

Fluorescence and Nonradiative Decay of Anthracene in Crystal and Solution

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4.5 ± 0.3 . For Cs^+ in NaNO_3 the same value as we have given (4.7 ± 0.3) is reported both by Kwak and Ketelaar and by Lantelme. Another comparison may be made for Na^+ in LiNO_3 , where our value is 4.2 ± 0.4 while Kwak and Ketelaar report 3.6 ± 0.2 compared with the value 4.4 ± 0.6 given by Lantelme.

The most striking information one gets from Table V is that all the apparent activation energies are very similar, especially if the errors are taken into account, although there is quite a difference between both the size and mass of the cations from one system to the other. This fact indicates the close equivalence of the potentials acting between the ions to restrict their diffusional migration in these molten salts.

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Fluorescence and Nonradiative Decay of Anthracene in Crystal and Solution*

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The marked decrease in fluorescent quantum yield of anthracene in going from crystal to solution is discussed theoretically. The relative importance of direct and indirect radiationless transitions from the excited singlet to the triplet manifold is calculated using a simple model.

I. INTRODUCTION

The marked increase in the intersystem-crossing rate for the fluorescing state of anthracene in going from crystal to solution is well known. The fluorescence yield ϕ_F changes from ~ 0.3 in solution to ~ 1.0 in the crystal. A nearby triplet state has been suggested as an explanation of this effect. Kellogg¹ confirmed the fact that in solution the second triplet of anthracene is $\sim 600 \text{ cm}^{-1}$ below the first singlet, (S_1), whereas in the crystal the order is reversed and T_2 is $\sim 600 \text{ cm}^{-1}$ above S_1 .² Kellogg suggested that this level inversion renders the $S_1 \rightarrow T_2$ process less probable in the crystal since the vibrationally relaxed S_1 state cannot decay to T_2 on energy considerations. Bixon and Jortner³ have considered this explanation in the context of their theory of radiationless transitions; however, the situation is more complicated than their analysis suggests, and we have thus re-examined the problem. A recent investigation⁴ of the deuteration effect on radiationless transitions contains much of the essentials of the model we will consider, but in the present work we will focus on the $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ ⁵ nonradiative routes and their relative importance in various cases. We will be considering nonradiative processes from the vibrationally relaxed S_1 state only.

II. MODEL

Consider the following zeroth-order model: The first singlet, S_1 , and second triplet, T_2 , are nearly degenerate states which are embedded in a dense manifold of highly excited vibronic levels of the first triplet T_1 . (We assume that the $S_1 \rightarrow S_0$ process is not important for internal conversion because of the relatively large energy gap.) The zeroth order vibronic states are eigensolutions of the "crude" adiabatic approximation.⁶ We consider the following set of states: ϕ_S , the lowest vibrational state of S_1 ; $\{\phi_T\}$, a small set of vibronic levels of T_2 (i.e., the lowest and first few vibrational states of T_2); the dense manifold of vibrationally excited states of T_1 , $\{\phi_i\}$, which are equally spaced in energy with spacing ϵ . (The density of states ρ_i is thus ϵ^{-1} .) The residual interaction between these states consists of spin-orbit interaction (between ϕ_S and $\{\phi_T\}$ and between ϕ_S and $\{\phi_i\}$) and vibronic interaction (between $\{\phi_T\}$ and $\{\phi_i\}$).^{3,6} For the cases we will consider, the manifold $\{\phi_i\}$ has two disjoint subsets: one of which interacts with ϕ_S through spin-orbital coupling and one of which interacts with $\{\phi_T\}$ via vibronic coupling. (This occurs because we will consider molecules with inversion symmetry. The states and the operators

of interest are such that these two subsets are those of g and u symmetry.) We will thus label those states of $\{\phi_i\}$ which interact with ϕ_S as $\{\phi_i'\}$ and those which interact with $\{\phi_T\}$ as $\{\phi_i''\}$. However, we will assume for simplicity that the vibrational overlap density between $\{\phi_i'\}$ and $\phi_S(\phi_T)$ is equal to that between $\{\phi_i''\}$ and $\phi_T(\phi_S)$.

