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DISSOCIATION OF $H_2^+$ BY ELECTRON IMPACT:
CALCULATED ANGULAR DISTRIBUTION

by

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The angular distribution of products in the electron impact dissociation of $\text{H}_2^+$ has been calculated following closely the Born approximation treatment of E. H. Kerner [Phys. Rev. 92, 1441 (1953)]. For "axial recoil" in which the fragments are ejected with considerable kinetic energy along the molecular axis, the leading term in the differential cross section shows a cosine-squared anisotropy peaked about the momentum transfer vector, independent of the initial rotational state of the molecule. This is in contrast to the findings of Kerner. The inclusion of higher order terms produces interference effects in the differential cross section, although the forward-backward scattering symmetry is preserved. Relevant electronic matrix elements have been evaluated by J. M. Peek [Phys. Rev. 134, A877 (1964)]. With increasing momentum transfer the angular distribution distorts from a cosine-squared dependence to one more nearly isotropic.
INTRODUCTION

Calculation of the differential cross section in dissociative electron impact appears quite formidable for the general case and most attention in the past has been confined to the dissociation of $\text{H}_2^+$. For this molecule there have been several Born approximation calculations$^{1,2,3,4}$ of the total cross section, but only the treatment due to Kerner$^1$ considers the excitation to specific rotational and vibrational states while treating the $1\sigma_g^+ - 2\pi_u^-$ electronic transition of $\text{H}_2^+$ from the $2^3\Pi_g$ ground state to the repulsive $2^3\Pi_u$ state. He finds that the angular distribution will be dominated by the term $P_{J+1,M}^M(\cos \Theta)$ where $\Theta$ is the polar angle measured from the momentum transfer vector $K$ to the recoiling fragments, and $J$ is the rotational quantum number for the ground state. Thus it is concluded that if the molecule is initially in the rotational ground state ($J = 0$) the angular distribution will have mainly a $\cos^2 \Theta$ dependence whereas for the $J = 1$ rotational state a spherically symmetric contribution will be important.

Recently Dunn and Kieffer$^5$ have studied the angular distribution of fast protons in the dissociative ionization of $\text{H}_2$ by electron impact. Near threshold, where dissociative ionization is expected to resemble dissociative excitation,$^5,6$ they find a nearly $\cos^2 \Theta$ anisotropy. Under their experimental conditions $\text{H}_2$ is predominantly in the $J = 1$ rotational state, and the observed angular distribution is in apparent disagreement with the calculations of Kerner.

In the closely related problem of molecular photodissociation Zare and Herschbach,$^7$ using a semi-classical procedure, found that for a $\sum - \sum$ transition the molecule has a preferred orientation for dissociation given by $\cos^2 \Theta$, where $\Theta$ is now measured from the polarization vector $\vec{E}$. If the molecule
dissociates in a time short compared to the rotational period with recoil energy considerably in excess of the molecular rotational energy, as is usually the case, the direction of departure of the atoms is along the molecular axis (the case of axial recoil) and the angular distribution of products will show a corresponding anisotropy. Moreover, the effect of the rotational motion of the recoiling fragments was explicitly taken into account and it was shown that the conservation of angular momentum forces normally only a slight blurring in the distribution.

A fully quantum mechanical description of the photodissociation mechanics has been completed which gives the quantum correspondence for small J of these semi-classical arguments. It is the purpose of this note to demonstrate that it follows from an analysis based on Kerner's work that the leading term in the angular distribution varies as \( \cos^2 \Theta \), independent of the rotational state J of the molecule, for the case of nearly axial recoil.

