THE FLUORESCENCE LIFETIME OF TETRACENE VAPOUR

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Received 23 October 1974

The fluorescence lifetimes of tetracene vapour as a function of excess vibrational energy in the first excited singlet state have been measured under collision free conditions. A very marked decrease in lifetime with increasing energy has been observed. We attribute this behaviour to enhanced internal conversion from vibrationally excited levels.

1. Introduction

The study of the vibrational energy dependence of radiative and radiationless processes has been a rich field for experiment and theory alike [1-8]. Although a good deal of progress has been made in both areas, there are many aspects of the problem which remain unclear. One of the most important of these aspects is the relative importance of internal conversion and intersystem crossing in determining the lifetime of the higher vibrational levels of the excited singlet state. From a theoretical point of view the problem seems insoluble at present because no accurate values of the electronic matrix elements for internal conversion and intersystem crossing have yet been calculated [9]. Consequently, theoretical calculations of radiationless transition rates have concentrated on the vibrational part of the problem and much effort has been put into calculations of Franck-Condon factors and densities of vibrational levels either separately [10,11] or, more recently, as weighted sums [2]. It is found both experimentally and theoretically that the rate of radiationless processes usually increases with increasing vibrational energy content of the excited singlet state. This has been explained [2,7] in terms of the increasing ability of the optical (totally symmetric) C-C modes to act as accepting modes as the vibrational energy content of the molecule is increased.

Two general conclusions from this work have appeared: (a) for large energy gap transitions the radiationless rate is a very sensitive function of vibrational energy whereas, for smaller energy gap transitions the energy dependence of the radiationless rate is not as marked [2,5,6]; (b) when the C-C displacement [11] between the two states involved in the transition is very small, the rate of the radiationless transition will be insensitive to the vibrational energy content of the molecule [7]. This second conclusion was used, along with earlier work on the energy dependence of radiative rates, to explain the insensitivity of anthracene fluorescence lifetime and quantum yield to excess vibrational energy [7]. Molecular orbital theory calculations suggest that the C-C bond lengths in S1 and T1 of anthracene should be almost identical [13]. Indeed, simple Hückel theory would predict zero displacement since S1 and T1 are of L2 symmetry in this case. The C-C displacement between S1 and T1 should be small in all aromatic hydrocarbons where S1 has L4 symmetry. Thus it should be possible to distinguish between internal conversion and intersystem crossing by a study of the wavelength dependence of the fluorescence lifetime under isolated molecule conditions.

Tetracene is a very interesting candidate for a study of this kind since, like anthracene, the S1 state has L2 symmetry so that little or no energy dependence of intersystem crossing would be expected. Also Kearvell and Wilkinson [14] have shown that a significant amount of internal conversion (\( \Phi_{IC} = 0.2 \)) occurs in tetracene, in ethanol and benzene solutions, at room temperature.
2. Experimental

The fluorescence decays were measured using the time-correlated single photon counting method [15, 16]. The light source used was a conventional high pressure free running spark source operating at 30 kV. The lamp filling was oxygen at a pressure of 4–5 atmosphere. This lamp was used for these experiments instead of the generally more useful thyatron-gated low pressure lamp [16] for two reasons: (a) the higher source intensity more than compensated for the lower repetition frequency (typically 2–3 kHz), since the maximum fluorescence photon collection rate possible with the free running source rarely approached a value where “pulse pile-up” became a problem (i.e., the ratio of stop to start rates was < 1%); (b) the emission spectrum of the high pressure lamp is significantly enhanced compared with the low pressure source, in the spectral region > 380 nm. The monochromator was an F/4 symmetrical Czerny Turner instrument (Applied Photophysics Ltd.). In all experiments the spectral bandpass was 5 nm and the detection system was similar to that previously described [16]. Time-base calibration was achieved using a commercial time-calibrator (Ortec 462) which uses a crystal oscillator as internal standard. This calibration was checked using standard delay lines.

When measuring lifetimes of < 10 ns it has been found that small amounts of scattered exciting light produce a marked reduction of the measured decay time without noticeably altering the deconvoluted decay function shape (i.e., deviations from exponentiality are negligible) [17]. This behaviour results from scattered light being predominantly detected in those channels of the MCA where the fluorescence intensity is a maximum and hence that portion of the decay where Poisson weighted fitting procedures are most sensitive. For this reason the emission from the tetracene was extensively filtered using a combination of a Corning 3-71 and a Schott BG12 filter. The 3-71 filter was found to fluoresce strongly with a short lifetime which for the reasons described above would induce serious errors in the measured lifetimes. The BG12 filter effectively removed this fluorescence. To remove further the scattered light the sample was sealed in a blacked quartz Woods horn. The Woods horn was evacuated and filled in a conventional mercury free and greaseless vacuum line at 10⁻⁴ torr. The temperature of the Woods horn was controlled using a double oven arrangement to avoid crystallisation of the tetracene on the cell windows. The temperatures of the ovens were 190 ± 1°C in the optical portion and 170 ± 1°C in the lower stem which corresponds to a pressure of tetracene of 0.05 torr [18]. At this pressure the tetracene can be considered to be “collision free” during its excited state lifetime.

