Photodissociation dynamics of triatomic molecules
Effect of predissociation on diatomic fragment fluorescence polarization

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Calculations are presented for the polarization anisotropy, $R = (I_x - I_y)/(I_x + 2I_y)$, of the fragment fluorescence ($AB^* \rightarrow AB + h\nu$) when a triatomic molecule ($ABC$) is photodissociated by a beam of linearly polarized radiation. Expressions are developed relating the polarization anisotropy to the predissociation lifetime $\tau$ of the $[ABC^*]$ complex under the assumptions that (1) the motion of the $[ABC^*]$ complex can be described by the classical motion of the prolate symmetric top, (2) the $AB^*$ excited fragment rotates in the plane of the $[ABC^*]$ complex at the time of dissociation and (3) the absorption and emission processes can be described by classical hertzian dipole oscillators. The time averaged autocorrelation function of a free symmetric top, $\langle D_{nn}(\bar{t})\rangle$, is used to find $R(\tau)$ for the dissociation of an $[ABC^*]$ complex in a single $J, K$ level and for this quantity averaged over a Boltzmann distribution of $J, K$ levels.

1. INTRODUCTION

The photodissociation of isolated small molecules continues to receive much attention as a prototype system for the study of reaction dynamics [1]. In this regard photodissociation may be considered as a half-collision in which the fragments recoil on a repulsive potential energy surface. When one of the fragments is in an electronically excited state, the dynamics may be readily studied by observing the subsequent fluorescence. In particular, the sign of the polarization of the fluorescence may be used to determine the symmetry of the excited surface and the magnitude of the polarization may be used to learn about the nature of the dissociation process on this surface. This method, originally developed by Chamberlain and Simons [2], has been applied to several triatomic systems, for example OH*(O*) from H$_2$O [2, 3] (D$_2$O) [3], CN* from XCN [4–9], HgBr* from HgBr$_2$ [10] and XeF* from XeF$_2$ [11],
and one polyatomic system, NH* from NH₄⁺ [12]. A simple generalization can be used for electron impact dissociation of H₂O [13, 14], D₂O [15], HCN [16], DCN [16] and BrCN [17]. Macpherson, Simons and Zare [18] have calculated the classical degree of polarization of the AB* excited diatomic fragment when a triatomic molecule ABC is photolysed by a beam of radiation. This treatment assumed that the photodissociation process was prompt, that is, direct dissociation occurred in a time much shorter than the rotational period of the [ABC*] complex. An analogous quantum mechanical calculation of direct dissociation has also been presented [19]. Subsequently Loge and Zare [20] considered the effect of rotational motion brought about by a finite predissociation lifetime on the observed degree of polarization. We consider here the same problem but using angular autocorrelation functions [21, 22] to obtain general analytical expressions for the dependence of the degree of polarization on the predissociation lifetime. This extends and in some cases corrects the previous work of Loge and Zare [20]. The present treatment has the virtue of presenting several simple physical models against which experimental observations can be readily compared.

\[ P = \frac{(I_\parallel - I_\perp)}{(I_\parallel + I_\perp)} \]

Figure 1 shows the conventional orthogonal geometry for measuring the polarization of the fragment emission following photolysis. Here a beam of radiation travels along the laboratory X axis with its plane of polarization (electric vector) along the Z axis. A detector views the fragment fluorescence along the Y axis. The gas sample is located at the origin of the laboratory XYZ frame. The degree of polarization \( P \) is traditionally defined by

\[ R = \frac{(I_\parallel - I_\perp)}{(I_\parallel + 2I_\perp)} \]
Here $R$ and $P$ are simply related by

$$R = 2P/(3 - P).$$

The advantage of using $R$ is that its denominator is proportional to the fluorescence intensity integrated over all directions so that its properties are simpler, as will be shown below. In particular, when more than one process contributes to the fragment fluorescence, $R$ values for different processes are additive (which is not true for $P$ values) so that the observed $R$ value is the average of different $R$ values weighted by their cross sections (probabilities).

We consider for simplicity the classical high-$J$ limit in which the absorption and emission processes may be described by hertzian dipole oscillators, $\pmb{r}_{\text{abs}}$ and $\pmb{r}_{\text{em}}$, fixed in the molecular frames of the parent molecule and its excited fragment, respectively. Then the polarization anisotropy can be expressed as [20]

$$R = \frac{2}{3} \langle \pmb{P}_0 \cdot \pmb{r}_{\text{em}} \rangle,$$

where $\pmb{r}_{\text{abs}}(0)$ is a unit vector along the absorption oscillator at the time of absorption ($t = 0$) and $\pmb{r}_{\text{em}}(t)$ is a unit vector along the emission oscillator at the subsequent time $t$ when the fragment is produced, where the subsequent rotational motion of the diatomic fragment is simply included by taking the appropriate average angle between $\pmb{r}_{\text{em}}$ and $\pmb{r}_{\text{abs}}$. In equation (4) $P_0$ is the second order Legendre polynomial, $(3x^2 - 1)/2$, and the brackets $\langle \rangle$ represent a time average of $P_0$ over the ensemble of dissociating molecules, that is, the second Legendre moment of the dipole autocorrelation function.