**THEORY AND DISCUSSION**

According to the first Born approximation, the scattering amplitude for exciting the \( \text{H}_2^+ \) molecule from an initial state characterized by quantum numbers \( \nu J M \) to a final state \( \nu' J' M' \) in which the momentum of the incident electron is changed from \( \hbar k \) to \( \hbar k' \) is given by

\[
\begin{align*}
\Psi
f(\nu J M \rightarrow \nu' J'M') &= -\frac{i}{4\pi} \frac{2me}{\hbar} \\
\int \frac{d^3 \rho}{|\mathbf{R} - \mathbf{q}|} \Psi_{\nu J M}^* \Psi_{\nu' J'M'} d^3 \mathbf{R} d^3 \mathbf{q} d^3 \mathbf{\rho}
\end{align*}
\]

Here \( e \) and \( m \) are the charge and mass of the electron; \( \mathbf{K} = \mathbf{k} - \mathbf{k}' \) is the momentum transfer vector; and \( \mathbf{R}, \mathbf{q}, \mathbf{\rho} \) denote respectively the coordinates of
the incident electron, the bound electron and the molecular axis, the origin chosen at the midpoint of the molecule.

The bound state wavefunction may be written to good approximation in the form

$$\psi_{nvJM} = \psi_e^{n}(q, \rho) \ R_v^n(\rho) \ Y_{JM}(\theta, \phi)$$ (2)

where the electronic wavefunction $$\psi_e^{n}(q, \rho)$$ is seen to depend parametrically on the internuclear separation $$\rho$$, the vibrational wavefunction $$R_v^n(\rho)$$ describes the radial motion of the nuclei and the rotational wavefunction $$Y_{JM}(\theta, \phi)$$ is a spherical harmonic giving the orientation of the molecular axis with respect to the axis of quantization chosen along $$K$$. Eq. (2) corresponds to a stationary state of the molecule with definite values of the energy, angular momentum and projection thereof.

The continuum wavefunction $$\psi^*_{n'v'J'M'}$$ satisfies the boundary conditions for scattering, namely, that it has the asymptotic form of an outgoing plane wave plus outgoing spherical waves:

$$\psi^*_{n'v'J'M'}(\rho \rightarrow \infty) \rightarrow A[e^{-i\kappa \cdot \rho} + f(\beta)\frac{e^{ik\rho}}{\kappa \rho}]$$ (3)

where $$\kappa$$ is the propagation vector and $$\rho$$ the position vector. For dissociative excitation $$\kappa$$ points along the final recoil direction of the atoms and $$\rho$$ coincides with the molecular axis, as shown in Fig. 1. Then the continuum wavefunction may be put in a form similar to (2)

$$\psi^*_{n'v'J'M'} = \psi_e^{n'}(q, \rho) \sum_{J'}(2J' + 1)(-1)^{J'}e^{i\delta_{J'}J'}R_v^n(\rho) P_{J'}(\kappa \cdot \beta)$$ (4)
where the normalized vibrational wavefunction has the form at large separation of a sine wave

\[
\sin(\kappa \rho - J' \pi/2 + \delta_{J'})
\]  

(5)

with phase shift \( \delta_{J'} \), and the angles are measured between the unit vectors \( \hat{z} \) and \( \hat{\rho} \) and are not the same angles as those in Eq. (2). The continuum wavefunction given by (4) corresponds to a stationary state of the molecule with a definite value of the energy \( E = h^2 \kappa^2 / 2 \mu \), but not a definite state of angular momentum.

We take for the binding and anti-binding electronic wavefunctions the well-known linear combination of atomic orbitals

\[
\psi_e^n(q, \rho) = U(\rho)[u(q_1) + u(q_2)] 
\]  

(6-a)

\[
\psi_e^{n'}(q, \rho) = U'(\rho)[u(q_1) - u(q_2)] 
\]  

(6-b)

with \( u(q) = \pi^{-1/2} e^{-q} \); \( q_1 \) and \( q_2 \) radial distances measured from the protons as centers; \( U(\rho) \) and \( U'(\rho) \) normalization constants. Upon substituting (6) into (1) the integration over \( R \) and \( q \) are performed in a straightforward manner with the result

\[
f_{(nvJM + n'v'J'M')} \sim \int \sin(\frac{1}{2} K \cdot \rho) Y_{J'M'}(\theta, \phi) \sum_{J} (2J' + 1)(-1)^J \ e^{i \delta_{J'} \rho} \ e^{i \delta_{J'} \rho} 
\]

\[
[U(\rho) U'(\rho) \sum R_{\nu J}^n(\rho) R_{\nu, J'}^{n'}(\rho)] d\rho \sin \theta \ d\theta d\phi 
\]  

