INTERNAL CONVERSION FROM VIBRATIONALLY EXCITED LEVELS

G.S. BEDDARD, G.R. FLEMING, O.L.J. GIJZEMAN and G. PORTER
Davy Faraday Research Laboratory of The Royal Institution, London W1X 4BS, UK

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It is shown that internal conversion to the ground state can become an important pathway of radiationless decay, for molecules in excited vibrational levels. Changes in fluorescence quantum yield as a function of excitation energy have been calculated for the particular case of naphthalene and are found to agree well with experiment.

1. Introduction

The lifetimes [1-3] and fluorescence yields [4, 5] of naphthalene vapour have been shown to decrease with increasing energy of excitation in the pressure region where collisions of excited singlet states may be ignored. The triplet yield has been investigated as a function of pressure by Ashpole et al. [6] and found to be very small in the collision free region ($\phi_T \approx 0.08$). Thus the decrease in $\phi_F$ with excitation energy cannot be due to increasing triplet formation. Quantum yields of chemical change are negligible. Internal conversion to the ground state from high vibronic levels of $S_1$ therefore, seems the only possible explanation, despite clear experimental evidence [7] that internal conversion from the lowest vibrational levels of $S_1$ in solution is an unimportant process in most aromatic hydrocarbons. Benzene seems exceptional in this respect [8]. These findings would be accounted for if the rate of internal conversion increased more rapidly, with increasing vibrational energy, than that of intersystem crossing.

The change in the radiationless rate constant as a function of vibrational energy in the excited state has been studied theoretically by several authors. Fischer and Schlag [9] and Fischer et al. [10] concerned themselves with $\beta$-naphthylamine and naphthalene respectively. In both cases the radiationless rate constant for intersystem crossing was found to increase with increasing vibrational energy in the excited state. For a large energy gap these authors regard increasing the vibrational energy as being equivalent to decreasing the energy gap between the two states involved [10]. In the theory of Fischer and Schlag rapid intramolecular vibrational redistribution is assumed. Other authors [11-15] have derived expressions for the decay of single vibronic levels, i.e., assuming slow vibrational redistribution. All these authors, with the exception of Brailsford and Chang [11] considered the problem of intersystem crossing in benzene. Although their quantitative conclusions vary (see ref. [14] for comparison) the calculations all predict an increase of the intersystem crossing rate as vibrational energy in $S_1$ is increased.

In this note we wish to emphasise the possible importance of internal conversion to the ground state, as a means of radiationless decay for higher vibronic levels. It will be shown that, for a reasonable choice of molecular parameters, internal conversion increases more rapidly than intersystem crossing, and thus becomes a significant process from higher vibronic levels of $S_1$.

In aromatic hydrocarbons only the C-C and C-H totally symmetric stretching modes show significant displacements of their potential surfaces on excitation [16]. Thus only these modes will contribute significantly to the vibrational overlap integrals†. Therefore we have examined the variation of the Franck-Condon factors for these modes.

* Present address: Physical Chemical Laboratory, South Parks Road, Oxford, UK.
† Unless one (or more) of the undisplaced modes has a large frequency change between the two electronic states.
modes as a function of the upper state quantum number, and the electronic energy gap. Most previous work has been concerned with vibrationally relaxed excited states and the trends to be expected were not clear from the literature.

2. Franck-Condon factors

For a vibration, \( \alpha \), with identical frequencies in the two electronic states involved, the Franck-Condon factor is given by [14]

\[
| \langle m_a | n_a \rangle |^2 = \exp(-X_a) \left( \frac{1}{m_a} \right)^{1/2} X_a^{n_a-m_a} \left(L_{m_a}^{n_a-m_a}(X_a)\right)^2.
\]

(1)

Here \( m_a \) and \( n_a \) are the upper and lower state quantum numbers, \( X_a \) is the dimensionless displacement of equilibrium position between the two states, and \( L_{m_a}^{n_a-m_a} \) is the generalised Laguerre polynomial [17].

\[ X_a = \frac{1}{2} M_a \omega_a / h (\Delta Q_a)^2, \]

where \( M_a \) is the effective mass of the \( \alpha \) th mode and \( \Delta Q_a \) is the shift in equilibrium position between the upper and lower electronic states.