The model assumes the following very simple form for the matrix elements of H (the total molecular Hamiltonian):

$$\langle \phi_S | H | \phi_T \rangle \equiv V_{ST} S_{ST} = v_{ST} S_{ST}, \quad (1a)$$

$$\langle \phi_S | H | \phi_i' \rangle \equiv V_{Si'} S_{Si'} = v_{Si'} S_{Si'}, \quad (1b)$$

$$\langle \phi_T | H | \phi_i'' \rangle \equiv V_{Ti''} S_{Ti''} = v_{Ti''} S_{Ti''}, \quad (1c)$$

where $v_{S,T}$, $v_{S,i}$, and $v_{T,i}$ are electronic terms and $S_{S,T}$, $S_{S,i}$, and $S_{T,i}$ are vibrational overlap factors. Now, Eq. (1b) is the relevant matrix element for the $S_1 \rightarrow T_1$ (direct) nonradiative process; (1a) and (1c) are the relevant matrix element for the $S_1 \rightarrow T_2 \rightarrow T_1$ (indirect) nonradiative process.

We first deal with the case in which only one of these two processes is operative. If only the direct process is operative, then we may calculate the rate ($K_{S_1 \rightarrow T_1}$) of this process³ as

$$K_{S_1 \rightarrow T_1} = (2\pi/\hbar) v_{Si'}^2 S_{Si'}^2 \rho_i'. \quad (2)$$

The description of the indirect process is more complicated. We assume that $V_{S,i} = 0$ and just consider the indirect process. Then we have the situation of a discrete state, ϕ_S , interacting with $\{\phi_T\}$ which is broadened by interaction with $\{\phi_i''\}$. We diagonalize the Hamiltonian in two steps: First we diagonalize the triplet part of the Hamiltonian matrix, then we diagonalize the resulting matrix. The states which diagonalize the *triplet* block are

$$\psi_J = \sum_T a_{JT} \phi_T + \sum_i b_{Ji''} \phi_i''.$$

In the case in which the widths of the broadened ϕ_T states are much smaller than the separation between ϕ_T states, we can consider each ϕ_T state interacting with $\{\phi_i''\}$ independently. This is the approach we take in the present case, and so the a_{JT} can be found as the solution to the isolated resonance model.² Now, the ϕ_S interacts with the $\{\psi_J\}$ through spin-orbit interaction,

$$V_{SJ} = \langle \phi_S | H | \psi_J \rangle = \sum_T a_{JT} \langle \phi_S | H | \phi_T \rangle. \quad (3)$$

In the case in which ϕ_S is almost degenerate with one of the $\{\phi_T\}$ or in the case in which one of the matrix elements, $\langle \phi_S | H | \phi_T \rangle$, is dominant, then only one term need be considered in the above sum. Thus

$$V_{SJ} \approx a_{JT} V_{ST} S_{ST}. \quad (4)$$

If the above approximations are not valid, the problem becomes more complex. In the interest of simplicity

we will consider the simplest case. Thus the rate of $S_1 \rightarrow T_2 \rightarrow T_1$ ⁵ (indirect) process is given by

$$K_{S_1 \rightarrow T_2} = (2\pi/\hbar) V_{ST}^2 \rho_J. \quad (5)$$

We make the assumption that $\rho_J = \rho_i''$. From the isolated resonance theory, we have

$$|a_{JT}(E_J)|^2 = |V_{Ti''} v_{ib}|^2 / [\frac{1}{4} \Delta_T^2 + (E_J - E_T)^2], \quad (6)$$