(7)

where all extraneous constants have been omitted.
Eq. (7) admits of considerable simplification. Using the addition theorem for spherical harmonics we may rewrite \( P_{j'}(\xi, \Theta) \) as

\[
P_{j'}(\xi, \Theta) = \frac{4\pi}{2j' + 1} \sum_{m' = -j'}^{j'} Y_{j'm'}^* (\Theta, \Phi) \ Y_{j'm'} (\Theta, \Phi)
\]

(8)

where the angles \((\Theta, \Phi)\) give the orientation of the molecular axis with respect to \(K\) and \((\Theta, \Phi)\) locate with respect to \(K\) the direction of the recoiling atoms at large separation (Fig. 1). With the help of the expansion of a plane wave in terms of Legendre polynomials we find that

\[
\sin\left(\frac{1}{2} K \cdot \rho\right) = \frac{1}{2 j} \sum_{\ell = 0}^{\infty} (2\ell + 1) i^\ell \left[j_\ell \left(\frac{1}{2} K \rho\right) - (-1)^\ell j_\ell \left(\frac{1}{2} K \rho\right)\right] P_\ell (\cos \Theta)
\]

(9)

where the \(j_\ell \left(\frac{1}{2} K \rho\right)\) are spherical Bessel functions. The first non-vanishing term in (9) is for \(\ell = 1\), the next for \(\ell = 3\). It is apparent that \(\ell = 1\) is the leading term in (9) and strongly dominates for small angle scattering \((K \rightarrow 0)\) where \(j_\ell \left(\frac{1}{2} K \rho\right)\) may be replaced by \([\ell!/(2\ell + 1)!] (K \rho)^\ell\).

Upon replacing in Eq. (7) \(P_{j'}(\xi, \Theta)\) by Eq. (8) and \(\sin\left(\frac{1}{2} K \cdot \rho\right)\) by the leading term in Eq. (9), we note that the Born scattering amplitude may be decomposed into two parts:

\[
f(nvJM \rightarrow n'v'J'M') \sim \sum_{j'm'} \left\{ \int U(\rho) U'(\rho) (-i)^j J^i e^{\frac{i\delta}{\varepsilon} j^i j_1 (\frac{1}{2} K \rho)} R^n_{v'J'} (\rho) j_1 (\frac{1}{2} K \rho) R^n_{vJ} (\rho) d\rho \right\}

\[
\left[ \int Y^*_{j'm'} (\Theta, \Phi) Y_{10} (\Theta, \Phi) Y_{JM} (\Theta, \Phi) \sin \Theta d\Theta d\Phi \right] Y_{j'm'} (\Theta, \Phi)
\]

(10)
a radial term which governs primarily the band strength of the transition; and an angular term which is the rotational line strength factor for a specific JM → J'M' transition. The value of the first term in brackets depends on the magnitude of the phase shift \( \delta_{J'} \), which may be different for each J' appearing in the sum (J' = J ± 1). For nearly axial recoil, however, the scattering is almost classical and the phase shift \( \delta_{J'} \) may be estimated semi-classically to high accuracy. In the Appendix we show that

\[
\delta_{J'} = J' \pi / 2 - C
\]

(11)

where C is a constant to order \(( (J + 1/2) / \kappa r )^2 \). Then

\[
(-i)^{J'} e^{i \delta_{J'}} = e^{-iC}
\]

(12)

is nearly independent of J' and the radial term is roughly a constant over the rotational structure and may be taken outside the sum over J' and M' occurring in (10). With this approximation, which is exact for purely axial recoil, we see that the second term in (10) solely controls the form of the angular distribution.