Let us restrict ourselves to the photodissociation of a triatomic molecule $ABC$ by a beam of linearly polarized radiation to yield an excited diatomic fragment $AB^*$ and an atomic fragment $C$

$$ABC + h\nu \rightarrow [ABC^*] \rightarrow AB^* + C.$$  

We consider only isolated behaviour; we assume collision-free fluorescence of the $AB^*$ fragment and the absence of external fields, that is no electric or magnetic field depolarization of the fluorescence.

We assume that the $[ABC^*]$ complex dissociates with a predissociation lifetime $\tau$ so that the probability of dissociation at a time $t$ after excitation is given by a normalized Poisson distribution, that is $\exp(-t/\tau)/\tau$. In the limit as $\tau \rightarrow 0$ this corresponds to direct dissociation whereas the limit $\tau \rightarrow \infty$ corresponds to infinitely slow dissociation.

For the absorption and emission processes to be described by classical hertzian dipole oscillators, it is necessary for the angular momenta of the parent molecule and its fragment to be much larger than $\hbar$. This condition is usually well fulfilled. The peak of the rotational Boltzmann distribution of the parent molecule is usually larger than $10\hbar$ while that of the fragment normally exceeds that of the parent due to the torque exerted on the $AB^*$ diatomic molecule by the recoiling $C$ atom. We make the additional approximation that the angular momentum of $AB^*$ is so much larger than $[ABC^*]$ that the latter may be neglected. When this is the case, the only torque on $AB^*$ comes from the repulsive force between $AB^*$ and $C$. Because $AB^*$ and $C$ lie in the $[ABC^*]$ plane by definition, it follows that the plane of rotation for $AB^*$ coincides with the $[ABC^*]$ plane. This approximation has the consequence of reducing
significantly the computational effort and permits analytical expressions to be derived for the polarization anisotropy of the $AB^*$ fluorescence. While it is possible to treat this problem more exactly, this is not pursued here because we seek a simple description of the effect of the photodissociation dynamics on the fluorescence polarization.

We distinguish two different geometries for the $[ABC^*]$ complex, namely, linear and bent. In a linear configuration, when bending motion is ignored, the plane of rotation of the $AB^*$ fragment coincides with that of the $[ABC^*]$ complex. Consequently, predissociation cannot alter the time averaged angle between $\nu_{em}(t)$ and $\nu_{abs}(0)$. Hence, for this case, the polarization of the $AB^*$ fluorescence is unaffected by predissociation. We consider this case no further.

We approximate the rotational motion of the bent $[ABC^*]$ complex as that of a classical prolate symmetric top. Of course, any triatomic molecule is in actuality an asymmetric top since it cannot possess a threefold or higher symmetry axis. However, most triatomic molecules are well approximated by prolate tops in which the two larger moments of inertia are nearly equal. Moreover, in keeping with the high-$J$ limit, we treat the motion of the prolate top as classical.

In what follows we derive expressions for $R$ (see (4)) first for an individual $J$, $K$ level of the parent molecule, then for a case where the parent molecule has a Boltzmann distribution of $J$, $K$ levels. Various cases are distinguished based on the possible directions of the absorption dipole moment in the parent molecule and the emission dipole moment in the excited diatomic fragment.

2. POLARIZATION ANISOTROPY AS A FUNCTION OF PREDISSOCIATION LIFETIME

2.1. DISSOCIATION OF THE $[ABC^*]$ COMPLEX IN A SINGLE $J$, $K$ LEVEL

Let the $[ABC^*]$ complex be prepared with a total angular momentum $J$ having a projection $K$ on the prolate top axis. Hence $K$ ranges from $-J$ to $J$ in unit steps and we denote by $\theta$ the angle the figure axis of the top makes with $J$. For a quantized top $\cos^2 \theta = K^2/J(J+1)$; for a classical top $\theta$ can take on any value between 0 and $\pi$ but $\theta = 0$, which implies that the rate of precession of the symmetric top axis about $J$ is constant. The vectors $\nu_{abs}(0)$ and $\nu_{em}(t)$ have the polar angles $(\theta_{abs}, \phi_{abs})$ and $(\theta_{em}, \phi_{em})$, respectively, defined in the molecular $xyz$ frame. We introduce a reduced lifetime

$$\tau = (J/|I|) \tau$$

where $I$ represents the larger moment of inertia of the prolate top, that is the moment about an axis perpendicular to the top axis, and $\tau$ is the predissociation lifetime. We also define the quantity

$$b = I/I_z - 1$$

where $I_z$ is the moment of inertia about the figure axis. We arbitrarily choose the $yz$ plane to coincide with the plane of the $[ABC^*]$ complex. Then (4) can be evaluated (see Appendix A) to yield the expression

$$R(\tau) = \frac{8\pi}{25} \sum_{m, n = -2}^{2} Y_{2m}^*(\theta_{em}, \phi_{em}) Y_{2m}(\theta_{abs}, \phi_{abs})[d_{mn}^{(3)}(\theta)]^2$$

$$\times \frac{1 - i(n + mb \cos \theta) \tau}{1 + (n + mb \cos \theta)^2 \tau^2} \frac{1}{\tau^2}$$

(8)
where $Y_{2m}(\theta, \phi)$ is a spherical harmonic of order 2 and $d_{mn}^{(\alpha)}(\theta)$ is the well known special case of the rotation matrix $D_{mn}^{(\alpha)}(0, \theta, 0)$ [23, 24].