where

$$\Delta_T = 2\pi |V_{Ti''} v_{ib}|^2 \rho_i''. \quad (7)$$

Thus,

$$K_{S_1 \rightarrow T_2} = \frac{2\pi |V_{Ti''} v_{ib}|^2 \rho_i'' |V_{ST} S_{ST}|^2}{\hbar [\frac{1}{4} \Delta_T^2 + (E_S - E_T)^2]} = \hbar^{-1} \Delta_T |V_{ST} S_{ST}|^2 [\frac{1}{4} \Delta_T^2 + (E_S - E_T)^2]^{-1}, \quad (8)$$

where we have put $E_J = E_S$ since the $\{\phi_J\}$ states close in energy to ϕ_S are the most important in this process.

We may now calculate the ratio of the two processes,

$$\frac{K_{S_1 \rightarrow T_2}}{K_{S_1 \rightarrow T_1}} = \frac{|V_{Ti''} v_{ib}|^2 |V_{ST} S_{ST}|^2}{|V_{Si'} S_{Si'}|^2 [\frac{1}{4} \Delta_T^2 + (E_S - E_T)^2]}, \quad (9)$$

where we have assumed that $\rho_i' \approx \rho_i''$. Using Eq. (1) and assuming for an order of magnitude estimate that $v_{S,T} \approx v_{S,i}$ (both are *electronic* spin-orbit matrix elements) and also assuming that $S_{S,i}^2 \approx S_{T,i}^2$, we find

$$K_{S_1 \rightarrow T_2} / K_{S_1 \rightarrow T_1} \approx v_{Ti''}^2 S_{ST}^2 / [\frac{1}{4} \Delta_T^2 + (E_S - E_T)^2]. \quad (10)$$

In the limit that $\frac{1}{2} \Delta_T > (E_S - E_T)$ (near degeneracy of ϕ_S and ϕ_T), we find

$$K_{S_1 \rightarrow T_2} / K_{S_1 \rightarrow T_1} \approx 4v_{Ti''}^2 S_{ST}^2 / \Delta_T^2 \approx S_{ST}^2 / S_{Ti''}^2 \rho_i'' \Delta_T. \quad (11)$$

Since $S_{S,T}^2$ is of the order of 0.1–1 and $\rho_S S^2 \Delta$ (the square of the *overlap per vibronic linewidth* at $\sim 11\,000$ cm^{-1} above T_1) can be estimated from the work of Robinson⁷ to be $\sim 10^{-3}$ for $V_{Ti''} \approx 100$ – 1000 cm^{-1} , then $K_{S_1 \rightarrow T_2}$ will be much greater than $K_{S_1 \rightarrow T_1}$ in the case of near degeneracy of ϕ_S and ϕ_T . Notice that the approximate result (11) is independent of the *ratio* of the matrix elements in contrast to the results of Bixon and Jortner.³

In the case in which $(E_S - E_T) > \frac{1}{2} \Delta_T$ we find

$$K_{S_1 \rightarrow T_2} / K_{S_1 \rightarrow T_1} \approx [v_{Ti''} S_{ST} / (E_S - E_T)]^2. \quad (12)$$

Thus the ratio of the rates of the two processes is strongly dependent on the energy separation between ϕ_S and ϕ_T .

III. APPLICATION TO ANTHRACENE

The $T_1 \rightarrow T_2$ absorption spectrum of anthracene in a glass was recorded by Kellogg,¹ the first band lies at $11\,200$ cm^{-1} . From the vibronic structure of the spectrum it appears that the $T_1 \rightarrow T_2$ transition is symmetry allowed, as no trace of a weak signal at lower energy was recorded, thus suggesting that the first band at $11\,200$ cm^{-1} is the 0–0 band. The vibra-