Integration over the triple product of spherical harmonics in (10) yields\(^{11}\)

\[
\left( \frac{3}{4\pi} \right)^2 \sum_{J', M'} \left[ \frac{2J + 1}{2J' + 1} \right]^2 C(J1J'; M0) C(J1J'; 00) Y_{J'M'}(\Theta, \Phi)
\]

(13)

where the C's are Clebsch-Gordan coefficients. The sum over J' and M' is readily performed by reference to the Clebsch-Gordan series\(^{11}\) and one finds that the
Born scattering amplitude is proportional to the product of two spherical harmonics:

\[ f(n\nu J M \rightarrow n'\nu' J' M') \sim Y_M(\Theta, \Phi) \ Y_{10}(\Theta, \Phi) \]  

(14)

The differential cross section is then obtained by squaring Eq. (14) and summing over all the indistinguishable \( M \) sublevels of the initial state:

\[ I(\Theta, \Phi) d\Omega = \sum_M |Y_M(\Theta, \Phi)|^2 |Y_{10}(\Theta, \Phi)|^2 \]  

(15)

By closure the differential cross section reduces to

\[ I(\Theta, \Phi) = |Y_{10}(\Theta, \Phi)|^2 = \cos^2 \Theta, \]  

(16)

which is independent of \( J \).

By the same arguments as above we may discuss the effect of including higher order terms of the plane wave expansion in (10). For the general case the result is

\[ I(\Theta, \Phi) = \left| \sum_{l=0}^{\infty} \alpha_{2l+1} P_{2l+1}(\cos \Theta) \right|^2 \]  

(17)

where the coefficients \( \alpha_{2l+1} \) depend on the detailed evaluation of the radial integrals occurring in (10). Eq. (17) is derived using approximate electronic wavefunctions (6) for the \( H_2^+ \) molecule. If the exact electronic wavefunctions are employed instead,\(^3,4\) it can be shown that the differential cross section has the same form as (17) but the constants \( \alpha_{2l+1} \) involve different radial integrals.
From Eq. (15) it is apparent that the differential cross section $I(\phi)$ for axial recoil possesses cylindrical symmetry about $K$, being independent of $\phi$; possesses forward and backward symmetry about a plane through the scattering center at right angles to $K$, since the cross section is an even function of $\phi$; and vanishes at $\phi = \pi/2$. The inclusion of higher order terms in (17) corresponds to the scattering of higher order partial waves. Although the $\cos^2 \phi$ term is the largest term in (17), these higher order terms produce interference. For $H^+$ the electronic and radial integrals may be evaluated numerically and the results of Peek (see Fig. 2 of his paper) indicate that the differential cross section changes from a cosine-squared dependence on $\phi$ at small values of $K$ to an eccentric-shaped distribution, the maximum in the distribution moving away from the poles ($\phi = 0, \pi$) towards the equator ($\phi = \pi/2$) with increasing momentum transfer change.

These conclusions are for nearly axial recoil of the dissociation fragments. When this approximation ($r >> J + \frac{1}{2}$) is no longer applicable, such as close to the threshold for dissociation or for the dissociation of very high rotational levels, one must evaluate the terms in (10) separately. This task appears quite formidable although certainly tractable. For large $J$, however, one finds from semi-classical considerations that the effect of this rotational momentum is to suppress the sharp features of the angular distribution at first, and in the extreme case where the fragments are ejected at right angles to the initial direction of the molecular axis to reverse the form of the anisotropy. It is also to be noted that for dissociative electron impact the angular distribution has been calculated with respect to the momentum transfer vector $K$. In general $K$ will have a range of orientations with respect to $k$, the direction of the electron beam. Close to threshold $k$ and $K$ will almost coincide whereas at high energy $k$ and $K$ are
nearly at right angles to each other.

So far no observations have been made of quantum mechanical interference effects in molecular dissociation. Indeed there appears to be presently no experimental information on the angular distribution of products in dissociative excitation. Undoubtedly this lack can be attributed in part to the difficulty of detecting and identifying slow neutral particles. The dissociation of molecular ions, however, does not suffer from this drawback and may hold promise for future work.