Note that $R$ is a real quantity ranging from $+1$ to $-\frac{1}{2}$; the summation over $m$ and $n$ cancels all imaginary terms in (8). In the limit of direct dissociation ($\tau \to 0$)

$$R(\tau \to 0) = \frac{8\pi}{25} \sum_{m} Y_{2m}^* (\theta_{em}, \phi_{em}) Y_{2m} (\theta_{abs}, \phi_{abs}) \sum_{n} [d_{mn}^{(\alpha)}(\theta)]^2$$

$$= \frac{2}{5} P_{\gamma} (\cos \gamma),$$

where

$$\cos \gamma = \cos \theta_{abs} \cos \theta_{em} + \sin \theta_{abs} \sin \theta_{em} \cos (\phi_{abs} - \phi_{em}).$$

Here we use the identity

$$\sum_{n} [d_{mn}^{(\alpha)}(\theta)]^2 = 1$$

and the spherical harmonic addition theorem [23, 24]. In (9) and (10) $\gamma$ denotes the average angle between $\mu_{abs}$ and $\mu_{em}$. Equation (9) is identical to the expression obtained for $R$ in the previous work [18]. On the other hand, as $\tau \to \infty$, for $\cos \theta \neq 0$ ($K \neq 0$) only the term with $m = 0$ and $n = 0$ contributes to (8) and $R$ becomes

$$R(\tau \to \infty) = \frac{8\pi}{25} Y_{20}^* (\theta_{em}, \phi_{em}) Y_{20} (\theta_{abs}, \phi_{abs}) [P_{\gamma} (\cos \theta)]^2,$$

while for $\cos \theta = 0$ ($K = 0$) only the terms with $n = 0$ contribute to (8) and $R$ becomes

$$R(\tau \to \infty) = \frac{8\pi}{25} \sum_{m=-2}^{2} Y_{2m}^* (\theta_{em}, \phi_{em}) Y_{2m} (\theta_{abs}, \phi_{abs}) \left[ d_{m0}^{(\alpha)} \left( \frac{\pi}{2} \right) \right]^2.$$ 

We consider next the (average) angle $\mu_{abs}$ makes with respect to $\mu_{em}$ for all possible cases where different orientations of the absorption and emission dipole oscillators occur. In a triatomic molecule having a bent equilibrium geometry, the direction of $\mu_{abs}$ belongs to either of the following cases for a transition between two prolate top states: (i) $\mu_{abs}$ lies in the molecular plane ($yz$ plane) and points along the figure axis $z$ (A-type transition); (ii) $\mu_{abs}$ lies in the molecular plane and is perpendicular to the figure axis (B-type transition); (iii) $\mu_{abs}$ is perpendicular to the molecular plane, that is lies along the $x$ axis (C-type transition). Then the orientation of $\mu_{abs}$ referred to the molecule-fixed frame is determined as follows: for an A-type transition $\theta_{abs} = 0$ and $\phi_{abs}$ is arbitrary and is denoted by $\phi_{abs} = \alpha$; for a B-type transition $\theta_{abs} = \pi/2$ and $\phi_{abs} = \pi/2$; for a C-type transition $\theta_{abs} = \pi/2$ and $\phi_{abs} = 0$.

Since the $AB^*$ fragment rotates in the $yz$ plane after dissociation, the direction of $\mu_{em}$ is either in this plane for an $R$ or $P$ line ($\Delta J = \pm1$) or perpendicular to it for a $Q$ line ($\Delta J = 0$). In the former, the average polar and azimuthal angles are $\theta_{em} = \pi/4$ and $\phi_{em} = \pi/2$; in the latter, $\theta_{em} = \pi/2$ and $\phi_{em} = 0$. The table lists the six possible cases for $\mu_{abs}$ relative to $\mu_{em}$. These cases are named $E$ through $J$ using the same nomenclature of Loge and Zare [20]. We also present in the table the values of $R$ obtained from (9) and (11) in the limit of direct dissociation and infinitely slow predissociation, respectively. These results are the same as those of Loge and Zare [20] except for the special case $K = 0$ in $G, H, I, J$. (Loge and Zare incorrectly performed the average over the angle $\chi_0$ in cases $G - J$ by taking the average of $\chi_0 = 0$ and $\chi_0 = \pi/2$, rather than
Different orientations of $\mu_{abs}$ and $\mu_{em}$ referred to the molecule-fixed frame of the $[ABC^\kappa]$ prolate top.