tional structure of the absorption can then be identified with a 590-cm^{-1} vibrational progression and a 1450-cm^{-1} vibration. The zero vibrational level of S_1 is 650 cm^{-1} above T_2 in solution, whereas in the crystal the order is reversed T_2 being 611 cm^{-1} above S_1 (these figures refer to the zero vibrational levels, assuming the assignment of Kellogg to be valid). Thus, in solution ϕ_S is actually almost degenerate with the first harmonic of the 590-cm^{-1} vibration ($|E_S^{\text{sol}} - E_T^{\text{sol}}| \cong 60\text{ cm}^{-1}$), whereas in the crystal the relevant energy separation between ϕ_S and the zero vibrational level of T_2 is 10 times larger ($|E_S^{\text{cryst}} - E_T^{\text{cryst}}| = 611\text{ cm}^{-1}$). Thus, from energy considerations, the $S_1 \rightarrow T_2$ process will be ~ 100 times faster in solution than in the crystal, assuming that the vibronic width of the $\{\phi_T\}$ is smaller or of the same order of magnitude as $|E_S - E_T|$ in solution (i.e., $\Delta_T \cong 60\text{ cm}^{-1}$) which is the experimental observation. The same considerations hold for the relative importance of the $S_1 \rightarrow T_2$ and $S_1 \rightarrow T_1$ non-radiative processes in solution and the crystal, since the $S_1 \rightarrow T_1$ is hardly affected in going from solution to crystal so that the over-all rate of nonradiative decay is expected to be $\approx 50\text{--}100$ times slower in the crystal. The experimental value as deduced from the quantum yields recorded by Kellogg is $70\text{--}200$.

However, serious difficulties previously overlooked are encountered at this point in the analysis, since S_1 is a ${}^1B_{2u}$ state and thus has no spin-orbit coupling with either T_1 being of ${}^3B_{2u}$ symmetry or with T_2 of ${}^3B_{1g}$ symmetry. (This last assignment was given by Kellogg on basis of vibronic structure of the spectrum and is in accord with Pariser's calculations.⁸) Thus, the rate of spin-orbit nonradiative routes for S_1 is predicted to be zero.

At this point we recall that actually there are more involved routes which have to be considered in this case, viz.,

- vibronically induced spin-orbital coupling,
- vibronic spin-orbital coupling, i.e., coupling through terms of the form $\partial H_{so}/\partial Q$. Both (a) and (b) are possible routes in the anthracene case and are in accord with the experimental data. In both cases, ϕ_S interacts with the first harmonic vibrational level of the active vibration. Thus if ϕ_S is approximately degenerate with and coupled to the first harmonic of ϕ_T in solution (i.e., the frequency of the active vibration is $600 \pm 200\text{ cm}^{-1}$), then the energy gap $E_S^{\text{cryst}} - E_T^{\text{cryst}}$ will be $|E_S - E_T| \approx 1000\text{--}1400\text{ cm}^{-1}$.

IV. A POSSIBLE MECHANISM IN ANTHRACENE

We will now make an order-of-magnitude calculation of the change in nonradiative rate in going from crystal to solution in the anthracene case according to the above model (i.e., that the effect of the solvent is only to shift the energy levels of the molecule). First, we must find a spin-orbit route for the interaction. Fröhlich and Mahr⁹ have investigated the g excited

states of anthracene crystal using the technique of two-photon spectroscopy. They suggest that there are two states of even parity at 3.5 and 3.6 eV. These states can be either the predicted A_{1g} and B_{1g} states in the molecule⁸ or they might be vibronic states of u electronic states (with a u vibrational mode). If we assume that these states are indeed molecular states of g symmetry, then there will be spin-orbit coupling between these and the second triplet state (ϕ_T). Thus the state ϕ_T contains a small amount of singlet character, and there will now be vibronic coupling between ϕ_S and ϕ_T (this is a different mechanism than proposed in Sec. II above). Let us write

$$\tilde{\phi}_T = \phi_T + \lambda^{\text{so}} \phi_S',$$

where ϕ_S' is the A_{1g} molecular state at 3.5 or 3.6 eV, and $\tilde{\phi}_T$ is the vibronic state of $\{\phi_T\}$ of appropriate symmetry closest to ϕ_S . Then, we write

