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Effect of Partial Deuteration and Temperature on Triplet-State Lifetimes

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The lifetime of the triplet state of aromatic molecules increases when deuterons are substituted for its protons. For naphthalene, our experiments and others show that the decay rate is linear with the number of protons and independent of the position of substitution. This result is shown to follow from Lin's theory of nonradiative decay of excited states.

INTRODUCTION

In previous papers¹ a general theory of radiationless processes has been presented. The crucial assumption was that the perturbation was due to the failure of the Born-Oppenheimer approximation. In this paper we discuss some experiments on the effect of partial deuteration and temperature on triplet-state lifetimes. The principal results are then shown to follow from the theory.

EXPERIMENT ON PARTIAL DEUTERATION

A dramatic increase occurs in the lifetime of the triplet state of aromatic hydrocarbons when they are completely deuterated.^{2,3} For example, at 77°K in a durene solid solution, naphthalene has a 2.5 sec lifetime vs 16.2 sec for naphthalene- d_8 . Since the initial discovery of this deuteration effect, Hirota and Hutchison⁴ have made lifetime measurements on three naphthalenes which were partially deuterated. We have measured the lifetimes of two others and the combined data on seven isotopic species of naphthalene appear in Table I and is plotted in Fig. 1.

What is striking about the naphthalene results is that the decay rate (inverse of the lifetime) is linear with the number of deuterons in the molecule. Moreover, there is little or no dependence on the position of substitution even though the wave function of the unpaired electrons is considerably larger at the α than at the β positions.

Studies on two other systems suggest that this phenomenon is perfectly general. Lamola⁵ measured the lifetime of the triplet $\pi - \pi^*$ state of acetophenone

in H_3PO_4 at 77°K and two of its deuterated derivatives. The results are quoted in Table I and in Fig. 1. Although admittedly there are only three points they lie within experimental error in a straight line. This straight line is presumably fortuitously almost parallel to the naphthalene straight line. In other hydrocarbons² the line passing through the two available data points for no-deuteron and all-deuteron substitution has a strongly varying slope.

Heller⁶ measured the phosphorescence intensity of a number of rare-earth ions (Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺) in D₂O solution as a function of added H₂O. The phosphorescence quenching is strictly linear with the concentration of H_2O . In other words an H_2O molecule is exactly twice as effective as an HDO molecule in relaxing an excited state of a rare-earth ion.

The various experiments referred to tell us that:

(1) In many molecules the high-frequency hydrogenatom stretching mode is an important sink for the electronic energy.7

(2) The total effectiveness of these modes depends only on their number and not on the specific location of the protons. These general conclusions will now be derived from the theory.

EXPERIMENTAL

1-Deuteronaphthalene and 1,4-dideuteronaphthalene were prepared by the method of Leitch et al.,^{8,9} which consists of agitating the corresponding bromocompound with zinc dust and CaO in an excess of boiling D₂O for several hours. We were not able to prepare the 2-deuterocompound in this way. We are indebted to Eisinger and Lamola of the Bell Telephone Laboratories for measuring the phosphorescence decay curves and for suggestions concerning the syntheses.

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DISCUSSION OF THE RADIATIONLESS TRANSITION RATE

In the Franck-Condon approximation, the probability of the radiationless transition from the initial state (bv') to the final state (av'') of a molecule embedded in a solvent molecular lattice was derived¹ in the form

$$\begin{split} W(bv' \rightarrow av'') &= (2\pi/\hbar) \sum_{i} \mid R_{i}(ab) \mid^{2} \mid \langle \Theta_{av''} \mid \partial/\partial Q_{i} \mid \Theta_{bv'} \rangle \mid^{2} \delta(E_{av''} - E_{bv'}) \\ &= (2\pi/\hbar) \sum_{i} \mid R_{i}(ab) \mid^{2} \mid \langle X_{av_{i}} \mid' \mid \partial/\partial Q_{i} \mid X_{bv_{i}'} \rangle \mid^{2} \prod_{j} \mid \langle X_{av_{j}} \mid' \mid X_{bv_{i}'} \rangle \mid^{2} \delta(E_{av''} - E_{bv'}), \end{split}$$

where

$$R_i(ab) = -\hbar^2 \langle \Phi_a \mid \partial/\partial Q_i \mid \Phi_b \rangle$$

is the perturbation matrix element due to the normal mode i that causes the electronic relaxation to take place between the electronic states Φ_a and Φ_b . $\Theta_{av''}$ and $\Theta_{bv'}$ designate the wavefunctions of both intraand intermolecular vibrations of the system and are expressed as the product of the wavefunctions of each normal mode, $X_{avi''}$, $X_{bvi'}$ etc. There may be more than one normal mode i which is effective in inducing the electronic relaxation, i.e., there will be more than one process contributing to the electronic relaxation.