**APPENDIX**

If the phase shift $\delta_J$ for scattering is expressed in increasing powers of Planck's constant, the first term in the series is $^{13}$

$$\delta_J = (J + \frac{1}{2}) \pi/2 - \hbar^{-1} \left\{ \frac{1}{(2\mu E)^{2}} r_0 \right. \left. + \int_{r_0}^{\infty} \left\{ [2\mu (E - U(r)) - (J + \frac{1}{2})^2 / r^2]^2 - (2\mu E)^2 \right\} dr \right\}$$

(A-1)

where $E$ is the energy of the scattered particle, $U(r)$ is the potential and $r_0$ is the value of $r$ for which $E = U(r_0) + (J + \frac{1}{2})^2 / r_0^2$ (the classical turning point). The next term of this expansion enters with the power $\hbar^{-3}$ and expressions for all higher order members are given elsewhere. $^{14}$

We wish to show for large recoil energies that $\delta_J - J\pi/2$ is nearly independent of $J$. Let us define the momentum variables $\hbar^2 k^2 = 2\mu [E - U(r)]$ and $\hbar^2 k^2 = 2\mu E$. Then (A-1) may be put in the form

$$\delta_J = (J + \frac{1}{2}) \pi/2 - kr_0 + \int_{r_0}^{\infty} \left\{ k[1 - (J + \frac{1}{2})^2 / r^2 k^2]^2 - k \right\} dr$$

(A-2)
from which it is apparent that

$$-kr_0 + \int_{r_0}^{\infty} \kappa \left[ 1 - \frac{(J + \frac{1}{2})^2}{r^2} \right]^{\frac{1}{2}} - \kappa \right] \ dr \tag{A-3}$$

is independent of J to terms of order \((J + \frac{1}{2})^2/r\kappa\)^2. This proves the assertion.

Alternatively\(^{15}\) we may differentiate Eq. (A-1) with respect to J (bearing in mind that \(r_0\) depends on J). We find that

$$\frac{\partial \delta J}{\partial J} = \frac{\pi}{2} - \int_{r_0}^{\infty} \frac{J + \frac{1}{2}}{r^2 \left( \kappa - \frac{(J + \frac{1}{2})^2}{r^2} \right)^2} \ dr \tag{A-4}$$

where the right hand side of (A-4) is recognized as one-half the classical deflection angle, \(\theta/2 = \pi/2 - \chi\). Calculations for \(\chi\) have been performed previously for the photodissociation of NaI. It was shown that \(\chi\) was close to zero and insensitive to variations in J for nearly axial recoil.\(^7\)

It might be questioned whether the phase shift given by (A-1) is valid for very small J. Most derivations of the semi-classical phase shift in the past have used the approximation that \(J(J + 1)\) may be replaced by \((J + \frac{1}{2})^2\) for large J. However, it has been demonstrated that this additional assumption is not required to derive (A-1) and that the factor \((J + \frac{1}{2})\) arises naturally if the appropriate boundary conditions are imposed.\(^{14}\) Furthermore the quantum mechanical phase shifts calculated by R.B. Bernstein\(^{16}\) for a Lennard-Jones potential at high energy but small angular momentum show the behavior described above \(|\delta_{J+1} - \delta_J| = \pi/2\) to \(\leq 1\) radians or better) for a wide range of conditions and suggest the general validity of these results for nearly axial recoil.
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REFERENCES

8. For \( \text{H}_2^+ \) the kinetic energy of the fragments varies widely from about 10 eV for dissociation of the ground vibrational level to less than 0.1 eV for dissociation of the highest vibrational level. The \( \text{H}_2^+ \) molecule is typical in that the minimum in its bound state potential curve lies under a strongly sloping portion of the repulsive state potential curve.
12. Drs. J.M. Peek and T.A. Green inform us that detailed calculations of the angular distribution have been under way for some time.
15. Reference 12 develops a power series expansion in $\tilde{H}$ for the difference in phase shifts $\delta_{j+1} - \delta_j$. It is shown that this is equal to $\pi/2 - x + \frac{1}{4} \frac{3x}{\partial x}^j$ to first order in $\tilde{H}$.

Fig. 1. The recoiling atom (whose classical trajectory is indicated by the dotted line) is scattered by the repulsive molecular potential. The quantization axis $\kappa$ is along the $Z$ axis; the propagation vector $\kappa$ is along the asymptote of the recoiling atom; and the position vector $\rho$ coincides with the molecular axis. For molecular dissociation the recoiling fragments generally have considerable kinetic energy so that $\kappa$ and $\rho$ nearly coincide throughout.