos\Theta), \qquad (12)$$

$$R_3 = \frac{2z_a{}^3}{\pi^2}\exp(-i\boldsymbol{K}.\tfrac{1}{5}\boldsymbol{R})I_3 I_4$$
$$= \sum_n\sum_l L_3(l)(2n+1)(-i)^n j_n(\tfrac{1}{5}KR)P_n(\cos\Theta)P_l(\cos\Theta), \qquad (13)$$

where

$$I_3 = \frac{4\pi^{3/2}}{\sqrt{2K}}\sum_{l=0}^{\infty}i^l(2l+1)P_l(\cos\Theta)[\{\int_0^R J_{l+\frac{1}{2}}(Kr_{1a})\exp(-z_a r_{1a})$$
$$\times r_{1a}f_{l_1}(R,r_{1a},z_b)dr_{1a}+\int_R^\infty J_{l+\frac{1}{2}}(Kr_{1a})\exp(-z_a r_{1a})$$
$$\times r_{1a}f_{l_2}(R,r_{1a},z_b)dr_{1a}\}], \qquad (14a)$$

and

$$I_4 = 4\pi \int_0^\infty \exp(-z_a r_{2a}) f_0(z_b, r_{2a}, R) r_{2a}^2 dr_{2a}, \qquad \ldots (14b)$$

$$R_4 = \frac{512}{27\sqrt{6}} \frac{z_a^4}{(4z_a^2 + K^2)^2} \exp(-iK \cdot \tfrac{1}{5} R)$$

$$= L_4 \sum_n (2n+1)(-i)^n j_n(\tfrac{1}{5} KR) P_n(\cos \Theta), \qquad \ldots (15)$$

$$R_5 = \frac{2 \sin\left[3 \tan^{-1}\left(\frac{2K}{3}\right)\right]}{K\sqrt{6} \, (\tfrac{9}{4} + K^2)^{3/2}} \exp(iK \cdot \tfrac{4}{5} R)$$

$$= L_5 \sum_n (2n+1) i^n j_n(\tfrac{4}{5} KR) P_n(\cos \Theta), \qquad \ldots (16)$$

$$R_6 = \frac{z_a^3}{\pi^2 \sqrt{96}} \exp(iK \cdot \tfrac{4}{5} R) \, I_6 I_4$$

$$= \sum_n \sum_l L_6(l)(2n+1) i^n j_n(\tfrac{4}{5} KR) P_n(\cos \Theta) P_l(\cos \Theta), \qquad \ldots (17)$$

where

$$I_6 = -\frac{4\pi^{3/2}}{\sqrt{2K}} \sum_{l=0}^\infty i^l (2l+1) P_l(\cos \Theta) \Big\{ \int_0^R J_{l+\frac{1}{2}}(Kr_{1b})$$

$$\times \exp(-z_b r_{1b}/2) r_{1b}^2 f_{l2}(R, r_{1b}, z_a) dr_{1b}$$

$$+ \int_R^\infty J_{l+\frac{1}{2}}(Kr_{1b}) \exp(-z_b r_{1b}/2) r_{1b}^2 f_{l2}(R, r_{1b}, z_a) dr_{1b} \Big\} \qquad \ldots (18)$$

$$R_7 = \frac{z_a^3}{\pi^2 \sqrt{96}} \exp(-iK \cdot \tfrac{1}{5} R) I_3 I_5$$

$$= \sum_n \sum_l L_7(l)(2n+1)(-i)^n j_n(\tfrac{1}{5} KR) P_n(\cos \Theta) P_l(\cos \Theta), \qquad \ldots (19)$$

and

$$I_8 = 4\pi \int_0^\infty \exp(-z_a r_{2a}) f_0(z_b/2, r_{2b}, R) r_{2b} dr_{2b}. \qquad \ldots (20)$$