One should distinguish clearly in Eq. (1) between the *promoting* modes i, responsible for the electronic transition, and the *accepting* modes j, which are a sink for the electronic energy. When the electronic excitation energy is transformed into the vibrational energy of the final electronic state, the number of vibrational quanta which can be put into a normal mode j is dependent on the Franck-Condon factor which in turn depends on the anharmonicity, the modifications of the normal coordinate and frequencies between the two electronic states under consideration.

TABLE I. Triplet lifetimes of partially deuterated molecules.

Compounds	Position of deuterons	Lifetime (sec)	Ref.
Naphthalene in	None	2.5 ± 0.1	2
durene at 77°K	1	$2.8 {\pm} 0.1$	This work
	2 (in durene- d_{14})	2.6 ± 0.1	2
	1,4	$3.4{\pm}0.1$	This work
	1, 4, 5, 8	5.4 ± 0.2	2
	2, 3, 6, 7 (in durene- d_{14})	4.8±0.2	2
	1, 2, 3, 4, 5, 6, 7, 8	16.2±0.3	2
Acetophenone in	None	1.51	5
H₃PO₄ at 77°K	α, α, α	1.85	5
	2, 3, 4, 5, 6	2.25	5

Whether part of the electronic energy can be directly converted into the lattice modes (intermolecular vibrations) or not also depends on the Franck-Condon factor and in some cases on the perturbation $R_i(ab)$. For large molecules there are many ways of distributing the electronic energy over the normal modes of vibration of the final electronic state and each distribution is weighted by a Franck-Condon factor. Thus if the radiationless transitions originate from a Boltzmann distribution of vibrational levels of the initial electronic state, then the total radiationless transition probability can be obtained from Eq. (1) by summing over all initial vibration states v' weighted by the Boltzmann factor and then summing over all the possible distributions of the electronic plus the thermal energy over the final vibrational states v'' consistent with energy conservation.

A NEW EXPRESSION FOR THE RADIATIONLESS TRANSITION RATE

In a previous paper, the radiationless transition rate was derived in terms of a mean frequency and mean phase factor, whose physical meaning was difficult to interpret. Here a new expression is derived



FIG. 1. Rate of phosphorescence decay (sec⁻¹) vs number of deuterons in the molecule.

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using the same theory but without the above objections. For this purpose we begin with an equation equivalent to Eq. (32) of the previous paper¹:

$$W(b \rightarrow a) = \sum_{i} \frac{1}{\tilde{\hbar}^{2}} |R_{i}(ab)|^{2} \exp\left[-\sum_{j} \frac{1}{2} \left[\beta_{j}'^{2}(d_{j}''-d_{j}')^{2}\right] \coth\frac{\tilde{\hbar}\omega_{j}'}{2kT}\right]$$

$$\times \int_{-\infty}^{\infty} dt \exp(i\omega_{ab}t) \frac{\omega_{i}'}{4h} \left[\left(\coth\frac{\tilde{\hbar}\omega_{i}'}{2kT}+1\right) \exp(i\omega_{i}'t) + \left(\coth\frac{\tilde{\hbar}\omega_{i}'}{2kT}-1\right) \exp(-i\omega_{i}'t)\right]$$

$$\times \exp\left[-\sum_{j} \frac{1}{2} i\rho_{j}\omega_{j}'t \coth\frac{\tilde{\hbar}\omega_{j}'}{2kT} + \sum_{j} \frac{1}{2} \beta_{j}'^{2}(d_{j}''-d_{j}')^{2} \operatorname{csch}\frac{\tilde{\hbar}\omega_{j}'}{2kT} \cos\left(\omega_{j}'t-i\frac{\tilde{\hbar}\omega_{j}'}{2kT}\right)\right]. \quad (2)$$

The quantities in Eq. (2) are defined as follows:

$$Q_{i}' = Q_{i} - d_{i}', \qquad Q_{i}'' = Q_{i} - d_{i}'', \qquad \omega_{i}'' = \omega_{i}'(1 - \rho_{i}), \qquad \beta_{j}' = (\omega_{j}'/\hbar)^{1/2}, \tag{3}$$

referring respectively to the variations (assumed small) of the normal coordinates and normal frequencies in the two electronic states. The assumptions leading to Eq. (2) are that $|\rho_i| \ll 1$, the vibrational relaxation time $\ll 1/W$, and the normal vibrations are harmonic. Whenever these assumptions do not hold, one has to use the original expression, Eq. (1).

