PHOTOFRAGMENT ANGULAR DISTRIBUTIONS FROM ORIENTED SYMMETRIC-TOP PRECURSOR MOLECULES

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The fragment angular distribution is calculated for photodissociation by a beam of plane-polarized radiation of an ensemble of oriented symmetric-top molecules selected in a specific $|JKM\rangle$ state. For prompt dissociation the resulting expression, proportional to $(e/4\pi) P_{JKM}(\cos \theta) [1 + \beta \hat{P}_x(\cos \theta)]$, where $P_{JKM}(\cos \theta)$ is the probability of finding the symmetric-top precursor molecule with its figure axis in a given orientation, agrees with that given previously by Choi and Bernstein (J. Chem. Phys. 85 (1986) 150).

1. Introduction

A large body of indirect evidence points to the strong dependence of chemical reactions upon the approach geometry of the reagents. Increasingly, direct evidence is becoming available through scattering experiments employing oriented molecular beams [1-3]. In particular, Bernstein and coworkers [4-11] have made notable progress using a hexapole electrostatic field followed by an orienting (homogeneous) electric field to produce intense pulsed beams of symmetric-top molecules in essentially a pure $|JKM\rangle$ eigenstate.

For a proper analysis of the subsequent gas-gas or gas-surface collision experiments, it is necessary to know the orientational distribution function of these molecules. In particular, when nonzero nuclear spins are present, hyperfine recoupling of the randomly oriented nuclear spins with the oriented molecular framework leads to a partial loss [12-14] of the spatial orientation of these symmetric tops as the $|JKM\rangle$-selected molecules pass from the strong-field regime of the hexapole lens assembly to the weak-field regime of the orienting electric field. These effects are further complicated by how rapid is this passage, which is readily described in the sudden or adiabatic limits (see ref. [12]). Recently, Gandhi, Curtiss, and Bernstein [6] demonstrated that the degree of orientation of symmetric-top molecules in their beam could be experimentally determined by polarized laser-induced photodissociation. In their procedure [6], the mass-selected photofragmentation signals $S^+$ and $S^-$ are recorded in the $+z$ ("up") and $-z$ ("down") hemispheres when the electric vector of the photolysis beam points along the orienting electric field direction. The $S^+/S^-$ "up-down" asymmetry ratio indicates the degree of orientation of the molecules in the beam prior to photodissociation. As a reference and as a calibration, $S^+/S^-$ is also recorded when the electric vector of the photolysis beam points perpendicular to $z$. Under these conditions, the up-down asymmetry ratio ideally should be unity.

This procedure has been applied by Gandhi, Curtiss, and Bernstein [6] to study the resulting degree of orientation achieved when different $|JKM\rangle$ states of methyl iodide (CH$_3$I) are selected. They observe the hemispherical up-down anisotropy of the I($2P_{1/2}$) photofragments, which are detected via a 2+1 REMPI process at the same wavelength used to cause photodissociation of CH$_3$I [14]. In a similar manner, Xu, Jung, and Bernstein [9] have investigated the degree of orientation of state-selected beams of $t$-butyl iodide ($t$-C$_4$H$_9$I), observing both the $t$-butyl and I fragments. These results may be compared with the predictions of Choi and Bernstein [16] who derived an expression for the photofragment angular distribution following the photolysis of an ensemble of symmetric-top molecules in a single $|JKM\rangle$ state. The theoretical treatment by Choi and
Bernstein is based on some intuitive assumptions; its validity has been questioned by Gandhi [17]. This Letter presents an independent derivation of the photofragment angular distribution from symmetric-top precursor molecules selected in a $|JKM\rangle$ state. The resulting expression agrees with that found previously by Choi and Bernstein [16]. The treatment presented here is quite simple. It has the virtue of being readily extended to more complex situations of possible interest, such as the use of an elliptically polarized photolysis beam or the application to asymmetric-top molecules.

2. Theory

When an ensemble of isolated randomly oriented target molecules is photodissociated by a beam of plane-polarized radiation, the resulting photofragment intensity, $I$, has an angular distribution of the form

$$I(\theta, \phi) = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)]$$

for a one-photon, electric-dipole-allowed transition, where $\sigma$ is the total cross section, $\beta$ is the asymmetry parameter, $P_2(\cos \theta)$ is the second-order Legendre polynomial, and $\theta$ is the angle between the final recoil direction of the fragments and the electric vector of the light beam. Eq. (1) was first derived by Zare and Herschbach [18] and a simple development of this result may be found in ref. [19, pp. 120–122]. What follows is adapted from the latter treatment.