The Franck-Condon factor for frequency shifted and displaced harmonic oscillators has been given by Burland and Robinson [18]. In their equation (7) the argument of one of the Hermite polynomials will always be complex, but their equation can be rewritten for the two cases \( f_a = \omega_a / \omega_a' > 1 \) or \( f_a < 1 \) (the prime refers to the upper state).

\[
\begin{align*}
\langle m_a | n_a \rangle &= \left( \frac{2 f_a^{1/2}}{1 + f_a} \right)^{1/2} \left( \frac{1}{n_a! 2^{n_a}} \right)^{1/2} \left( \frac{1}{m_a! 2^{m_a}} \right)^{1/2} \exp \left[ -X_a \left( \frac{f_a}{1 + f_a} \right) \right] \sum_l (l! - 1)^{-1} \frac{m_a!}{(m_a - l)!} \frac{n_a!}{(n_a - l)!} \left( \frac{4 f_a^{1/2}}{1 + f_a} \right) \\
&\times \left( \frac{1 - f_a}{1 + f_a} \right)^{(m_a + n_a)/2 - l} \left( \frac{2 X_a}{1 - f_a^2} \right)^{1/2} \left( \frac{2 X_a f_a}{1 - f_a^2} \right)^{1/2} \left( \frac{2 X_a f_a}{1 - f_a^2} \right)^{1/2}, \quad f_a < 1;
\end{align*}
\]

and

\[
\begin{align*}
\langle m_a | n_a \rangle &= \left( \frac{2 f_a^{1/2}}{1 + f_a} \right)^{1/2} \left( \frac{1}{n_a! 2^{n_a}} \right)^{1/2} \left( \frac{1}{m_a! 2^{m_a}} \right)^{1/2} \exp \left[ -X_a \left( \frac{f_a}{1 + f_a} \right) \right] \sum_l (l! - 1)^{-1} \frac{m_a!}{(m_a - l)!} \frac{n_a!}{(n_a - l)!} \left( \frac{4 f_a^{1/2}}{1 + f_a} \right) \\
&\times \left( \frac{1 - f_a}{1 + f_a} \right)^{(m_a + n_a)/2 - l} \left( \frac{2 X_a f_a}{1 - f_a^2} \right)^{1/2} \left( \frac{2 X_a f_a}{f_a^2 - 1} \right)^{1/2} \left( \frac{2 X_a f_a}{f_a^2 - 1} \right)^{1/2}, \quad f_a > 1;
\end{align*}
\]

\[ F_n(x) = i^n H_n(ix) = -2 x F_{n-1}(x) + 2(n - 1) F_{n-2}(x). \]

(2)

It is seen that these two equations involve only real quantities\(^\dagger\). A useful check on Franck-Condon factor calculations is to take the sum over \( n_a \) for a reasonable number of terms of \( | \langle m_a | n_a \rangle |^2 \) and to see how closely this sum approaches unity. This test was first suggested by Manneback [19]. Generally, using eqs. (1) and (2) sums differing from unity by \( 10^{-10} \) were obtained.

\(^\dagger\) This is the same formula as eq. (3.14) of ref. [14], but in ref. [14] there are some typographical errors. Also table 2 of that reference is incorrect. The ratios in table 1 are only slightly affected.
Table 1

Variation of Franck-Condon factors with upper state quantum number

<table>
<thead>
<tr>
<th>C-H vibrations</th>
<th>C-C vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁ - S₀</td>
<td>S₁ - T₁</td>
</tr>
<tr>
<td>Xₐ = 0.044, fₐ = 1.02</td>
<td>Xₐ = 0.002, fₐ = 0.97</td>
</tr>
<tr>
<td>mₐ</td>
<td>nₐ</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