<table>
<thead>
<tr>
<th>Case</th>
<th>Case</th>
<th>$(\phi_{abs}$, $\phi_{abs})$</th>
<th>$(\phi_{em}$, $\phi_{em})$</th>
<th>$R(\tau \to 0)$</th>
<th>$\cos \theta = 0(K = 0)$</th>
<th>$\cos \theta \neq 0(K \neq 0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$(0, \alpha)$</td>
<td>$(\pi/2, 0)$</td>
<td>$\frac{1}{3}$</td>
<td>$-\frac{1}{8}$</td>
<td>$-\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>$(0, \alpha)$</td>
<td>$(\pi/4, \pi/2)$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>$(\pi/2, \pi/2)$</td>
<td>$(\pi/2, 0)$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>$(\pi/2, \pi/2)$</td>
<td>$(\pi/4, \pi/2)$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>$(\pi/2, 0)$</td>
<td>$(\pi/2, 0)$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
<tr>
<td>$J$</td>
<td>$(\pi/2, 0)$</td>
<td>$(\pi/2, 0)$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}(P_2(\cos \theta))^2$</td>
<td></td>
</tr>
</tbody>
</table>

Integrating from 0 to $2\pi$. If the latter prescription is followed, then a term $\frac{1}{8}(1 - \cos \phi_2)^2 \sin^4 \phi \cos 2\phi_2$ must be added to their expression for $\langle |\mathbf{x} \cdot \mathbf{y}'| \rangle$ and subtracted from their expression for $\langle |\mathbf{x} \cdot \mathbf{x}'| \rangle$. The Laplace transform of this term is

$$\frac{1}{8} \sin^4 \theta \left[ \frac{3}{2(1 + 4\tilde{\chi}^2 \tau^2)} + \frac{1}{1 + (2\tilde{\chi} + \phi^2)^2 \tau^2} \right] - \frac{1}{2(1 + 4\tilde{\chi}^2 \tau^2)}$$

$$+ \frac{1}{2(1 + 4\tilde{\chi}^2 \tau^2)} \left[ \frac{1}{1 + 4(\tilde{\chi} + \phi^2)^2 \tau^2} + \frac{1}{1 + 4(\tilde{\chi} - \phi^2)^2 \tau^2} \right].$$

This should be added to $\mathcal{L} \langle |\mathbf{x} \cdot \mathbf{y}'| \rangle$ and $\mathcal{L} \langle |\mathbf{y} \cdot \mathbf{x}'| \rangle$ and subtracted from $\mathcal{L} \langle |\mathbf{x} \cdot \mathbf{x}'| \rangle$ and $\mathcal{L} \langle |\mathbf{y} \cdot \mathbf{y}'| \rangle$ in their Table 4. When this is done, the procedure of Loge and Zare gives the same results for $R$ as presented here.) A comparison of the value of $R$ at $\tau = 0$ to that at $\tau \to \infty$ shows that predissociation always

![Figure 2](image_url)

Figure 2. Plot of $R(\tau)$ for case $F$ in which $\mu_{abs}$ lies along the top axis of the $[ABC^\kappa]$ complex and $\mu_{em}$ lies in the plane of rotation of the $AB^\kappa$ excited fragment. The behavior of various $J, K$ levels are shown where $\cos^2 \theta = K^2/J(J + 1)$. Here $R(\tau)$ is independent of $b = (I - I_z)/I_z$.  

FOR ANY VALUE OF $b$

Polarization Anisotropy, $R$

Reduced Lifetime, $\tau$
has the effect of decreasing the magnitude of the polarization anisotropy but $R$ does not necessarily vanish. For all cases except case $H$ the polarization anisotropy is unaltered in sign by predissociation. In case $H$, $\mu_{\text{abs}}$ lies in the molecular plane along the $y$ axis while $\mu_{\text{em}}$ lies uniformly distributed in the same plane. Let us specialize to the situation where $K=J$, that is $\cos \theta = 1$. At $\tau = 0$, $\cos^2 \gamma = \frac{1}{2}$ and $R = \frac{1}{20}$. As $\tau \rightarrow \infty$, $\mu_{\text{abs}}$ and $\mu_{\text{em}}$ lie uniformly distributed in two orthogonal planes, the $xy$ plane for $\mu_{\text{abs}}$ and the $yz$ plane for $\mu_{\text{em}}$. Hence $\cos^2 \gamma = \frac{1}{4}$ and $R = -\frac{1}{20}$. Note that the form of $R$ for $\cos \theta \neq 0$ does not approach the value of $R$ for $\cos \theta = 0$. This may seem at first glance to be surprising. However, the rotational motion of a bent prolate top with $K=0$

![Diagram](image)

Figure 3. Plot of $R(\tau)$ for case $H$ in which $\mu_{\text{abs}}$ lies in the plane of the $ABC$ molecule perpendicular to the top axis and $\mu_{\text{em}}$ lies in the plane of rotation of the $AB^*$ excited fragment. The behaviour of various $J, K$ levels as a function of $b$ is shown where $\cos^2 \theta = K^2 / J(J+1)$ and $b = (I_2 - I_2)/I_2$. 
should be distinguished from that with \( K \neq 0 \). An infinitesimal precession rate about the top \( z \) axis causes a finite reorientation of the top given a sufficiently long predissociation lifetime; this clearly differs from the case where there is no rotation about the top \( z \) axis \((K = 0)\).