Suppose a symmetric-top molecule in the state $|JKM\rangle$ is dissociated by a beam of linearly polarized radiation causing a one-photon, electric-dipole-allowed transition from a bound state to a repulsive state, such as occurs in the photodissociation of CH$_3$I and t-C$_4$H$_9$I. Let $(\phi, \theta, \chi)$ denote the Euler angles that describe the molecule-fixed axes relative to the space-fixed axes. Let the $z$ axis of the space-fixed frame lie along the electric vector $E$ of the light beam and the $z$ axis of the molecule-fixed frame lie along the transition dipole moment $\mu$ of the molecule (which for a symmetric top is assumed for convenience to coincide with the figure axis, as is the case for t-C$_4$H$_9$I and CH$_3$I). Then the probability of making a dissociative transition is proportional to $|\mu \cdot E|^2$. For a given orientation $R = (\phi, \theta, \chi)$ of the molecular frame with respect to the space frame

$$P(\phi, \theta, \chi) = \sigma(3 \cos^2 \theta/8\pi^2) = \sigma[1 + 2P_2(\cos \theta)]/8\pi^2 = \sigma[D^J_{00}(R) + 2D^J_{0\theta}(R)]/8\pi^2,$$

where $P$ has been normalized to the total cross section $\sigma$:

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\chi P(\phi, \theta, \chi) = \sigma.$$

Here $D^J_{\ell\mu\nu}(R)$ is a Wigner rotation matrix element [19].

A symmetric-top molecule in the state $JKM$ has a rotational wave function given by [19]

$$|JKM\rangle = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D^J_{MK}(\phi, \theta, \chi).$$

The probability $P_{JKM}(\theta)$ of finding the $JKM$-selected symmetric-top molecule with its molecular axis pointing between $\theta$ and $\theta + d\theta$ is readily evaluated to be

$$P_{JKM}(\theta) = \frac{2J+1}{8\pi^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta D^J_{MK}(\phi, \theta, \chi) D^J_{MK}(\phi, \theta, \chi)$$

$$= \frac{2J+1}{2} [d^J_{MK}(\theta)]^2 = (-1)^{M-K} \frac{2J+1}{2} \sum_{n=0}^{2J} (2n+1) \binom{J}{M} \binom{J}{n} \binom{J}{K} \binom{J}{n} P_n(\cos \theta),$$

\[5\]
where the \( (\ell_2, \ell_3, \ell_4) \) are 3-j symbols [16,19]. For a random distribution of symmetric-top molecules the molecular axis should point uniformly in all directions. This implies that \( P_{J,K,M}(\theta) \) should be independent of \( \theta \) when summed over all \( M \) values:

\[
\sum_{M} P_{J,K,M}(\theta) = \frac{2J+1}{2} \delta_{M,K}.
\]  

Let \( f(\theta_m, \phi_m) \) denote the final recoil direction of the fragments of interest in the molecular frame. Here \( (\theta_m, \phi_m) \) are the polar and azimuthal angles about the \( z \) axis (the direction of \( \mu \)). We expand \( f(\theta_m, \phi_m) \) in the complete set of spherical harmonics

\[
f(\theta_m, \phi_m) = \sum_{k,q} b_{kq} Y_{kq}(\theta_m, \phi_m),
\]

where the expansion coefficients are given by

\[
b_{kq} = \int_0^{2\pi} d\phi_m \int_0^\pi \sin \theta_m d\theta_m \ Y_{kq}^*(\theta_m, \phi_m) f(\theta_m, \phi_m).
\]

For prompt photodissociation, we make use of the axial recoil approximation [18,20]; then \( f(\theta_m, \phi_m) \) takes the particularly simple form

\[
f(\theta_m, \phi_m) = \delta(\theta_m - 0)/(2\pi \sin \theta_m)
\]

and the expansion coefficients are given by

\[
b_{k0} = \int_0^{2\pi} d\phi_m \int_0^\pi \sin \theta_m d\theta_m (-1)^q Y_{k-q}(\theta_m, \phi_m) \delta(\theta_m - 0)/(2\pi \sin \theta_m).
\]

It follows that for \( q \neq 0 \) the \( b_{kq} = 0 \), and for \( q = 0 \)

\[
b_{k0} = Y_{k0}(0, \phi_m) = \left( \frac{2k+1}{4\pi} \right)^{1/2} P_k(1) = \left( \frac{2k+1}{4\pi} \right)^{1/2}.
\]

