

ON THE EFFECT OF HYDROGEN BONDING ON THE EXCITED STATES OF COUMARINS

COUMARIN molecules have close lying $\pi\pi^*$ and $n\pi^*$ states which are perturbed by changes in substituents, solvents and by hydrogen bonding. In the present study, the effect of hydrogen bonding is investigated by taking the coumarins in two types of solvents: (1) proton donating and (2) proton accepting. Five different coumarin derivatives have been used. The quantum yield of fluorescence and the frequencies of the absorption and emission spectra have been obtained. The absorption and emission spectra were recorded with a Perkin-Elmer spectrophotometer and an Aminco-Bowman spectrofluorophotometer respectively. The quantum yield of fluorescence has been calculated from the area of the emission spectrum curve and the relative absorption for the exciting wavelength.

Table I gives a summary of the experimental results. It is clear from the results that the relative quantum yield of fluorescence is generally higher in proton donating solvents than in proton accepting solvents. This indicates the possible effect of hydrogen bonding on the excited states of coumarins. As in all fluorescent aromatic molecules, $\pi\pi^*$ is the lowest excited singlet state in coumarins^{1,2}, and $n\pi^*$ is very close to it. A close examination of the correlation between fluorescence quantum yield and frequency of emission indicates that the effect of the perturbation is such that as the quantum yield of fluorescence increases the corresponding frequency of fluorescence emission decreases. This leads to the conclusion that hydrogen bonding while perturbing the close lying $\pi\pi^*$ and $n\pi^*$ singlet states of the coumarin molecules increases the energy gap between $\pi\pi^*$ and $n\pi^*$ and still leaves the $\pi\pi^*$ as the lowest state⁵. It may

TABLE I

Solute	Solvent	5, 6-dihydroxy-4-methyl coumarin	4, 7-dimethyl coumarin	7, 8-dimethoxy-4-methyl coumarin	7-Acetyloxy coumarin	5-methoxy-4-phenyl coumarin
Water	..	28980* 21740 0.20 ..	{ 31540 34720 26320 0.102	{ 31260 20740 0.65 ..	{ 31060 25640 15380† 0.69	{ 32780 19480 Good yield ..
Formamide	..	26040 21560 0.20	{ 31540 34840 26100 0.320 ..	{ 31060 27780† 21660 15460† 0.68	{ 31060 25640 0.96	{ 32680 26370† 21180 0.23 ..
Ethanol	..	28160 22720 0.29	{ 31740 35460 26320 15430† 0.062	{ 31260 27780† 21840 15290† 0.30	{ 31060 25640 15200† 0.50 ..	{ 32780 27400† 21660 0.11 ..
Butanol 23260 0.37	{ 31740 35460 26320 15870† 0.115	{ 31260 28010† 22120 15380† 0.24	{ 30860 25780 0.53	{ 32900 27400† 23040 0.073 ..
Acetone 23580	{ .. 24630 13870† ..	{ .. 27400† 24500 0.18	{ .. 25120 14600† ..	{ .. 25000 14410† ..
Dioxane	..	28980 23800 0.062 ..	{ 31840 35720 30580 0.082	{ 32240 27320 25000† 0.073	{ 31250 25900 14790† 0.20	{ 32460 27320 14810† 0.10

* For each solvent and solute, the data is entered in the following order: $\bar{\nu}_a$, $\bar{\nu}_f$, Q_f , which are the wavenumbers of the maxima of longest wavelength absorption, the maxima of fluorescence and the relative quantum yield of fluorescence, respectively, † Very weak peak.

also be mentioned that the effect of hydrogen bonding on the excited states is similar to the other perturbing effect due to the substituents³⁻⁵.