$$v_1 = \langle \phi_S | H | \tilde{\phi}_T \rangle,$$

$$v_2 = \langle \tilde{\phi}_T | H | \phi_l \rangle, \quad \text{all } l.$$

We diagonalize in the triplet manifold first (i.e., $\{\phi_l\}$ and $\tilde{\phi}_T$) to find new states $\{\phi_J\}$ which interact with ϕ_S . The nonradiative rate of ϕ_S to the triplet manifold is

$$K_{S_1 \rightarrow T_2} = \Delta_{S_1 \rightarrow T_2} / \hbar = (2\pi/\hbar) |v_1|^2 |a_{JT}(E_S)|^2 \rho,$$

where $|a_{JT}(E)|^2$ is given by

$$|a_{JT}(E)|^2 = |v_2|^2 / [(E - E_T)^2 + (\pi v_2^2 \rho)^2]$$

(ρ is the density of states in the manifold). We now assume that the active state, ϕ_T , is the vibronic state of the $\{\phi_T\}$ manifold corresponding to the first harmonic of the active vibration which couples ϕ_S and ϕ_S' . Taking

$$|E_S - E_T| \cong 1000\text{--}1400\text{ cm}^{-1} \text{ in crystal}$$

$$\cong 100\text{--}200\text{ cm}^{-1} \text{ in solution.}$$

We estimate v_2 (a vibronic coupling matrix element) as before⁶ to be $\sim 1000S\text{ cm}^{-1}$ where S^2 is the Franck-Condon factor between ϕ_T and ϕ_l . We estimate ρS^2 to be $\sim 10^{-5}\text{ cm}$. Using these, we find that $\Delta \approx 60\text{ cm}^{-1}$ (in close agreement with the experiment¹); then,

$$K_{S_1 \rightarrow T_2}(\text{solution}) = (0.3\text{--}1)v_1^2 \times 10^9\text{ sec}^{-1},$$

$$K_{S_1 \rightarrow T_2}(\text{crystal}) = (0.5\text{--}1)v_1^2 \times 10^{17}\text{ sec}^{-1}.$$

Now, v_1 is given by

$$v_1 = \lambda^{\text{so}} \langle \phi_S | H | \phi_S' \rangle,$$

where $\langle \phi_S | H | \phi_S' \rangle$ is a vibronic coupling matrix element and λ^{so} is given by

$$\lambda^{\text{so}} = \langle \phi_T | H_{so} | \phi_S' \rangle / (E_S' - E_T)$$

$$\approx \langle \phi_T | H_{so} | \phi_S' \rangle / 2000\text{ cm}^{-1},$$

if we take ϕ_S' to be the state at 3.5 eV. If we take as

an order-of-magnitude estimate that $\langle \phi_T | H_{so} | \phi_S' \rangle \approx 1 \text{ cm}^{-1}$ and $\langle \phi_S | H | \phi_S' \rangle \approx 100\text{--}1000 \text{ cm}^{-1}$, we find

$$v_1 \approx 0.05\text{--}0.5 \text{ cm}^{-1}.$$

Thus

$$K_{S_1 \rightarrow T_2}(\text{solution}) \approx 1 \times 10^6\text{--}3 \times 10^8 \text{ sec}^{-1},$$

$$K_{S_1 \rightarrow T_2}(\text{crystal}) \approx 1 \times 10^4\text{--}3 \times 10^6 \text{ sec}^{-1}.$$

Hence, in solution the nonradiative rate will be faster than or of the same magnitude as the radiative decay,¹⁰ while in the crystal on the other hand, the radiative decay will be faster, in agreement with experiment.

V. CONCLUSIONS

In conclusion we wish to emphasize several points related to the above discussion.