Hence, for axial recoil

\[
f(\theta_m, \phi_m) = \sum_k \left( \frac{2k+1}{4\pi} \right)^{1/2} Y_{k0}(\theta_m, \phi_m).
\]

Let \( I_{JK,M}(\theta_s, \phi_s) \) denote the angular distribution of the fragments of interest in the lab frame where \( (\theta_s, \phi_s) \) are the polar and azimuthal angles about the \( Z \) axis (the direction of \( E \)). A particular molecular orientation \( R = (\phi, \theta, \chi) \) makes the contribution \( P(\phi, \theta, \chi)f(\theta_m, \phi_m) \) to \( I_{JK,M}(\theta_s, \phi_s) \). Weighting by the probability \( P_{JK,M}(\theta) \) of finding the symmetric-top molecule in the orientation \( (\phi, \theta, \chi) \) with its axis pointing between \( \theta \) and \( \theta + d\theta \), the angular distribution is given by

\[
I_{JK,M}(\theta_s, \phi_s) = \int_0^{2\pi} d\phi \ \sin \theta d\theta \ \int_0^{2\pi} d\chi P_{JK,M}(\theta) P(\phi, \theta, \chi) f(\theta_m, \phi_m).
\]

Substitution of eq. (12) into eq. (13) yields

\[
I_{JK,M}(\theta_s, \phi_s) = \int_0^{2\pi} d\phi \ \sin \theta d\theta \ \int_0^{2\pi} d\chi P_{JK,M}(\theta) P(\phi, \theta, \chi) \sum_k \left( \frac{2k+1}{4\pi} \right)^{1/2} Y_{k0}(\theta_m, \phi_m).
\]
But

\[ Y_{\lambda \theta} (\theta_m, \phi_m) = \sum_{q'} D_{q'}^{k} (\phi_m, \chi) Y_{kq} (\theta_m, \phi_m), \]

where we have expressed the spherical harmonic \( Y_{\lambda \theta} (\theta_m, \phi_m) \) in the molecule-fixed frame as a sum over spherical harmonics of the same rank in the space-fixed frame. Then by substitution of eqs. (2), (5) and (15) into eq. (14) it follows that

\[ L_{JM} (\phi, \chi) = \sigma (-1)^{M-k} \frac{2J+1}{2} \sum_{n=0}^{2J} (2n+1) \binom{J}{M} \binom{J}{-M} \binom{n}{0} \binom{n}{0} \frac{2k+1}{4\pi} \]

\[ \times \left[ \int \sin \theta d \theta \int d \chi D_{\lambda 0} (\phi, \theta, \chi) D_{\lambda 0} (\phi, \theta, \chi) + 2D_{\lambda 0} (\alpha, \theta, \chi) \right] D_{\alpha \theta} (\phi, \theta, \chi) Y_{kq} (\theta, \phi), \]

where we have replaced \( P_{\alpha} (\cos \theta) \) by \( D_{\lambda 0} (\phi, \theta, \chi) \).

From ref. [19], eq. (3.118),

\[ \int d\Omega D_{M1M2} (R) D_{M3M4} (R) D_{M,1M4} (R) = 8\pi^2 \binom{J_1}{M_1} \binom{J_2}{M_2} \binom{J_3}{M_3} \binom{J_4}{M_4} \binom{J}{M} \binom{J}{-M} \binom{n}{0} \binom{n}{0} \binom{2k+1}{4\pi} \]

Thus, the sum over \( q' \) in eq. (16) vanishes except for \( q' = 0 \). Dropping the subscript \( s \) and taking into account that the photofragment distribution is independent of the azimuthal angle \( \theta \),

\[ L_{JM} (\theta) = \sigma (-1)^{M-k} \frac{2J+1}{2} \sum_{n=0}^{2J} (2n+1) \binom{J}{M} \binom{J}{-M} \binom{n}{0} \binom{n}{0} \frac{2k+1}{4\pi} \]

\[ \times \left[ \left( k \quad 0 \quad n \right)^2 + 2 \left( k \quad 2 \quad n \right)^2 \right] P_k (\cos \theta), \]

where we have replaced \( Y_{\lambda \theta} (\theta, \phi) \) by \( \left( (2k+1)/4\pi \right)^{1/2} P_\alpha (\cos \theta) \).