F(S₁-15) = 2.7 × 10⁻³
F(0-10) = 5.8 × 10⁻⁴
F(0-7) = 9.3 × 10⁻²

For a 3000 cm⁻¹ C-H mode ten quanta are sufficient to make up the electronic energy gap S₁-S₀ in naphthalene (32020 cm⁻¹), and thus the series 0–10, 1–11, ... will involve approximately isoenergetic levels. The S₁-T₁ gap is 10720 cm⁻¹ and so in this case the series 0–3, 1–4, ... is appropriate. For a 1500 cm⁻¹ C-C mode the appropriate series are 0–21, 1–22, ... (S₁–S₀) and 0–7, 1–8, ... (S₁–T₁). The result of typical calculations of Franck-Condon factors for this series of levels is shown in table 1. The general conclusion for both kinds of vibration is the same. Although much smaller in absolute magnitude, the Franck-Condon factors for the large energy gap (S₁–S₀) increase much more rapidly with increasing quantum number in S₁, than do the S₁–T₁ Franck-Condon factors. This is in disagreement with the conclusions of Ware et al. [20].

From this preliminary calculation it seems reasonable to infer that internal conversion will increase more rapidly with increasing vibrational energy than will intersystem crossing. This model, however, may not be a very realistic one. An improved model has been proposed by Heller et al. [14] and will be discussed in the next section.

3. The radiationless transition rate

Considering only totally symmetric C-C and C-H modes, the nonradiative rate can be written, in the harmonic approximation and assuming the statistical limit as [14, 21]

\[
k_{S \rightarrow T} (m_a) = \frac{(2\pi)^{1/2}}{\hbar^2} \beta^2 n_a \exp \left\{ -\frac{\Delta E_k^{n_a} / \hbar \omega_m}{\gamma_{n_a}} \right\},
\]

with

\[
b_{n_a} = (\omega_m \Delta E_k^{n_a} / \hbar)^{1/2}, \quad \gamma_{n_a} = \log \left( \Delta E_k^{n_a} / \sum_{m=1}^{d} X_m \hbar \omega \right)^{-1},
\]

\[
\Delta E_k^{n_a} = \Delta E - \hbar \omega_k^{(t)} + m_a \hbar \omega_a^{(S)} - n_a \hbar \omega_a^{(t)} + \sum \hbar / 2 \left( \omega_j^{(S)} - \omega_j^{(t)} \right)
\]

\[
\Delta E = E_0^{S} - E_0^{T}.
\]

Here \(a\) is the optical mode excited with \(m_a\) quanta, \(\omega_k\) is the promoting mode, \(\omega_m\) is the frequency, \(X_m\) the displacement and \(d\) the number of (nearly) degenerate, totally symmetric C-H modes. In benzene \(d = 1\), in naphthalene \(d = 2\). The final state, \(I\), can be either \(T_1\) or \(S_0\).
When relative rates of the form $k(m_a)/k(0)$ are considered, the constants and $\beta^2$, the electronic matrix element (assumed constant with vibrational energy) can be removed. Since we are interested only in qualitative trends we have calculated rates for $m_a$ values up to 10, although the harmonic approximation is not expected to be quantitatively valid for values of $m_a > 4$.

For the calculations on naphthalene, the ground state vibrational frequencies were taken from Hollas [22], frequencies in $S_1$ from Craig et al. [23], and the normal coordinate analysis of Freeman and Ross [24] was used to identify vibrations with particular nuclear motions. We have calculated rates of intersystem crossing and internal conversion for progressions in two totally symmetric skeletal stretching modes $a_g (4)$ ($\omega_{S_0} = 1460 \text{ cm}^{-1}$, $\omega_{S_1} = 1435 \text{ cm}^{-1}$) and $a_g (7)$ ($\omega_{S_0} = 1025 \text{ cm}^{-1}$, $\omega_{S_1} = 987 \text{ cm}^{-1}$). The displacements for $S_1 - S_0$ were taken from the estimates of Byrne et al. [16] and Siebrand [15]. For $S_1 - T_1$ the displacements were estimated from those given in ref. [14] for benzene. The promoting mode frequency for internal conversion was taken as 1000 cm$^{-1}$.