(a) The present model asserts that the $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ nonradiative processes are independent in the sense that S_1 actually decays into two disjoint sets of levels in the manifold of T_1 . Thus interference effects between $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ processes are not possible in this case. However, if the final states of the $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ processes (i.e., ϕ_l' and ϕ_l'') were the same, as was assumed by Bixon and Jortner, then interference effects will result. If destructive interference effects occur when S_1 is *above* T_2 , then constructive interference occur if S_1 is *below* T_2 , or vice versa. This can be seen by noticing that in this case

$$\begin{aligned} \psi_J &= \sum a_{JT} \phi_T + \sum_l b_{Jl} \phi_l \\ &\cong a_{JT} \phi + \sum_l b_{Jl} \phi_l \end{aligned}$$

(where the primes have been omitted). The $a_{JT}(E_J)$ changes sign on passing from energy values E_J *below* E_T to the energy region *above* E_T , whereas the $\{b_{Jl}\}$ do not change sign. Notice that if the mechanism involving $(\partial H_{so}/\partial Q)$ were also present, interferences *could* result.

(b) In the case when T_2 is below S_1 , and thus ϕ_S lies among $\{\phi_T\}$, interference effects might lead to the inhibition of nonradiative decay, since if the $\{\phi_T\}$ are members of the same progression of one of the totally symmetric vibrations then the a_{JT} will add in opposite sign where for simplicity we consider the case where only two adjacent levels are important. This phenomenon resembles the situation where a dip might occur in the absorption spectrum when two adjacent resonances interact with the same manifold.

(c) An inverse or retarded deuteration effect was

recently predicted by the authors for the $S_1 \rightarrow T_2$ process when $|E_{S_1} - E_{T_2}| \approx \Delta_T$ i.e., in the region where the $S_1 \rightarrow T_2$ process might dominate over $S_1 \rightarrow T_1$ when the electronic matrix elements v_{S_1} and $v_{S_1 T_2}$ are assumed to be of the same order.

(d) The diagonalization scheme adopted by us differs from that previously used. The main difference in the results occurs when ϕ_S is degenerate with one of the $\{\phi_T\}$. In this case Bixon and Jortner predict the ratio of the nonradiative rates to be given by

$$K_{S_1 \rightarrow T_2}/K_{S_1 \rightarrow T_1} \approx \left[\frac{1}{2} + (V^{\text{vib}}/V^{\text{so}}) + \frac{1}{2}(V^{\text{vib}}/V^{\text{so}})^2 \right],$$

which is dependent on the ratio $(V^{\text{vib}}/V^{\text{so}})^2 \approx 10^6\text{--}10^8$ whereas our result is independent of the ratio of the matrix elements.

(e) We have not discussed the effect of temperature on our prediction for the pure crystal of anthracene. If we assume that there is an equilibrium distribution of molecules in the vibrational states of S_1 , then there will be some molecules which will rapidly cross into the triplet manifold. These molecules will have to be in vibronic states close in energy to states in the triplet manifold (T_2) with which they may interact. A simple calculations predicts that $\sim 2\%\text{--}5\%$ of the molecules will be in states of the correct symmetry at 298°K; this means that even if we assume that *all* of these states have intersystem-crossing rates comparable to the solution rate, we still predict that the solution rate will be $\sim 20\text{--}50$ times the crystal rate. This is clearly an underestimate.

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† A. P. Sloan Foundation Fellow.

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² These numbers are calculated from Kellogg's paper. He has $E_{S_1} = 26\,700 \text{ cm}^{-1}$ in solution, $E_{S_1} = 25\,439$ in the crystal, and $E_{T_2} = 26\,050 \text{ cm}^{-1}$.

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⁵ In the present work, the $S_1 \rightarrow T_2$ process (or $S_1 \rightarrow T_2 \rightarrow T_1$) is the process of nonradiative decay from S_1 to the quasicontinuum (T_1) via the intermediate T_2 . This occurs if T_2 is above S_1 or below S_1 .

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