In the above expressions (11) to (20)

$$L_1 = \frac{16 z_u^4}{(4z_a^2 + K^2)^2}, \qquad \ldots (21a)$$

$$L_2 = \frac{16}{(4 + K^2)^2}, \qquad \ldots (21b)$$

$$L_3(l)P_l(\cos\Theta) = \frac{2z_a{}^3}{\pi^2} I_3 I_4, \qquad \qquad \dots (21c)$$

$$L_4 = \frac{512}{27\sqrt{6}} \frac{z_a{}^4}{(4z_a{}^2 + K^2)^2}, \qquad \qquad \dots (21d)$$

$$L_5 = \frac{2\sin\left[3\tan^{-1}\left(\frac{2K}{3}\right)\right]}{K\sqrt{6}(9/4 + K^2)^{3/2}}, \qquad \qquad \dots (21e)$$

$$L_6(l)P_l(\cos\Theta) = \frac{z_a{}^3}{\pi^2\sqrt{96}} I_6 I_4, \qquad \qquad \dots (21f)$$

$$L_7(l)P_l(\cos\Theta) = \frac{z_a{}^3}{\pi^2\sqrt{96}} I_3 I_5, \qquad \qquad \dots (21g)$$

$$f_{l1}(R, r_{1a}, z_b) = -\frac{1}{\sqrt{Rr_{1a}}} \left[-\frac{R}{2} I_{l+\frac{1}{2}}(z_b r_{1a})\{K_{l-\frac{1}{2}}(z_b R) + K_{l+3/2}(z_b R)\} \right.$$

$$\left. +\frac{r_{1a}}{2} K_{l+\frac{1}{2}}(z_b R)\{I_{l-\frac{1}{2}}(z_b r_{1a}) + I_{l+\frac{1}{2}}(z_b r_{1a})\} \right], \qquad \text{for } R > r_{1a}$$

$$f_{l2}(R, r_{1a}, z_b) = -\frac{1}{\sqrt{Rr_{1a}}} \left[\frac{R}{2} K_{l+\frac{1}{2}}(z_b r_{1a})\{I_{l+3/2}(z_b R) + I_{l-\frac{1}{2}}(z_b R)\} \right.$$

$$\left. -\frac{r_{1a}}{2} I_{l+\frac{1}{2}}(z_b R)\{K_{l-\frac{1}{2}}(z_b r_{1a}) + K_{l+3/2}(z_b r_{1a})\} \right], \qquad \text{for } R < r_{1a}.$$

$$\dots (22)$$

Similarly, the expressions for $f_0(R, r_{2a}, z_b)$ can be obtained by putting $l = 0$ in eq. (22).

To avoid elaborate calculations, the upper state radial wavefunction has been replaced by a normalized δ-function, $N\delta(R - R_0)$ where R_0 is the internuclear equilibrium distance for the ground state of the HeH⁺ ion. The axial-recoil approximation has been assumed which results in considerable simplifications in the calculations.

For the numerical evaluation of f_{s1} the following n and l values have been used

$$n = 0, 1 \quad \text{and} \quad l = 0, 1.$$

Sample calculations have shown that the contributions of the higher order terms to f_{s1} are small and may therefore be neglected. For a certain combination of n and l values, only certain particular values of J' will contribute in the summation over J', the final rotational quantum number.

Therefore, f_{s_1} can be written as

$$f_{s_1}(K, \Theta, \Phi) = \sum_{n=0}^{1} \sum_{l=0}^{1} f_{nl}, \qquad \ldots (23)$$

where

$$
\begin{aligned}
f_{nl} = &\{(2n+1)i^n \exp(-iC)F^{\circ}{}_{vJ}(R_0)R_0{}^2 Y_{JM}(\Theta, \Phi)Y_{n0}(\Theta, \Phi)\} \\
&[(L_2+L_5)j_n(\tfrac{4}{5}KR_0)+(-1)^n(L_1+L_4)j_n(\tfrac{1}{5}KR_0) \\
&+(2l+1)i^l Y_{l0}(\Theta, \Phi)\{L_6(l)j_n(4/5KR_0)+(-1)^n[L_7(l)+L_3(l)] \\
&j_n(\tfrac{1}{5}KR_0)\}].
\end{aligned} \qquad \ldots (24)
$$