Relative rates are rather insensitive to the precise value of the promoting mode [14].

The results of some representative calculations are shown in figs. 1 and 2.

The parameters with the largest uncertainties are the displacements and optical frequency in the triplet state. For reasonable choices of these parameters, internal conversion can increase as much as 20 times more than intersystem crossing for excess vibrational energies between 0 and 10000 cm$^{-1}$. In the curves in figs. 1 and 2 we have made the reasonable assumption that $\omega_{T_1} - \omega_{S_1} < \omega_{S_0} - \omega_{S_1}$. If $\omega_{T_1} - \omega_{S_1} > \omega_{S_0} - \omega_{S_1}$, the rates for internal conversion and intersystem crossing increase at approximately equal rates. But even when $\omega_{T_1} = \omega_{S_1}$ the rate for internal conversion still increases slightly more rapidly than $k(m_a)$ for intersystem crossing.

![Fig. 1. Calculated ratios, $k(m_a)/k(0)$, of the radiationless rate constants for internal conversion and intersystem crossing.](image-url)
Fig. 2. Calculated ratios, $k(m_a)/k(0)$, of the radiationless rate constants for internal conversion and intersystem crossing, as a function of the upper state quantum number ($m_a$), for the $a_g(7)$ 987 cm$^{-1}$ vibration. Parameters: Curve A ($S_1\rightarrow S_0$) $X_a = 0.1, f_a = 1.0385, X_m = 0.044$. Curve B ($S_1\rightarrow T_1$) $X_a = 0.025, f_a = 1.01, X_m = 0.001$. Curve C ($S_1\rightarrow T_1$) $X_a = 0.025, f_a = 0.97, X_m = 0.002$.

4. Discussion

Although we have calculated radiationless rates as a function of two progressions, in reality the 3200Å band of naphthalene shows no progressions with significant intensity in more than two members [23]. Also above 3890 cm$^{-1}$ of excitation in $S_1$, $S_2$ will be optically populated [25]. Although it seems reasonable to assume that $S_2$ undergoes rapid internal conversion to $S_1$ [4, 26] the resulting states in $S_1$ will not represent any single progression in one mode. However, increasing the excess vibrational energy will always result in an increased population of some vibrational modes. The radiationless rate constant of each of these modes will then be enhanced, giving, at least qualitatively, the effects discussed above. Since the calculations are most easily done for progressions of some mode and considering the approximations inherent in eq. (3), we feel that our present approach is realistic and should at least give qualitatively correct results.

The ratio of $\beta_{S_1\rightarrow S_0}^2$ and $\beta_{S_1\rightarrow T_1}^2$ has been variously given as $10^6$ (Kasha), $10^8$ [18, 27] and $10^{10}$ [18]. Table 2 shows values for the ratio $k_{S_1\rightarrow T_1}(0)/k_{S_1\rightarrow S_0}(0)$, calculated without the factor $[(2\pi)^{1/2}/\hbar^2] \beta^2$, for different values of $X_m$. It can be seen that the absolute value of the rate is very sensitive to the value of the C–H displacement but for reasonable values of $X_m$, the ratio $k_{S_1\rightarrow T_1}(0)/k_{S_1\rightarrow S_0}(0)$ is $10^6-10^8$. Thus it seems reasonable to suppose that the actual internal conversion and intersystem crossing rates are of comparable orders of magnitude. In table 2 $f_a$ and $X_a$ have been kept constant. These two parameters have little effect on the absolute magnitude of the rate (but a very strong effect on the rate of increase of $k(m_a)$ as a function of $m_a$).