We note that

\[ \left( k \quad 0 \quad n \right)^2 = \frac{1}{2n+1} \delta_{kn} \]

and

\[ D_{\lambda 0} (R) D_{\lambda 0} (R) = \sum_k (2k+1) \binom{2}{0} \binom{n}{0} \binom{k}{0} D_{\lambda 0} (R). \]

Hence, we can rewrite eq. (18) as

\[ L_{JM} (\theta) = (-1)^{M-k} \frac{2J+1}{2} \sum_{n=0}^{2J} (2n+1) \binom{J}{M} \binom{J}{-M} \binom{n}{0} \binom{n}{0} \frac{2k+1}{4\pi} [1 + 2P_2 (\cos \theta)] P_k (\cos \theta) \]

\[ = \sigma \frac{4\pi}{4\pi} P_{JM} (\cos \theta) \left[ 1 + 2P_2 (\cos \theta) \right]. \]

A similar treatment where the final recoil distribution of the fragments in the molecular frame is general [19] causes eq. (21) to be replaced by

\[ L_{JM} (\theta) = \sigma \frac{4\pi}{4\pi} P_{JM} (\cos \theta) \left[ \cos \beta P_2 (\cos \theta) \right]. \]
where $\beta$ is the asymmetry parameter. Except for some differences in normalization, eq. (22) is the same as eq. (30) of Choi and Bernstein [16]. Thus, the photofragment angular distribution from state-selected $|J K M\rangle$ precursor molecules shows in general more oscillatory behavior as a function of angle than the usual $(\sigma/4\pi) [1 + \beta P_2(\cos \theta)]$ distribution pertaining to the photolysis of an ensemble of randomly oriented symmetric tops.

Suppose the dipolar orientation field is turned off so that the beam is $JK$-selected but its $M$ levels are equally populated, each with a weight of $(2J+1)^{-1}$. Then the intensity of a specified photofragment at the polar angle $\theta$ becomes

$$I_{JK}(\theta) = \sum_{M=-J}^{J} \frac{I_{JKM}(\theta)}{2J+1} = \frac{\sigma}{4\pi(2J+1)} [1 + \beta P_2(\cos \theta)] \sum_{M=-J}^{J} P_{JKM}(\cos \theta) = \frac{\sigma}{8\pi} [1 + \beta P_2(\cos \theta)] ,$$

(23)

where we have made use of eq. (6). Of special interest is a measurement at the angle $\theta=0^\circ$, for

$$P_{JKM}(1) = \frac{2J+1}{2} [d_{JK}(0)]^2 = \frac{2J+1}{2} \delta_{MK} .$$

(24)

Thus, the ratio of the photofragments at $\theta=0^\circ$ from a beam of oriented symmetric-top molecules selected in the state $|JKM\rangle$ to a beam of $JK$-selected symmetric-top molecules having no orientation is

$$\frac{I_{JKM}(0)}{I_{JK}(0)} = (2J+1) \delta_{MK} .$$

(25)

This result is the same as eq. (32b) of Choi and Bernstein [16]. As Choi and Bernstein have pointed out [16], "this implies that the rotational quantum number $J$ of an oriented symmetric top molecule can be determined from photofragmentation data alone". This result is not being advocated as a new type of molecular spectroscopy but rather as a lovely connection between molecular spectroscopy and photofragmentation dynamics.

Examination of eq. (22) shows that the dipole angular momentum of the photon in the photofragmentation process is simply transformed into the factor $1 + \beta P_2(\cos \theta)$. The factor $P_{JKM}(\theta)$ merely expresses the probability of finding the symmetric top having the orientation $\phi, \theta, \chi$ with its axis pointing between $\theta$ and $\theta + d\theta$. For many molecular systems, such as CH$_3$I, nonzero nuclear spin is present, causing hyperfine depolarization. However, provided that the separation of the photofragments is much faster than the nuclear spin recoupling time in the (repulsive) excited state, i.e. prompt dissociation as opposed to predissociation, then the hyperfine depolarization may be taken into account by considering only its effect on the ground state [12-14]. This causes $P_{JKM}(\theta)$ to be replaced by some other function of $\theta$ which we denote by $P_{JKM}(\theta)$. Here $P_{JKM}(\theta)$ represents the probability of finding the symmetric top with its axis pointing between $\theta$ and $\theta + d\theta$ properly averaged over all $F$ levels arising from a given $J$ level.

In the above treatment we have assumed that the excited state is purely repulsive, leading to direct photodissociation. However, it may also be the case that the excited state may be bound but that it interacts with a repulsive state to lead to fragmentation (predissociation). There is then the possibility of interference between direct photodissociation and predissociation (which can occur whenever the intermediate state and the final state are both connected to the ground state by the electric dipole operator). Treatments taking this complication into account may be found elsewhere [21,22].

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References