In order to carry out the t integral of Eq. (2) we must expand the last factor of the integrand into a series of exponentials proportional to t:

$$\exp\left[\sum_{j} \frac{1}{2} (\beta_{j}'^{2}) (d_{j}'' - d_{j}')^{2} \operatorname{csch} \frac{\hbar \omega_{j}'}{2kT} \cos\left(\omega_{j}'t - i\frac{\hbar \omega_{j}'}{2kT}\right)\right]$$
$$= \left(\sum_{n=0}^{\infty} (n!)^{-1} \left[\sum_{k} a_{k}^{2} \operatorname{csch} \frac{\hbar \omega_{k}'}{2kT} \exp\left(\frac{\hbar \omega_{k}'}{2kT} + i\omega_{k}'t\right)\right]^{n}\right)$$
$$\times \left(\sum_{m=0}^{\infty} (m!)^{-1} \left[\sum_{p} a_{p}^{2} \operatorname{csch} \frac{\hbar \omega_{p}'}{2kT} \exp\left(\frac{-\hbar \omega_{p}'}{2kT} - i\omega_{p}'t\right)\right]^{m}\right), \quad (4)$$

where $a_k = \frac{1}{2}\beta_k'(d_k'' - d_k')$. Using the multinomial expansion

$$\left(\sum_{k}c_{k}\right)^{n}=\sum_{n_{k}}^{\Sigma_{n_{k}}=n}n!\prod_{k}\frac{c_{k}^{n_{k}}}{n_{k}!},$$
(5)

Eq. (4) becomes

$$\exp\left[2\sum_{j}a_{j}^{2}\operatorname{csch}\frac{\hbar\omega_{j}'}{2kT}\cos\left(\omega_{j}'t-i\frac{\hbar\omega_{j}'}{2kT}\right)\right] = \left(\sum_{n=0}^{\infty}\sum_{n_{k}}^{\sum n_{k}=n}\prod_{k}\frac{\left[a_{k}^{2}\operatorname{csch}(\hbar\omega_{k}'/2kT)\exp(\hbar\omega_{k}'/2kT)\right]^{n_{k}}}{n_{k}!}\right)$$
$$\times \left(\sum_{m=0}^{\infty}\sum_{m_{p}}^{\sum m_{p}=m}\prod_{p}\frac{\left[a_{p}^{2}\operatorname{csch}(\hbar\omega_{p}'/2kT)\exp(\hbar\omega_{p}'/2kT)\right]^{m_{k}}}{m_{p}!}\right)\exp\left[it(\sum_{k}n_{k}\omega_{k}'-\sum_{p}m_{p}\omega_{p}')\right].$$
(6)

Substituting Eq. (6) into Eq. (2) and integrating over time gives

$$W(b \rightarrow a) = \sum_{i} \frac{\pi \omega_{i}'}{2\hbar^{2}} |R_{i}(ab)|^{2} \exp\left(-2\sum_{j} a_{j}^{2} \coth\frac{\hbar\omega_{j}'}{2kT}\right) \\ \times \left(\sum_{n=0}^{\infty} \sum_{n_{k}}^{2n_{k}=n} \prod_{k} \frac{\left[a_{k}^{2} \operatorname{csch}(\hbar\omega_{k}'/2kT) \exp(\hbar\omega_{k}'/2kT)\right]^{n_{k}}}{n_{k}!}\right) \\ \times \left(\sum_{m=0}^{\infty} \sum_{m_{p}}^{2m_{p}=m} \prod_{p} \frac{\left[a_{p}^{2} \operatorname{csch}(\hbar\omega_{p}'/2kT) \exp(-\hbar\omega_{p}'/2kT)\right]_{m_{p}}}{m_{p}!}\right) \\ \times \left\{\left(\coth\frac{\hbar\omega_{i}'}{2kT}+1\right)\delta\left(\hbar\omega_{ab}+\hbar\omega_{i}'-\frac{1}{2}\hbar\sum_{j}\rho_{j}\omega_{j}' \coth\frac{\hbar\omega_{j}'}{2kT}+\hbar\sum_{k}n_{k}\omega_{k}'-\hbar\sum_{p}m_{p}\omega_{p}'\right) \\ +\left(\coth\frac{\hbar\omega_{i}'}{2kT}-1\right)\delta\left(\hbar\omega_{ab}-\hbar\omega_{i}'-\frac{1}{2}\hbar\sum_{j}\rho_{j}\omega_{j}' \coth\frac{\hbar\omega_{j}'}{2kT}+\hbar\sum_{k}n_{k}\omega_{k}'-\hbar\sum_{p}m_{p}\omega_{p}'\right)\right\}.$$
(7)

