

## RESEARCH NOTE

### Fluorescence polarization of a diatomic fragment following photodissociation of a triatomic precursor

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(Received 26 February 1990; accepted 7 March 1990)

Calculations are presented for the polarization anisotropy  $R = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$  of the fragment fluorescence ( $AB^* \rightarrow AB + h\nu$ ) when a linear triatomic molecule ( $ABC$ ) is photodissociated by a beam of linearly polarized radiation ( $ABC + h\nu \rightarrow AB^* + C$ ). An expression is derived relating the polarization anisotropy  $R(\tau)$  to the predissociation lifetime  $\tau$  of the bent  $[ABC^*]$  complex in the high- $J$  limit. The time-averaged autocorrelation function of a prolate symmetric top,  $\langle D_{mm}^{(2)}(\delta\Omega(t)) \rangle$ , is used to find  $R(\tau)$  for the dissociation of an  $[ABC^*]$  complex in a single  $(J, K)$  level.

#### 1. Introduction

The photodissociation dynamics of triatomic molecules continues to be a topic of active research interest because such small systems can be characterized in great detail and because experimental results can be compared with increasingly sophisticated theoretical calculations. Of particular interest is the alignment of the photo-fragment following photodissociation by a beam of plane-polarized light [1]. The degree of alignment is readily measured when the fragment is produced in an excited state that fluoresces. This experimental method, originally developed by Chamberlain and Simons [2], has been applied to many systems.

There have been several studies predicting the degree of polarization of an  $AB^*$  excited fragment when  $ABC$  is photolysed by a beam of radiation [3-6]. In particular, Nagata *et al.* [6] derived expressions for the polarization anisotropy as a function of predissociation lifetime when a single  $(J, K)$  level of the  $[ABC^*]$  complex dissociates. The  $[ABC^*]$  complex involves a transition from a linear ground state ( $J'', K'' = 0$ ) to a bent excited state  $(J, K)$ . Six cases could be distinguished, based on treating the  $[ABC^*]$  complex as a prolate symmetric top, depending on the orientation of the absorption transition dipole moment with respect to the emission transition dipole moment. Nagata *et al.* assumed that the initial distribution of the angular-momentum vector  $\mathbf{J}$  of the  $[ABC^*]$  complex could be expressed as

$$W(\mathbf{J}) \propto \delta(J - J_0)\delta(\theta - \theta_0), \quad (1)$$

on the basis of the idea that the  $x$  and  $y$  axes could not be distinguished in a prolate top (see equation (A 10) of [6]). This is correct for a type-A transition ( $\Delta J = \pm 1$ ,  $\Delta K = 0$ ), but incorrect for a type-B or a type-C transition ( $\Delta K = 1$ ). In the latter

two cases, (1) must be modified to read

$$W(\mathbf{J}) \propto \delta(J - J_0)\delta(\theta - \theta_0)\delta(\phi - \phi_0) \quad (2)$$

because the projection of the angular-momentum vector  $\mathbf{J}$  in the  $(x, y)$  plane is not uniformly distributed. This paper extends the previous treatment of Nagata *et al.* to type-B and type-C transitions.

## 2. Theory

We use the same notation as in [6]. We take as a starting point equation (A 5) of [6], namely

$$R(t) = \frac{8\pi}{25} \sum_{m, m' = -2}^2 Y_{2m'}^*(\theta_{cm}(0), \phi_{cm}(0)) Y_{2m}(\theta_{abs}(0), \phi_{abs}(0)) \langle D_{mm'}^{(2)}(\delta\Omega(t)) \rangle, \quad (3)$$

where

$$\langle D_{mm'}^{(2)}(\delta\Omega(t)) \rangle = \int \langle D_{mm'}^{(2)}(\delta\Omega(t)) \rangle_{\mathbf{J}} W(\mathbf{J}) d\mathbf{J}. \quad (4)$$

Here  $\langle D_{mm'}^{(2)}(\delta\Omega(t)) \rangle_{\mathbf{J}}$  is given in equation (A 7) of [6], and  $W(\mathbf{J})$  has the functional form (2) instead of (1). The integration over  $\mathbf{J}$  in (4) then gives

$$\langle D_{mm'}^{(2)}(\delta\Omega(t)) \rangle = \exp[i(m' - m)\phi_0] \sum_n \exp[-i(n + m'xb)\bar{t}] d_{mn}^{(2)}(\theta_0) d_{m'n}^{(2)}(\theta_0), \quad (5)$$

where  $\bar{t} = (J_0/I)t$ ,  $x = \cos \theta_0$  and  $b = I/I_x - 1$ . Here  $I$  is approximated by  $\frac{1}{2}(I_x + I_y)$  when  $I_x \neq I_y$ . By averaging  $R(t)$  over the lifetime  $\tau$  of the [ABC\*] complex, we have