Assuming the axial recoil approximtion to be valid, the factor $(-i)^{J'} \exp(i\delta_{J'})$ equals $\exp(-iC)$ where C is a constant to order $[(J'+\tfrac{1}{2})/\kappa r]^2$ and the sum over J' and M' can be readily performed.

Since $f_{s_1} = f_{s_2}$ numerically, we can put $f_s = 2f_{s_1}$.

The Born differential scattering cross section may be written as,

$$I_s(K, \Theta, \Phi) = \frac{k_f}{k_i} \sum_M |f_s(K, \Theta, \Phi)|^2, \qquad \ldots (25)$$

where (Θ, Φ) are the polar angles for $\mathbf{R}$ which is the direction of fragmentation according to the axial recoil approximation (figure 2). Eq. (25) depends on the magnitude of the momentum transfer vector, which is given by,

$$K^2 = k_i{}^2 + k_f{}^2 - 2k_i k_f \cos \omega, \qquad \ldots (27)$$

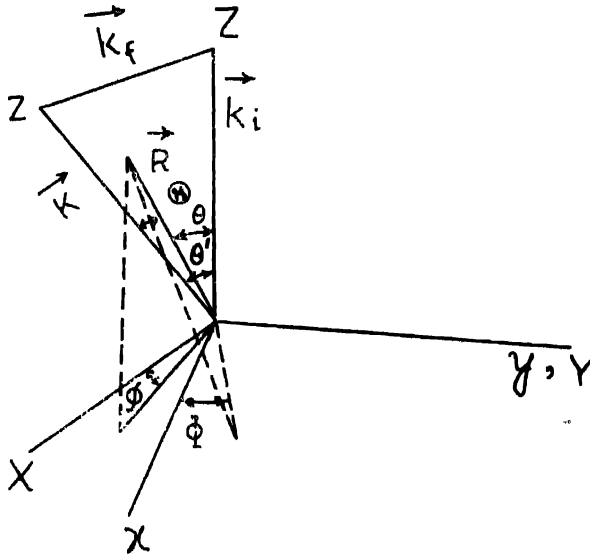ω being the angle between k_i and k_f.

Fig. 2.   Coordinate system showing the relation between scattering angles in the *momentum transfer* and *electron beam* frames. Dissociation fragments ejected along $\mathbf{R}$ are described by the polar angles (Θ, Φ) and (θ, ϕ) in the two respective frames.

. In order to make the differential cross-section for ejected fragments independent of the angle of the scattered electrons, the cross-section $I_s(K, \Theta, \Phi)$ should be integrated over $\sin \omega \, d\omega \, d\phi_0$. Thus one can obtain

$$I_s(\Theta, \Phi) = \frac{2\pi}{k_i^2} \int_{K_{min}}^{K_{max}} \Sigma \mid f_s(K, \Theta, \Phi) \mid^2 K dK \qquad (27)$$

where $K_{min} = k_i - k_f$; $K_{max} = k_i + k_f.$

Using eqs. (23) to (27) one can obtain

$$\underset{M}{\Sigma} \mid f_{s1}(K, \Theta, \Phi) \mid^2 \approx m + q \cos^2 \Theta + p \cos^4 \Theta. \qquad (28)$$