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Here the representation for the Dirac delta function has been used:

$$\delta(E_a - E_b) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp\left[\frac{it}{\hbar} \left(E_a - E_b\right)\right].$$
(8)

As the temperature, T approaches zero, $\coth \hbar \omega_j'/2kT$ approaches unity and $\operatorname{csch} \hbar \omega_j'/2kT$ approaches zero. Thus as T=0, the only terms in Eq. (7) which survive are those for which m=0, and Eq. (7) reduces to

$$W(b \rightarrow a) = \sum_{i} \frac{\pi \omega_{i}'}{\hbar^{2}} | R_{i}(ab) |^{2} \exp\left(-2\sum_{j} a_{j}^{2}\right) \left(\sum_{n=0}^{\infty} \sum_{n_{k}}^{2n_{k}=n} \prod_{k} \frac{(2a_{k}^{2})^{n_{k}}}{n_{k}!}\right) \delta(\hbar \omega_{ab} + \hbar \omega_{i}' + \hbar \sum_{k} n_{k} \omega_{k}' - \frac{1}{2} \hbar \sum_{j} \rho_{j} \omega_{j}').$$
(9)

This equation can also be obtained directly from Eq. (2) by taking the limit $T \rightarrow 0$. The summations over n, n_k , m, and m_p in Eqs. (9) and (7) imply that all the possible ways of distributing the electronic energy plus thermal energy (if the temperature is not zero) among the normal vibrations of the final electronic states should be included.

DISCUSSION OF DEUTERATION

The fundamental expression Eq. (7) contains factors from sets of modes, one of which promotes the radiationless transition and the other which accepts the energy. The promoting modes are characterized by the nonvanishing integral $\langle av_i'' | \partial / \partial Q_i | bv_i' \rangle$ and the accepting modes by the nonvanishing integral $\langle X_{av_i}^{\prime\prime} | X_{bv_i}^{\prime} \rangle$. To some extent, of course, the two sets are overlapping but here we wish to emphasize their different characteristics. Each contribution to the matrix element consists of a factor associated with a single promoting mode and a factor associated with a large number of accepting modes. The promoting mode changes its quantum number according to the selection rules for the integral $\langle av_i'' \mid \partial/\partial Q_i \mid bv_i' \rangle$; whereas the accepting modes are limited in their change of quantum number only by the Franck-Condon factors. The pronounced effect of total deuteration on triplet lifetimes makes it clear that the acceptor modes are largely those sensitive to the hydrogen mass, namely the C-H stretching modes. On the other hand, as we will show, the partial deuteration experiments prove that the C-H modes are not promoting modes. The latter are presumably the C-C stretching modes.7,10

From Eqs. (7) and (9) we see that in the harmonic oscillator approximation no mode can be an acceptor mode unless there is a modification of the corresponding normal coordinate, i.e., unless $a_k \neq 0$. The quantity a_k^2 is the same as the parameter γ discussed by Siebrand. The magnitude of this quantity is of major importance for the acceptor modes. If we write $d_k'' - d_k' = \mu_k \delta r_k$, where μ_k is a mass associated with the kth acceptor mode and is a change in equilibrium value of a linear coordinate between the ground and excited state, then

$$2a_{k}^{2} = \frac{1}{2}\beta_{k}^{\prime 2}(d_{k}^{\prime \prime} - d_{k}^{\prime})^{2} = \frac{1}{2}k_{f}(\delta r_{k})^{2}/\hbar\omega_{k}^{\prime}, \qquad (10)$$

¹⁰ E. F. McCoy and I. G. Ross, Australian J. Chem. 15, 573 (1962).

where k_f is a force constant defined by $\omega_k = (k_f/\mu_k)^{1/2}$. a_k^2 is just the dimensionless ration of the extra potential energy in the excited state divided by the vibrational quantum. As shown by Siebrand, a_k^2 for a C-C stretch is ~1.5. Equation (7) shows that the important acceptor modes will be those for which a_k^2 is large.