$$\begin{aligned} R(\tau) &= \int_0^\infty R(t) \exp\left(-\frac{t}{\tau}\right) d\left(\frac{t}{\tau}\right) \\ &= \frac{8\pi}{25} \sum_{\substack{m, m' = -2 \\ m, m' \neq \pm 1}}^2 Y_{2m'}^*(\theta_{cm}(0), \phi_{cm}(0)) Y_{2m}(\theta_{abs}(0), \phi_{abs}(0)) \exp[i(m' - m)\phi_0] \\ &\quad \times \sum_{n=-2}^2 \frac{1 - i(n + m'b \cos \theta_0)\bar{\tau}}{1 + (n + m'b \cos \theta_0)^2 \bar{\tau}^2} d_{mn}^{(2)}(\theta_0) d_{m'n}^{(2)}(\theta_0), \end{aligned} \quad (6)$$

where  $\bar{\tau} = (J_0/I)\tau$ .

We next consider the orientation of  $\mathbf{J}$  with respect to the molecular frame of the [ABC\*] complex. As mentioned in [6], we arbitrarily choose the  $(y, z)$  plane to coincide with the plane of the [ABC\*] complex. In the framework of the high- $J$  limit, the direction of  $\mathbf{J}$  is either parallel to that of  $\mu_{abs}$  for a Q line ( $\Delta J = 0$ ), or perpendicular to it for a P or R line ( $\Delta J = \pm 1$ ). In a type-B or type-C transition, however, the above situations are *not* completely realized because of the selection rule for  $K$  ( $\Delta K = 1$ ). However,  $J_0 \gg K$ , and this implies that the limiting direction of  $\mathbf{J}$  is approached very closely. Table 1 shows the 10 distinguishable cases for the orientations of  $\mu_{abs}$ ,  $\mu_{cm}$  and  $\mathbf{J}$ . Note that cases 1 and 2 correspond respectively, to cases E and F of [6], which are not affected by the present extension. The values of  $R(\tau)$  are listed in table 2 for the two limiting cases of dissociation, direct dissociation

Table 1. Orientation of  $\mu_{\text{abs}}$  and  $\mu_{\text{em}}$  referred to the molecule-fixed frame of the [ABC\*] complex.

Case	Transition	Branch	$(\theta_{\text{abs}}, \phi_{\text{abs}})^\dagger$	$(\theta_{\text{em}}, \phi_{\text{em}})$
1	A type	P, R	(0, a)	$(\frac{1}{2}\pi, 0)$
2	A type	P, R	(0, a)	$(\frac{1}{4}\pi, \frac{1}{2}\pi)$
3	B type	Q	$(\frac{1}{2}\pi, \frac{1}{2}\pi)$	$(\frac{1}{2}\pi, 0)$
4	B type	P, R	$(\frac{1}{2}\pi, \frac{1}{2}\pi)$	$(\frac{1}{2}\pi, 0)$
5	B type	Q	$(\frac{1}{2}\pi, \frac{1}{2}\pi)$	$(\frac{1}{4}\pi, \frac{1}{2}\pi)$
6	B type	P, R	$(\frac{1}{2}\pi, \frac{1}{2}\pi)$	$(\frac{1}{4}\pi, \frac{1}{2}\pi)$
7	C type	Q	$(\frac{1}{2}\pi, 0)$	$(\frac{1}{2}\pi, 0)$
8	C type	P, R	$(\frac{1}{2}\pi, 0)$	$(\frac{1}{2}\pi, 0)$
9	C type	Q	$(\frac{1}{2}\pi, 0)$	$(\frac{1}{4}\pi, \frac{1}{2}\pi)$
10	C type	P, R	$(\frac{1}{2}\pi, 0)$	$(\frac{1}{4}\pi, \frac{1}{2}\pi)$

$\dagger$  For an A-type transition,  $\phi_{\text{abs}}$  is arbitrary and is denoted by 'a'.

( $\tau \rightarrow 0$ ) and the limit of  $\tau \rightarrow \infty$ . In the latter case,  $R(\tau \rightarrow \infty)$  values are evaluated on the basis that  $J_0 \gg K$ , and hence  $\cos \theta_0$  approaches zero.

Intermediate behaviour depends on the values of  $b$  and  $\tau$ . The figure illustrates the behaviour of  $R(\tau)$  for various values of  $b$  in the range  $0 < \tau < \infty$ . Here case 6 is chosen because this case corresponds to the photodissociation of HCN [7]. It should be noted that  $R(\tau)$  approaches a different asymptote for large  $\tau$  according to the value of  $J$  and  $K$ . Other intermediate cases can easily be worked out if desired.