The values of the coefficients in eq. (28) can be easily obtained from the preceding relations. So far, the angular distribution of fragments has been calculated in *momentum transfer* frame i.e., where the momentum transfer vector K is along Z-axis. In order to compare these results with experiments one must transfer the cross section to the *electron beam* frame, where the electron beam direction
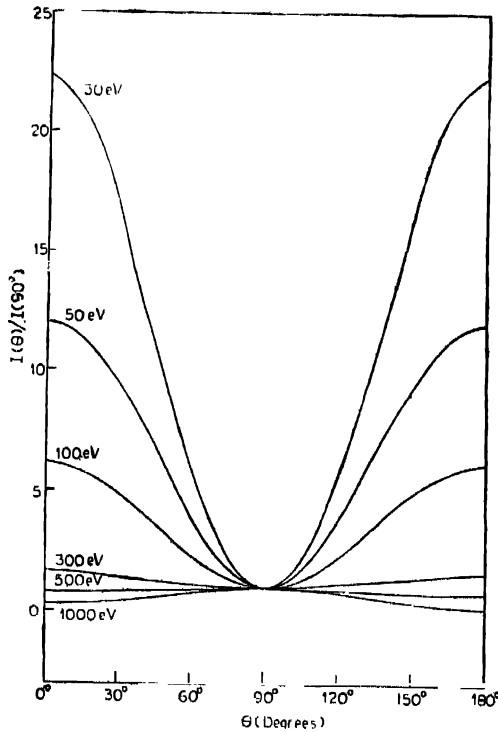

Fig. 3. Angular distribution of dissociation fragments of HeH+ ion ($X^1\Sigma \rightarrow A^1\Sigma$ transiton) for different electron bombardment energies.

k_i is taken along z-axis as shown in figure 2. This transformation can be done by substituting

$$\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \phi,$$

and

$$\Phi = \sin^{-1}(\sin \theta \sin \phi / \sin \Theta), \qquad \qquad \ldots \ (29)$$

where (Θ, Φ) and (θ, ϕ) are the polar angles of R in the two different frames and (θ', ϕ') are the polar angles for k_i with respect to K. In this case $\phi' = 0$, since the Y-axis for the two frames have been made to coincide. Averaging over the angle ϕ, the differential scattering cross section for the fragments in the k_i-frame is given by,

$$I(\theta) = \frac{1}{2\pi} \int_0^{2\pi} I(\theta, \phi) \mathrm{d}\phi.$$

Therefore, the angular distribution of the fragments is symmetrical in the forward and backward directions and the angle-dependent part is superimposed on an angle-independent term.

3. Discussion of Results

The nature of $I(\theta)/I(90°)$ curves for the angular distribution of the fragments produced from $X^1\Sigma \to A^1\Sigma$ transition of HeH$^+$ ion is similar to the curves for the homonuclear H$_2{}^+$ dissociation. In the lower energy range the ratio is expected to increase considerably when exchange is taken into account. This has been shown by Saha et al (1972) for the dissociation of HD$^+$ ion. The differential cross-section for fragments of the heteronuclear ion is obtained as a sum of an angle-independent term with a combination of cosine square term and the square of a cosine square term.

The experiments performed for the dissociation of HeH$^+$ ion by electronic excitation indicate that both $X^1\Sigma \to A^1\Sigma$ and $X^1\Sigma \to a^3\Sigma$ transitions are energetically possible (Schopman et al 1971). The latter transition although optically forbidden is possible when excitation takes place by collision with another particle. However, from the available data it is not possible to ascertain experimentally the relative importance of the two transitions mentioned above. It is not possible to obtain scattering amplitude for $X^1\Sigma \to a^3\Sigma$ transition using Born approximation. Therefore, exchange scattering should be considered for the singlet-triplet transition.

For the ground $X^1\Sigma$ state of HeH$^+$ ion no ionic term has been included in the wavefunction although this state is known to be strongly ionic (Michels 1966). The ionic term will affect the magnitude of the differential cross-section of the fragments and the results reported by us as ratios are not likely to be affected significantly by this approximation. It can also be shown that if a purely ionic

wave function is chosen for ground state, the resulting differential cross section has the similar angle dependence as that for the non-ionic wave function.

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