Because of the factors $n_k!$, $m_p!$ it is not favorable to distribute too many vibrational quanta into any single acceptor mode. Thus the normal modes with high frequencies will be favored in the electronic relaxation. This implies that in aromatic molecules the C-H stretching modes are important in radiationless transitions and deuteration of the solute molecules will slow down the rate of the electronic relaxation because of the lower C-D frequencies. Moreover, the acceptor mode must be simultaneously shared by a relatively large number of modes. On experimental grounds one can show this. Suppose, for example, we had a 30 000 cm^{-1} electronic quantum whose energy was placed, by assumption, in a single C-H stretching mode. The vibrational quantum number would be ten and upon deuteration there have to be fourteen quanta in that mode. There would then be a ratio of $\sim 14!/(10!2^7)$ in the nonradiative transition rates in the two cases. The actual ratio, while not known with certainty, is far smaller.

The C-H stretching contribution of the promoting modes $\sim \langle a \mid \partial/\partial Q_i \mid b \rangle$ would be expected to be sensitive to the position of deuteration because the wavefunction varies over the molecule. The available data as discussed before indicate that the radiationless transition rate depends only on the number of deuterons and not on their specific positions. Thus the C-H stretching modes are not, in general, promoting modes. Their weak promoting contribution can be gauged from the small differences in decay rate of the pairs α - and β -D-naphthalene and α_4 -D- and β_4 -D-naphthalene (cf., Fig. 1).

DISCUSSION OF TEMPERATURE DEPENDENCE

At T=0, all m_p values in Eq. (7) have to be zero. This means that the excited vibrational states of the initial electronic state are not populated. As T increases, some of the m_p 's take values other than zero, i.e.,

some of the normal modes of the initial electronic state will be thermally excited, particularly those of lower frequency. Thus, in addition to the processes of electronic relaxation originating from the ground vibrational states of the initial electronic state there will be some other processes in which the electronic energy plus the extra thermal energy will be relaxed into the vibrational energy of the final electronic state. One should notice however that not all the normal modes which are thermally excited can be acceptor modes. The acceptor modes are, as already emphasized, those whose Franck-Condon factors are appreciable, i.e., in the harmonic oscillator approximation those whose a_k 's are large. The a_k values of the lattice modes may be appreciable because the two electronic states of the given solute molecules may interact differently with the solvent molecules and the molecular geometry may be different in the two states.

Because of the large number of modes which must necessarily enter into the transition rate of Eq. (7)it is not easy to extract a simple functional form for

the temperature dependence. The important acceptor modes which are of high frequency do not contribute to the temperature dependence. If we assume the temperature is low and expand all the temperature dependent terms of Eq. (7) in powers of $\exp(-\hbar\omega j/kT)$ and retain only the lowest terms, we arrive at an expression in the form of a sum of exponentials which can be abbreviated in the Arrhenius form

$$1/\tau = 1/\tau_0 + a/\tau_0 e^{-\theta/T}$$
. (11)

Kellogg and Schwenker³ measured the triplet lifetime of octadeuteronaphthalene in several plastics as a function of temperature. Their data can be fitted to Eq. (11) with values of $\theta = 901^{\circ}$ K, $a/\tau_0 = 0.710$. The value of θ is equivalent to a vibrational quantum of 617 cm⁻¹. This suggests that some of the lower-frequency intramolecular vibrations (out-of-plane bends) may be responsible for the temperature dependence. This conclusion is tentative however because the constants in Eq. (11) are mean values with a qualitative significance.

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Internal Compression Effects. II. Frequency and Intensity Changes in Charge-Transfer and Hydrogen-Bonded Complex Spectra*

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Some effects on spectra of weak molecular complexes due to compression of the complex bond were investigated. Changes in the charge-transfer (CT) frequency and intensity with changing bond length in model tetracyanoethylene-aromatic complexes have been estimated. These changes are related to a reduction of the complex bond length by internal compression forces of solvent (or by high external pressure). Variation of CT band frequency with compressional forces in various nonpolar solvents was studied, as was the stretching frequency of H bonds. It is concluded that solvent forces can contribute importantly to vapor-to-liquid spectral changes in weak complexes.

I. INTRODUCTION

Available work comparing vapor-phase electronic spectra of molecules to that in solution leads one to expect for strong, allowed transitions a red shift of about 40 to 400 cm⁻¹ in the band maximum and an intensity increase (or decrease) of 0% to 20% on going from the vapor phase into a nonpolar solvent.¹⁻⁸ These effects are observed in electronic spectra of single molecules such as phenol blue,⁴ benzene,⁵ fluorobenzene,⁵ isoprene,⁷ piperylenes,⁷ and cyclopentadiene.⁸ The red shifts have been explained as being due to a lowering of excited-state energy by transition dipole and dispersive interactions with polarizable solvent

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