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A METHOD FOR DETERMINING AN EXPLICIT VALUE OF CHEMICAL SHIFT IN γ -RESONANCE ABSORPTION BY SOLIDS

In the γ -resonance absorption by solids, the relative change in the energy of the isomeric states (absorber and source) due to the charge distribution of S-electrons around the Mössbauer nucleus is measured along with the shift in γ -ray energy due to second order Doppler effect. The total shift is called as centre shift¹. The independence of isomer shift with temperature is known from the work of Preston *et al.*². So in the resonance absorption of gamma-rays, elimination of the contribution of second order Doppler effect to centre shift is possible, if there is a definite difference of temperatures between the source and absorber when the Mössbauer isotopes are located in different host lattices which then will give an explicit value for isomer shift (chemical shift).

The energy E_s of the emitted γ -ray by a Mössbauer source incorporated in a host lattice can be given as a sum of transition energy E_0 , the chemical shift ΔE_c and the second order Doppler shift ΔE_D ³

$$E_s = E_0 + \Delta E_c + \Delta E_D \quad (1)$$

and similarly for the absorbing nucleus in another environment

$$E_A = E_0 + \Delta E_c' + \Delta E_D' \quad (2)$$

Substituting values⁴ for ΔE_c and ΔE_D the energy shift in the γ -rays emitted by the source relative to the absorber can be given as

$$\begin{aligned} E &= (E_A - E_s) \\ &= \frac{2\pi ze^2}{5} (R_{ss}^2 - R_{ad}^2) \{ |\psi(0)|_A^2 - |\psi(0)|_s^2 \} \\ &\quad + \frac{E_0}{2c^2} (\langle v^2 \rangle_A - \langle v^2 \rangle_s) \end{aligned} \quad (3)$$

where $\langle v^2 \rangle_s$ and $\langle v^2 \rangle_A$ are the mean square velocities of the emitting and absorbing nuclei respectively and the rest notations are well known. Since the Mössbauer isotope forms an impurity in the host lattice, the values of $\langle v^2 \rangle_s$ and $\langle v^2 \rangle_A$ are not equal in general. Evaluation of the values of $\langle v^2 \rangle_s$ and $\langle v^2 \rangle_A$ are rather complicated at low temperatures but somewhat simpler at the high temperature limit⁵. For a cubic crystal, in harmonic approximation, at high temperature limit, we can write $\langle v^2 \rangle$ as

$$\langle v^2 \rangle \cong \frac{3KT}{M'} \left\{ 1 + \frac{1}{20} \frac{M}{M'} \left(\frac{\theta_D}{T} \right)^2 \right\} \quad (4)$$

Here M is the mass of the host atom and M' is the mass of the impurity and other notations are well known. Thus relation (3) can be written as

$$\begin{aligned} \delta E &\cong \frac{2\pi ze^2}{5} (R_{ss}^2 - R_{ad}^2) \\ &\quad \times \{ |\psi(0)|_A^2 - |\psi(0)|_s^2 \} \\ &\quad + \frac{E_0}{2c^2} \left[\left(\frac{3K_B T'}{M'} - \frac{3K_B T}{M'} \right) \right. \\ &\quad + \left\{ \frac{3K_B T'}{M'} \frac{1}{20} \frac{M''}{M'} \left(\frac{\theta_D^A}{T'} \right)^2 \right. \\ &\quad \left. \left. - \frac{3K_B T}{M'} \frac{1}{20} \frac{M}{M'} \left(\frac{\theta_D^S}{T} \right)^2 \right\} \right] \end{aligned} \quad (5)$$

The second term in (5) gives the second order Doppler shift relative to the absorber and will be zero under two conditions.

(i) If the source and absorber are at the same temperature and are located in the same host lattices, then the second term in (5) will vanish. In this case the first term will also be zero and so the resonant absorption will occur exactly at zero velocity of the source relative to the absorber.

(ii) If the source and the absorber are located in different host lattices and the Mössbauer experiment is performed at high temperature and the condition

$$\begin{aligned} T' \left[1 + \frac{M''}{20M'} \left(\frac{\theta_D^A}{T'} \right)^2 \right] \\ = T \left[1 + \frac{M}{20M'} \left(\frac{\theta_D^S}{T} \right)^2 \right] \end{aligned} \quad (6)$$

is satisfied, then the contribution in energy shift due to second order Doppler effect will be zero in the resonant absorption spectrum. In