In the preceding we have concentrated our attention on the two extreme limits, \( R(\tau \to 0) \) and \( R(\tau \to \infty) \). Intermediate values of \( R(\tau) \) are readily calculated using (8). Figures 2-4 illustrate the behaviour of \( R(\tau) \) for various values of \( b \) ranging from \( b = 0 \) (spherical top) to \( b \to \infty \) (linear top). We choose to
Triatomic photodissociation dynamics

examine an A-type transition (figure 2), a B-type transition (figure 3) and a C-type transition (figure 4) and in each only for (parallel-type) emission of P and R lines by the excited diatomic fragment, corresponding to cases F, H and J in the table, respectively. Note that in most cases there is only a narrow range of \( \gamma \) for which \( R(\gamma) \) is not well approximated by its two limiting values. Consequently, the extremes of direct dissociation and infinitely slow predissociation often represent two useful physical models for describing the effect of predissociation on the polarization anisotropy.

Closer examination of figures 2–4 shows the following behaviour. When \( \theta = 90^\circ \) (\( K = J \) in high \( J \) limit), \( R(\gamma) \) is independent of the value of \( b \), as would be expected since \( b \) only appears in the term \( mb \cos \theta \) in (8). At the magic angle (\( \theta = 54.7^\circ \)) \( R(\gamma) \) approaches the value of zero when \( b \neq 0 \). This is a consequence of the fact that as \( \gamma \to \infty \), \( R(\gamma) \) is proportional to \( |P_2(\cos \theta)|^2 \) for \( b \neq 0 \), as can be seen from inspection of (8). In figure 2 note that \( R(\gamma) \) does not depend on the value of \( b \), while \( R(\gamma) \) varies with \( b \) for the other cases (when \( \theta \neq 90^\circ \)). The reason for this behaviour is that in case \( F \), \( \mu_{\text{abs}} \) lies along the top axis and the rotational motion about this axis cannot alter the angle between \( \mu_{\text{abs}} \) and \( \mu_{\text{em}} \). Since \( R(\gamma) \) only depends on this angle (see (4)), it is unaffected by the value of \( b \). The opposite behaviour appears in figures 3 and 4 where \( R(\gamma) \) shows a rather impressive dependence on \( b \) for large \( b \) values. As \( b \) increases in magnitude the [\( ABC^* \)] complex approaches a linear top with a large angular velocity along the top axis. Hence for small \( \gamma \) values \( R(\gamma) \) approaches the limiting value for \( \theta = 0^\circ \). However, as \( \gamma \) increases, \( R(\gamma) \) must then approach its limiting behaviour \( R(\gamma \to \infty) \) for whatever \( \theta \) value applies.

2.2. Dissociation of the [\( ABC^* \)] complex averaged over different \( J, K \) levels

In the most general case the \( ABC \) parent molecule is found in many \( J, K \) levels in the ground electronic state with some arbitrary distribution. When the sample is exposed to nearly monochromatic radiation, the [\( ABC^* \)] complex is prepared with a complicated distribution of \( J, K \) levels, each of which contributes to the observed polarized fragment emission. Clearly, the evaluation of \( R \) under such circumstances is a formidable task requiring much additional information. Instead, we consider a restricted case where the internal energy level population of the parent molecule may be described by a Boltzmann distribution at the temperature \( T \) and where the parent molecule has a linear geometry in the ground electronic state but a bent (prolate top) geometry in the excited state. This restricted case includes many practical examples of photodissociation. Moreover, its consideration leads to a rather simple expression for the polarization anisotropy. In the electronic ground state the molecule rotates about an axis perpendicular to the molecular axis. According to the selection rule for \( \Delta K \) in excitation, the [\( ABC^* \)] complex may receive only a small component of angular momentum along its figure axis so that \( \theta \simeq \pi/2 \). (For a \( 1\Sigma \) electronic ground state, the quantum number \( K' \) of the angular momentum about the symmetry axis is equivalent to \( l' \), the quantum number of the vibrational angular momentum of the two degenerate bending modes. Hence the selection rules for \( \Delta K \) are \( K' - l' = 0 \) for a \( \parallel \) band and \( K' - l' = \pm 1 \) for a \( \perp \) band.) Let us assume that the photolysis source causes broad band excitation, that is, is flat over those wavelengths pumping the various rotational levels of a given vibrational band. Then the rotational kinetic
energy distribution in the complex is almost the same as that in the ground electronic state because of the $\Delta J=0, \pm 1$ selection rule. When these conditions are met, then the angular momentum distribution of the $[ABC^*]$ complex can be approximated by a Boltzmann distribution

$$W(J)\, dJ = (8\pi I k T)^{-3/2} \exp \left(-J^2/2I k T\right) \delta(\cos \theta) J^2 \, dJ \, d(\cos \theta) \, d\phi,$$