3. Results and discussion

The exponential fluorescence decay times of tetracene vapour as a function of excitation wavelength are shown in Table 1. These lifetimes were extracted from the observed decay by convolution with the instrumental response function [16]. The data show a rapid decrease in the fluorescence lifetime as the excess vibrational energy content of the molecule is increased. In fact, the decrease in lifetime of tetracene, with excess energy, is more rapid than for any of the polycyclic aromatic hydrocarbons previously studied [7]. This is illustrated in fig. 1.

In order to explain these observations it is necessary to consider the energy dependence of the radiative and non-radiative decay rates. There was no evidence for permanent photochemical product formation. Reversible isomerisation cannot be ruled out. There is, however, no evidence for the occurrence of such processes in polyacenes. It seems extremely unlikely that the decrease in lifetime could be caused by a rapidly increasing radiative rate since for a symmetry allowed radiative transition (such as $S_1 \rightarrow S_0$ in tetracene), the radiative rate is expected to be very in-

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**Table 1**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Excess energy (cm⁻¹)</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0</td>
<td>5.5 a)</td>
</tr>
<tr>
<td>427</td>
<td>1197</td>
<td>4.1</td>
</tr>
<tr>
<td>422</td>
<td>1474</td>
<td>2.5</td>
</tr>
<tr>
<td>398</td>
<td>2903</td>
<td>2.3</td>
</tr>
<tr>
<td>377</td>
<td>4303</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a) This value is possibly shorter than the true lifetime because of transmissio of exciting light through the filters (see experimental section).
The sensitive to the vibrational energy content of the excited state. This is confirmed in the case of anthracene, where both lifetimes [7, 19] and quantum yields [4] are reported to be independent of exciting wavelength in S₁. However, even if the radiative rate does change with excess energy, this change will produce an increase in the lifetime with increasing vibrational energy [3] because the optical mode vibrational frequency is lowered on excitation to S₁ [18]. This behaviour is the reverse of the experimental observations.

The S₁ → T₁ intersystem crossing rate should also show little or no excess dependence because, in tetracene, both S₁ and T₁ are of L₂ symmetry thus the C-C displacement is expected to be very small [7]. Therefore the ability of the totally symmetric C-C vibrations to act as accepting modes in T₁ will be independent of the degree of vibrational excitation in S₁ [7]. The small energy gap between S₁ and T₁ etc. seems to rule out the possibility of significant energy dependence of intersystem crossing via this route [3, 6, 20, 21]. Further, no step function change in the lifetime is observed, in contrast with the results of Laor et al. for anthracene [19]. These authors attribute this behaviour to the onset of intersystem crossing to higher triplet states. This interpretation has recently been criticised by Fischer and Lim [4] who argue that changes in the vibrational distribution of S₁ following S₁ → S₀ internal conversion are responsible for the effect.

We have previously shown that S₁ → S₀ internal conversion should increase very rapidly with increasing excess energy [6]. This conclusion has recently been confirmed by other workers [5, 22]. The C-C displacement between S₁ and S₀ must be significant in tetracene since the absorption spectrum shows a moderately extensive totally symmetric C-C progression [18]. This displacement will favour a rapid increase in S₁ → S₀ internal conversion with increasing excess energy [6, 7]. Although it is not yet possible to calculate the absolute magnitude of non-radiative rates [6, 10], if the Boltzmann population of S₁ shows significant internal conversion then there seems little doubt that, at higher excess energies, internal conversion will be the dominant decay route [5, 6]. Kearvell and Wilkinson [14] have shown that tetracene in ethanoll and benzene solution undergoes a measurable amount of internal conversion (ΦINC ≈ 0.2) in contrast with the other molecules shown in fig. 1, for which ΦINC + ΦΦ ≈ 1 [23]. Also Siebrand and Williams [24] have predicted that tetracene will show significant S₁ → S₀ internal conversion in solution.

We therefore conclude that the results shown in table 1 are attributable to the rapid excess energy dependence of internal conversion. We believe that these results represent the first direct measurement of the energy dependence of internal conversion for an aromatic molecule.

Acknowledgement

We thank Dr. David Phillips for the loan of the Corning Filter and Mr. Christopher Buckley for technical assistance. Graham R. Fleming thanks S.R.C. and Colin Lewis thanks Applied Photophysics for financial support.
References