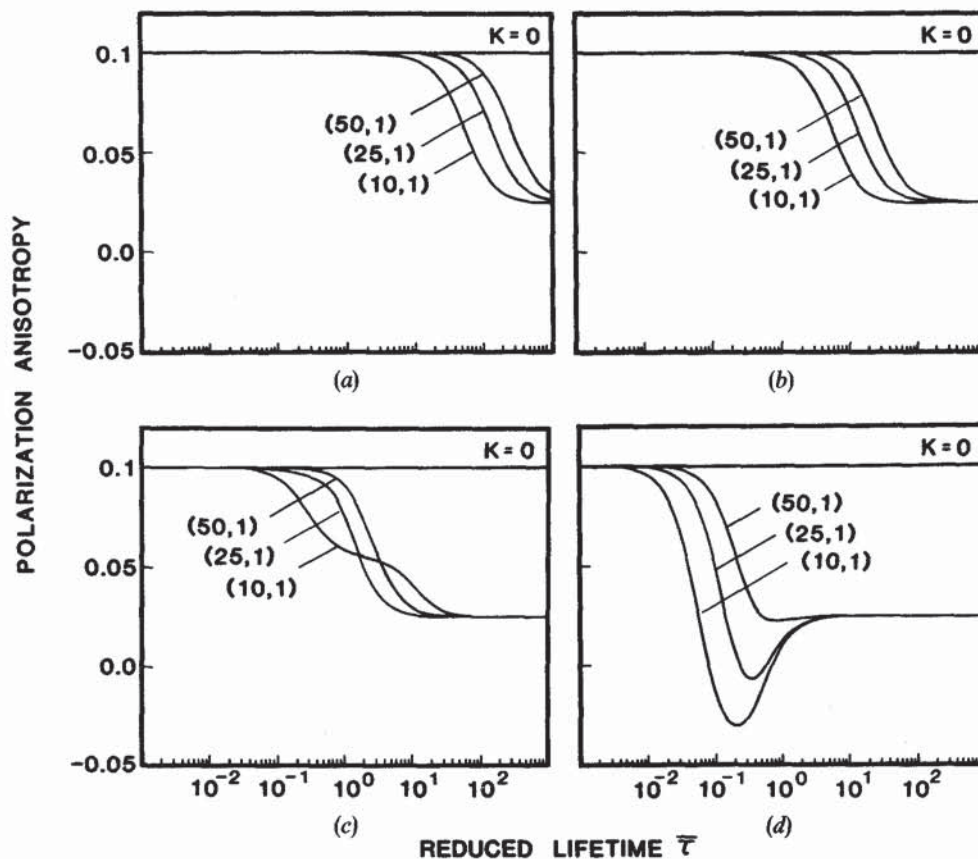
It is also possible to compute the ensemble average, assuming an initial thermal distribution of the ABC precursors. This has been described in [6]. However, the development of VUV coherent light sources as well as the use of multiphoton absorption suggest that future experiments can select individual ( $J, K$ ) levels of the [ABC\*] complex. Such studies will be particularly informative, since, as this paper has shown, measurement of the fluorescence polarization anisotropy may be used to infer the direction of the various transition moments as well as the approximate lifetime of the [ABC\*] complex prior to dissociation.

Table 2.

$(\theta_0, \phi_0)^\dagger$	$R(\tau \rightarrow 0)$	$R(\tau \rightarrow \infty)^\ddagger$
$(\frac{1}{2}\pi/2, u)$	$-\frac{1}{3}$	$-\frac{1}{20}$
$(\frac{1}{2}\pi, u)$	$\frac{1}{10}$	$\frac{1}{40}$
$(\theta, \frac{1}{2}\pi)$	$-\frac{1}{3}$	$-\frac{1}{3}$
$(\theta, 0)$	$-\frac{1}{3}$	$-\frac{1}{3}$
$(\theta, \frac{1}{2}\pi)$	$\frac{1}{10}$	$\frac{1}{10}$
$(\theta, 0)$	$\frac{1}{10}$	$\frac{1}{10}$
$(\theta, 0)$	$\frac{2}{3}$	$\frac{2}{3}$
$(\theta, \frac{1}{2}\pi)$	$\frac{2}{3}$	$\frac{1}{10}$
$(\theta, 0)$	$-\frac{1}{3}$	$-\frac{1}{3}$
$(\theta, \frac{1}{2}\pi)$	$-\frac{1}{3}$	$-\frac{1}{20}$

$\dagger$  For an A-type transition,  $\mathbf{J}$  is uniformly distributed in the ( $x, y$ ) plane, and hence  $\phi_0$  is denoted by 'u'. In other cases, the direction of  $\mathbf{J}$  is well defined, with  $\cos^2 \theta = K^2/J_0(J_0 + 1)$ .

$\ddagger$   $R(\tau \rightarrow \infty)$  values is the limit  $J_0 \gg K$  ( $\cos \theta_0 \rightarrow 0$ ).



Plot of  $R(\tau)$  as a function of  $b$  for various  $(J, K)$  levels for case 6 (see table 1 for definition):  
 (a)  $b = 0.1$ ; (b) 1; (c) 10; (d) 100.

#### References

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