ON THE EFFECT OF DEUTERATION ON NON-RADIATIVE PROCESSES IN LARGE MOLECULES*

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It is shown that the non-radiative decay of the fluorescing state of large polyatomic molecules might exhibit an inverse or retarded deuteration effect.

It is presently accepted that the rate of "non-radiative" processes in aromatic hydrocarbons tend to decrease upon deuteration. However, conclusive experimental evidence for this effect is known only for the process of intersystem crossing from the first excited triplet state (T_1) to the ground state (S_0), where the quantum yield of phosphorescence is enhanced upon deuteration [11]. Studies [2] of the fluorescence of these molecules in condensed media have failed to observe an isotopic effect. Recently [3], however, the rate of intersystem crossing in the fluorescing state ($^1B_{2u}$) of benzene was found to be two fold greater in C_6H_6 than in C_6D_6, a similar effect was recorded for azulene [4].

The major routes of this non-radiative process are assumed to be $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$, with the $S_1 \rightarrow S_0$ assumed to be unimportant. The effect of the second triplet state is clear from the drastic enhancement of the fluorescent yield in anthracene in going from solution to solid (where the major change is the relative positions of S_1 and T_2). The rate of the $S_1 \rightarrow T_2$ process depends on the energy separation between the electronic states S_1 and T_2; this separation is known to be small in benzene and anthracene (≈ 1000 cm^{-1}) and may indeed be small in similar molecules.

According to the model for radiationless transitions in polyatomic molecules, there is a simple relation between the non-radiative rate and the width of the optical absorption to the relaxing state [5]. This line width is caused by the interaction between the zeroth order vibronic state of the upper state (ϕ_S) and the manifold of highly excited vibronic levels (ϕ_l) of the lower electronic state which are degenerate with it. The eigenstates (ψ_n) of the molecular hamiltonian are taken to be superpositions of ϕ_S and ϕ_l:

$$\psi_n = a_S^n \phi_S + \sum_l b_l^n \phi_l . \tag{1}$$

If the manifold of levels (ϕ_l) are considered to be equally spaced with energy separation ϵ, and if it is assumed that the hamiltonian matrix elements of ϕ_S with the (ϕ_l) quasi degenerate with it are constant and equal to V, then the coefficient a_S^n is given by

$$|a_S^n|^2 = \frac{V^2}{(E_n - E_S)^2 + (\pi V^2 \rho)^2} , \tag{2}$$

provided that $V\rho = V/\epsilon \gg 1$. This gives a lorentzian line with width Δ given by

$$\Delta = 2\pi V^2 \rho . \tag{3}$$

The interaction matrix element, V, can be written as the product of the Franck–Condon factor, S, and an electronic part K.

Using the same theory, it was shown [5] that the rate of the non-radiative process $\phi_S \rightarrow \phi_l$ is given by $K_{nr} \equiv 1/\tau = \Delta/\hbar$. The isotopic deuteration effect for these processes is due to the ρS^2 term in K_{nr}. It has been shown [11] that the ρS^2 term is sensitive to deuteration only for large electronic energy separations.

In the present note, we will discuss the effect of deuteration on the $S_1 \rightarrow T_2$ process (for which the electronic energy separation is small). We shall show that if the $S_1 \rightarrow T_2$ process is dominant

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over the $S_1 \rightarrow T_1$ process, then the non-radiative decay rate is *enhanced* upon deuteration (we should perhaps write the $S_1 \rightarrow T_2$ process as $S_1 \rightarrow T_2 \rightarrow T_1$ since T_1 provides the manifold of states for the non-radiative process).

In essence the situation for the case of interest is the following: we assume a set of zeroth order vibronic levels which consist of the following vibronic wavefunctions

(a) the lowest vibronic wave function ϕ_S of the first excited singlet S_1,

(b) the ground vibronic level ϕ_T of the second triplet state T_2, which is nearly degenerate with ϕ_S.

(c) a dense (quasi continuum) manifold $\{\phi_i\}$ of vibrationally highly excited vibronic levels of the first triplet state T_1.

The compound eigenstates of the molecular hamiltonian consist of superpositions of the zeroth order molecular states; i.e.,

$$\psi_n = a_S^n \phi_S + a_T^n \phi_T + \sum_i b_i^n \phi_i \,. \tag{4}$$

The off-diagonal matrix elements of the molecular hamiltonian in the crude adiabatic representation are given by:

$$\langle \phi_S | H | \phi_T \rangle = V_{SO} \,, \tag{5}$$

$$\langle \phi_S | H | \phi_i \rangle = V_{SO}^i \,, \tag{6}$$

$$\langle \phi_T | H | \phi_i \rangle = V_{vib}^i \,, \tag{7}$$

where V_{vib}^i and V_{SO}^i refer to vibronic and spin orbital coupling respectively. Assuming $V_{vib}^i \gg V_{SO}^i$ which is usually the case, we first construct the compound states $\{\phi_J\}$ which are the superpositions of ϕ_T and $\{\phi_i\}$ which diagonalize the triplet sub-matrix of the molecular hamiltonian; hence,