(12)

where $\delta(\cos \theta)$ expresses the constraint that $\mathbf{J}$ is perpendicular to the $x$ axis (figure axis) of the $[ABC^*]$ complex. As shown in Appendix B, the resulting expression for the polarization anisotropy is

$$R(\tau; \bar{\omega}) = \frac{8\pi}{25} \sum_{m=-2}^{2} Y_{2m}^{*} \left(\theta_{em}, \phi_{em}\right) Y_{2m} \times \left(\theta_{abs}, \phi_{abs}\right) \sum_{n=-2}^{2} Q_n \left[d_{mn}^{(2)} \left(\frac{\pi}{2}\right)\right]^2,$$

(13)

where

$$Q_0 = 1$$

$$Q_{\pm 1} = \frac{1}{\tau_T} \int_{0}^{\infty} \left(1-x^2\right) \exp \left(-x^2/2-x/\tau_T\right) \, dx,$$

$$Q_{\pm 2} = \frac{1}{\tau_T} \int_{0}^{\infty} \left(1-4x^2\right) \exp \left(-2x^2-x/\tau_T\right) \, dx$$

(14)

and

$$\tau_T = \bar{\omega} \tau, \quad x = \bar{\omega} t.$$

(15)

In (13)-(15)

$$\bar{\omega} \equiv (kT/\hbar)^{1/2}$$

is the average angular velocity. The $Q_n$ integrals cannot be written in closed form but they are readily evaluated numerically.

Figure 5 presents some representative plots of $R(\tau; \bar{\omega})$ for the six possible cases $E-J$. In each case $R(\tau; \bar{\omega})$ approaches its asymptotic value in a time of the order of the rotational period of the $[ABC^*]$ complex. Again there is a fairly narrow range of time $\tau_T$ about $\tau_T=1$ for which $R(\tau; \bar{\omega})$ is not well described by the two extremes of direct dissociation ($\tau \rightarrow 0$) and infinitely slow predissociation ($\tau \rightarrow \infty$). In the limit of direct dissociation the $R(\tau; \bar{\omega})$ curves coincide for the cases $E$ and $G$ ($Q$ branch emission) and the cases $F$ and $H$ ($P$ and $R$ branch emission); however, it is possible to distinguish the $A$-type transitions (cases $E$ and $F$) from the $B$-type transitions (cases $G$ and $H$) of the $ABC$ parent when the predissociation lifetime $\tau_T$ is of the order of unity or larger. On the other hand, the $C$-type transitions (cases $H$ and $I$) are easily distinguished from the $A$-type and $B$-type transitions because the former give values of $R(\tau; \bar{\omega})$ of the opposite sign.

For any $\tau_T$ the polarization anisotropy for a $Q$ branch transition (see figures 5 (a), (b)) has twice the magnitude and the opposite sign from that obtained for the corresponding $P$ or $R$ branch transition (see figures 5 (c), (d)) of the fragment fluorescence. This result is a consequence of the fact that $\mathbf{p}_{em}$ points along $\mathbf{J}$ for a $Q$ branch transition while $\mathbf{p}_{em}$ rotates in a plane perpendicular to $\mathbf{J}$ for a $P$ or $R$ branch transition. Consequently, when it is possible to resolve the fragment fluorescence, the largest $R(\tau; \bar{\omega})$ values are expected for molecular transitions having strong $Q$ branches, that is for perpendicular-type transitions.
3. CONCLUSIONS

Calculations have been presented which show that the polarization anisotropy $R$ of the fluorescence of an excited diatomic photofragment is directly related to the dynamics of a dissociating triatomic molecule in a photo-excited state. Based on these calculations, a precise measurement of the magnitude of $R$ can provide detailed information on the predissociation lifetime as well as the symmetry of the photo-excited state. The present treatment can be extended to dissociation processes of a triatomic molecule arising from electron, ion or metastable atom dissociative impact. In these cases the interaction between the impinging particles and the target molecules are more complicated than in...
photodissociation, but a knowledge of the excitation probabilities should enable calculations to be carried out analogous to those of the present study.

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APPENDIX A

Expression for the polarization anisotropy \( R(\tau) \) obtained from a single \( J, K \) level with a predissociation lifetime \( \tau \)

In this Appendix we evaluate (4) to obtain an analytical expression for \( R(\tau) \) when an \([ABC^*]\) complex in a single \( J, K \) level dissociates with a predissociation lifetime \( \tau \). We begin by rewriting (4) as

\[
R(\tau) = \int_0^\infty R(t) \exp \left( -t/\tau \right) dt/\tau
\]  