Apparently one serious shortcoming of the present theory is its failure to account for the absolute magnitude of the observed rates. Multiplying the values in table 2 by the appropriate constants $[(2\pi)^{1/2}/\hbar^2] \beta^2$ yields rates of approximately 1 sec$^{-1}$, for both intersystem crossing ($\beta = 1$ cm$^{-1}$) and internal conversion ($\beta = 10^4$ cm$^{-1}$).
Table 2

<table>
<thead>
<tr>
<th>( X_m )</th>
<th>( X_m )</th>
<th>( k_{S_1-T_1}(0) )</th>
<th>( k_{S_1-S_0}(0) )</th>
<th>( k_{S_1-T_1}(0) )</th>
<th>( k_{S_1-S_0}(0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.044</td>
<td>0.001</td>
<td>( 4.8 \times 10^{-24} )</td>
<td>( 2.6 \times 10^{-32} )</td>
<td>( 1.8 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>0.088</td>
<td>0.002</td>
<td>( 3.9 \times 10^{-23} )</td>
<td>( 2.6 \times 10^{-29} )</td>
<td>( 1.5 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.001</td>
<td>( 4.8 \times 10^{-24} )</td>
<td>( 1.2 \times 10^{-38} )</td>
<td>( 4.0 \times 10^6 )</td>
<td></td>
</tr>
</tbody>
</table>

Table 3

Comparison of observed and calculated changes in the fluorescence quantum yield, \( \phi_F \), refers to the fluorescence quantum yield of the lowest vibrational level, \( \phi_F^{\prime} \), to the yield from levels with 10000 cm\(^{-1}\) of excess energy.

<table>
<thead>
<tr>
<th>( \phi_F )</th>
<th>( \phi_F^{\prime} )</th>
<th>( \phi_F/\phi_F^{\prime} )</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.06</td>
<td>3.4</td>
<td>4.0</td>
</tr>
<tr>
<td>0.65</td>
<td>--</td>
<td>--</td>
<td>2.0</td>
</tr>
<tr>
<td>0.92</td>
<td>&lt;0.23</td>
<td>&gt;4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Since these values must be considered upper limits a serious discrepancy exists between the observed (10\(^7\) sec\(^{-1}\)) and calculated rates. Including anharmonicities may change the Franck–Condon factor considerably \([18]\) (C–H Franck–Condon factors can be increased by as much as 10\(^3\)). However, these effects are difficult to include in the present model. Anharmonicities in the optical mode are not expected to be very important, since the rate determining Franck–Condon factors are already fairly large (0.1–0.9). As far as relative rates are concerned we feel that the present approach should give reliable results.

We can now investigate, for the isolated molecule, the effect on the fluorescence quantum yield, of the changes in intersystem crossing and internal conversion rate constants predicted by our calculations. For the lowest levels (310 nm) in the isolated molecule, \( \phi_F \) has been variously reported as 0.21 \([4]\), 0.65 \([28]\), and 0.92 \([5]\). The lifetime of the lowest levels, in the isolated molecule, is approximately 420 nsec \([28]\). In cyclohexane solution the lifetime is 120 nsec \([29]\). This implies that in solution the radiationless decay of the lowest vibrational state is enhanced in agreement with the arguments of Beddard et al. \([3, 5, 30]\) who proposed a collision dependent rate of intersystem crossing \( k_T \). Setting \( k_C \) (the rate of internal conversion) equal to \((1/10) k_T\), in solution, we arrive at \( k_C = (1/3) k_T \) for the lowest level of the isolated molecule.

Using the relation

\[
\phi_F = \frac{k_F}{(k_F + k_C + k_T)},
\]

where \( k_F \) is the radiative rate constant, the quantum yield decrease between zero and 10000 cm\(^{-1}\) of excess energy was calculated. The variation in \( k_F \) with excitation energy was taken from refs. \([4, 5]\), and the changes in \( k_T \) and \( k_C \) from figs. 1 and 2. The results are compared with the experimental values in table 3.

It can be seen that an increase of the internal conversion rate by approximately 30 times over an excess energy range of 10000 cm\(^{-1}\) is able to account for the observed decrease in the quantum yield (and lifetimes) as the excitation energy is increased.

The above considerations are likely to be of importance in the internal conversion of other large molecules. They may also be important at higher pressures and in condensed phases, where the Boltzman population of the upper vibrational levels would be expected to lead to increased rates of internal conversion at higher temperatures and consequently to lowered yields of fluorescence and of intersystem crossing. Further work along these lines is in progress in this laboratory.

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References