$$\phi_J = a_T^J \phi_T + \sum_i b_i^J \phi_i \,. \tag{8}$$

The molecular eigenstates ψ_n are then given by:

$$\psi_n = a_S^n \phi_S + \sum_J b_J^n \phi_J \,. \tag{9}$$

The relevant matrix elements are:

$$\langle \phi_S | H | \phi_S \rangle = E_S \,, \tag{10}$$

$$\langle \phi_J | H | \phi_{J'} \rangle = E_J \delta_{J,J'} \,, \tag{11}$$

$$\langle \phi_S | H | \phi_J \rangle = V_J \,. \tag{12}$$

The level ϕ_T is broadened due to the vibronic interactions with the manifold $\{\phi_i\}$, the width of the lorentzian amplitude distribution $|a_T^J|^2$ is given by:

$$\Delta_T = 2\pi V_{vib}^2 \rho_i \,. \tag{13}$$

The state ϕ_J is physically superimposed on the manifold $\{\phi_J\}$, this manifold density of states-ρ_J, is equal to ρ_i (to a good approximation) so that $\rho_J = \rho_i \equiv \rho$. The matrix element V_J can be displayed in the form *:

$$V_J = \sum_T a_T^J V_{SO} \cong a_T^J V_{SO} \tag{14}$$

neglecting the terms $V_{SO}^i b_i^J$ since we are assuming the $S_1 \rightarrow T_1$ process to be slow. Making use of the Lorentzian distribution of the amplitude $|a_T^J|^2$, i.e.

$$|a_T^J|^2 = \frac{V_{vib}^2}{(E_J - E_T)^2 + \frac{1}{4}\Delta_T^2} \,. \tag{15}$$

The rate of the $S_1 \rightarrow T_2$ process will be given by:

$$K_J \equiv 1/\tau_J = \Delta_J/\hbar \,, \tag{16}$$

where we have assumed that V_J is a constant and is equal to $V_J(E_J = E_S)$ (i.e. that essentially ϕ_S interacts only with the states in the J continuum close to E_S in energy). We are interested in Δ_J^H/Δ_J^D. For the region $\Delta E_{S,T} \ll \frac{1}{2}\Delta_T$ the following relation results.

$$\frac{K_J^H}{K_J^D} \equiv \frac{\Delta_J^H}{\Delta_J^D} \simeq \left(\frac{\Delta_T^D}{\Delta_T^H}\right) \leqslant 1 \,, \tag{17}$$

whereas for the region $\Delta E_{S,T} \gg \frac{1}{2}\Delta_T$ the ratio will be of the form:

$$\frac{K_J^H}{K_J^D} \simeq \frac{\Delta_T^H}{\Delta_T^D} \geqslant 1 \,. \tag{18}$$

* This approximation is valid when ϕ_S is superimposed on ϕ_T, or in the case where some Franck—Condon overlap factor dominates, the set $\{\phi_T\}$ refers to the lower vibronic levels of the second triplet state. In fact ϕ_T can be any vibronic level provided it is of the proper symmetry.

The turning point, i.e. the point for which $K_J^H = K_J^D$ will be given by:

$$\Delta E_{S,T} = \left\{ \frac{(\Delta_T^H)^2 \Delta_T^D - \Delta_T^H (\Delta_T^D)^2}{2(\Delta_T^H - \Delta_T^D)} \right\}^{1/2}. \quad (19)$$

Thus, the $S_1 \rightarrow T_2$ non-radiative process will show an inverse or retarded isotopic deuteration effect for small singlet triplet separation. Since this is the case for many aromatic molecules, we expect this effect to be of general importance. In fact it might be responsible, at least to some extent, for the absence of pronounced deuteration effect in many of these molecules. Tentatively this last argument applies for all cases where the fluorescing S_1 state lies below the second triplet state.

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Because of an error in the analytic expression for the dipolar integral for a 1s atomic orbital the following corrections should be made: On page 519 the principal components of the contact-dipolar coupling tensor for H_2 are $J^{(23)}_{xxHH'} = J^{(23)}_{yyHH'} = 19.55$ Hz, and $J^{(23)}_{zzHH'} = -39.10$ Hz. For $^{13}C-H$, $(J^{(23)}_{\parallel} - J^{(23)}_{\perp})_{CH} = -18.8$ Hz, and for CH_4,

$$J^{(23)}_{\alpha\beta\,^{13}C-H} = \begin{vmatrix} 21.8 & -1.3 & -2.5 \\ -1.3 & 25.0 & -3.2 \\ -2.5 & -3.2 & -46.8 \end{vmatrix} \text{ Hz.}$$

The second word of the last paragraph is vicinal. On page 520 the two tensors for ethylene are

$$2J^{(23)}_{\alpha\beta HH'} = \begin{vmatrix} -5.1 & 22.8 & 0.0 \\ 22.8 & 16.2 & 0.0 \\ 0.0 & 0.0 & -11.1 \end{vmatrix} \text{ and } \begin{vmatrix} -4.5 & 23.5 & 0.0 \\ 23.5 & 16.1 & 0.0 \\ 0.0 & 0.0 & -11.6 \end{vmatrix} \text{ Hz.}$$