(A 1)

where

\[
R(t) = \frac{8}{25} \langle \mathcal{P}_{2}[\hat{\theta}_{\text{em}}(t), \hat{\phi}_{\text{em}}(t)] \rangle
\]

\[
= \frac{8\pi}{25} \left\langle \sum_{m = -2}^{2} Y_{2m}^{*}(\hat{\theta}_{\text{em}}(t), \hat{\phi}_{\text{em}}(t)) Y_{2m}(\theta_{\text{abs}}(0), \phi_{\text{abs}}(0)) \right\rangle.
\]  

(A 2)

Here the polar and azimuthal angles of the emission and absorption hertzian dipoles, \((\theta_{\text{em}}(t), \phi_{\text{em}}(t))\) and \((\theta_{\text{abs}}(0), \phi_{\text{abs}}(0))\), are referred to the molecule-fixed frame at \( t = 0 \) and the bracket \( \langle \rangle \) in (A 2) represents an appropriate conditional and ensemble average over the initial angular momentum in the molecular frame.

The molecular rotation of the \([ABC^*]\) complex during a time interval \( t \) cause a spatial reorientation \( \delta \mathbf{R} \) whose Euler angles are \((\delta \alpha, \delta \beta, \delta \gamma)\). This reorientation transforms \( Y_{2m}^{*}(\theta_{\text{em}}(t), \phi_{\text{em}}(t)) \) according to

\[
Y_{2m}^{*}(\theta_{\text{em}}(t), \phi_{\text{em}}(t)) = \left[ \delta R^{-1} Y_{2m}(\theta'_{\text{em}}(t), \phi'_{\text{em}}(t)) \right]^{*}
\]

\[
= \sum_{\delta m} D_{mm'}^{(2)}(\delta \alpha, \delta \beta, \delta \gamma) Y_{2m'}^{*}(\theta'_{\text{em}}(t), \phi'_{\text{em}}(t)),
\]  

(A 3)

where \( D_{mm'}^{(2)}(\delta \alpha, \delta \beta, \delta \gamma) \) is a rotation matrix [23, 24] and the primes indicate the spherical polar coordinates in the molecule-fixed frame at time \( t \). Since the hertzian dipole oscillator is fixed to the molecular frame, the coordinates of \( \mu_{\text{em}}(t) \) relative to the frame at time \( t \) are identical with those of \( \mu_{\text{em}}(0) \) relative to the frame at \( t = 0 \); \( \theta'_{\text{em}}(t) = \theta_{\text{em}}(0) \) and \( \phi'_{\text{em}}(t) = \phi_{\text{em}}(0) \). Hence, (A 3) can be rewritten as

\[
Y_{2m}^{*}(\theta_{\text{em}}(t), \phi_{\text{em}}(t)) = \sum_{\delta m} D_{mm'}^{(2)}(\delta \Omega(t)) Y_{2m'}^{*}(\theta_{\text{em}}(0), \phi_{\text{em}}(0)),
\]  

(A 4)

where we identify \( \delta \Omega(t) \) with \((\delta \alpha, \delta \beta, \delta \gamma)\). Substitution of (A 4) into (A 2) yields

\[
R(t) = \frac{8\pi}{25} \sum_{\delta m} Y_{2m}^{*}(\theta_{\text{em}}(0), \phi_{\text{em}}(0)) Y_{2m}(\theta_{\text{abs}}(0), \phi_{\text{abs}}(0))
\]

\[
\times \langle D_{mm'}^{(2)}(\delta \Omega(t)) \rangle.
\]  

(A 5)
The averaged rotation matrix \( \langle D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) \rangle \) corresponds to the angular autocorrelation function. According to St. Pierre and Steele [21] this function is given by

\[
\langle D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) \rangle_{\mathbf{J}_0} = \int \langle D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) \rangle_{\mathbf{J}_0} W(\mathbf{J}_0) \, d\mathbf{J}_0,
\]

(A 6)

where

\[
\langle D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) \rangle_{\mathbf{J}_0} = \int D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) W(\delta \mathbf{\Omega}, \mathbf{J}(t), t; \mathbf{J}_0) \times d\mathbf{J}(t) \, d(\delta \mathbf{\Omega})
\]

(A 7)

\( \mathbf{J}_0 \) and \( \mathbf{J}(t) \) are the angular momentum variables at time 0 and \( t \), respectively, \( W(\mathbf{J}_0) \) is the initial probability distribution of angular momenta of the \( [ABC^*] \) complex and \( W(\delta \mathbf{\Omega}, \mathbf{J}(t), t; \mathbf{J}_0) \) is the propagator which gives the probability of the system at time \( t \). For a free-rotating symmetric top [21]

\[
W(\delta \mathbf{\Omega}, \mathbf{J}(t), t; \mathbf{J}_0) = \sum_{j=0}^{\infty} \sum_{n, \alpha} \frac{2j+1}{8\pi^2} \exp(inJ(t)I) \exp[i(r\phi_0-r'\phi)] \times D_{\alpha, \alpha}(\delta \mathbf{\Omega}) \exp(i\omega_0 t) d_{\alpha, \alpha}(\theta) d_{\alpha, \alpha}(\theta) \delta(\mathbf{J}(t) - \mathbf{J}_0)
\]

(A 8)

where \( I \) represents the moment of inertia about an axis perpendicular to the top axis, \( \theta \) and \( \phi \) are defined as polar and azimuthal angles of the angular momentum vector in the body-fixed frame (the subscript 0 is used for representing the variables at \( t=0 \)) and \( \omega_0 = (I-I_z) \cos \theta / I_z \) is the frequency of the precessing motion of the top. By performing the integration in (A 7) over \( \delta \mathbf{\Omega} \), there remain only the terms with \( j=2 \), \( r=-m \) and \( r'=-m' \) because of the orthogonality properties of rotation matrices [23, 24]. Hence

\[
\langle D_{mn, \alpha}(\delta \mathbf{\Omega}) \rangle_{\mathbf{J}_0} = \sum_{n} \exp(-inJ(t)I) \exp[i(m'-m)\phi_0] \exp(-im'\omega_0 t) \times d_{mn, \alpha}(\theta_0) d_{m'n, \alpha}(\theta_0).
\]

(A 9)

For an \( [ABC^*] \) complex in a single \( J, K \) level, the initial distribution of angular momenta \( \mathbf{J}_0 \) can be expressed as

\[
W(\mathbf{J}_0) \propto \delta(J_0 - J) \delta(\theta_0 - \theta)
\]

(A 10)

where \( \cos^2 \theta = K^2/J(J+1) \) for a quantized top. Then the integration over \( \mathbf{J}_0 \) in (A 6) gives

\[
\langle D_{mn, \alpha}(\delta \mathbf{\Omega}(t)) \rangle = \delta_{mn} \cdot \sum_{n} \exp\{ -i(n+mb \cos \theta)\bar{\tau} \} [d_{mn, \alpha}(\theta)]^2
\]

(A 11)

where

\[
i = (J/I)t, \quad b = I/I_z - 1.
\]

(A 12)

It then follows from (A 1), (A 5) and (A 11) that the polarization anisotropy is a function of the related predissociation lifetime \( \bar{\tau} = (J/I)\tau \) whose explicit form is

\[
R(\tau) = \frac{8\pi}{25} \sum_{m,n=-2}^{2} Y_{m,n}^{*}((\theta_{em}(0), \phi_{en}(0))) Y_{m,n}((\theta_{abw}(0), \phi_{abw}(0)))
\]

\[
\times [d_{mn, \alpha}(\theta)]^2 \frac{1-i(n+mb \cos \theta)\bar{\tau}}{1+(n+mb \cos \theta)^2 \bar{\tau}^2}
\]

(A 13)

Equation (A 13) is the same as (8) in the main text.
APPENDIX B

Expression for the polarization anisotropy $R(\tau, \bar{\omega})$ obtained from a Boltzmann distribution of levels having the same predissociation lifetime $\tau$ and average angular velocity $\bar{\omega}$

When the ensemble of the $[ABC^*]$ complex is described by a Boltzmann distribution at the temperature $T$, we need to perform an ensemble average of $R(\tau)$ over the distribution of the initial angular momenta. In this case, however, the procedure given in Appendix A is readily applied when the Boltzmann distribution (12)

$$W(J_\beta) \, dJ_\beta = (8\pi kT)^{-3/2} \exp(-J_\beta^2/2kT) \delta(\cos \theta)$$

$$\times J_\beta^2 \, dJ_\beta \, d(\cos \theta) \, d\phi$$  \hspace{1cm} (B 1)

is adopted instead of (A 10) in the integration over $J_\beta$. Using (B 1), we find in place of (A 11) the angular autocorrelation function

$$\langle D_{mm'}(\delta\Omega(t)) \rangle = \delta_{mm'} \sum_{n=-2}^{2} (1-n^2 \lambda^2) \exp(-n^2 \lambda^2/2) \left[ d_{mn}^{(2)} \left( \frac{\pi}{2} \right) \right]^2$$  \hspace{1cm} (B 2)

where

$$\lambda = \omega t, \quad \bar{\omega} = (kT/T)^{1/8}.$$  \hspace{1cm} (B 3)

The time-weighted average gives us for the polarization anisotropy the general expression

$$R(\tau; \bar{\omega}) = \frac{8\pi}{25} \sum_{m=-2}^{2} Y_{2m} \, \hat{\theta}_{1m}(\theta_{1m}(0), \phi_{1m}(0)) Y_{2m}(\theta_{abs}(0), \phi_{abs}(0))$$

$$\times \sum_{n=-2}^{2} Q_n \left[ d_{mn}^{(2)} \left( \frac{\pi}{2} \right) \right]^2$$  \hspace{1cm} (B 4)

where

$$Q_0 = 1,$$

$$Q_{\pm 1} = \frac{1}{\tau_T} \int_0^\infty (1-x^2) \exp(-x^2/2-x/\tau_T) \, dx,$$

with

$$\tau_T = \bar{\omega} \tau.$$  \hspace{1cm} (B 6)

Equations (B 4)–(B 6) are the same as (13)–(15) in the main text.

REFERENCES


