

DUAL FLUORESCENCE FROM AN AROMATIC MONOAZINE WITH CLOSE-LYING ${}^1n,\pi^*$ AND ${}^1\pi,\pi^*$ STATES

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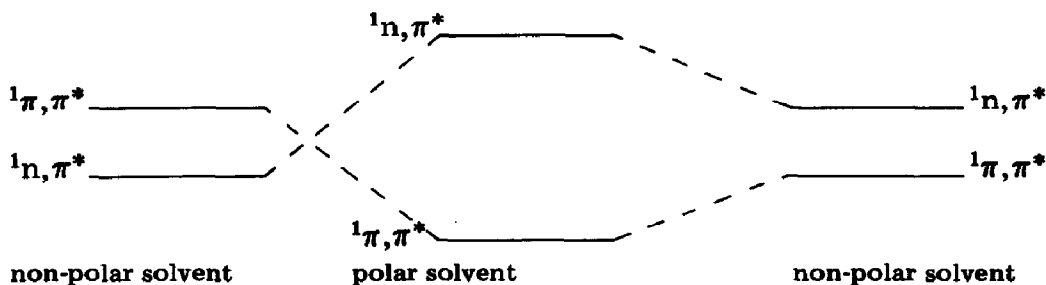
Summary

A variable-temperature fluorescence study of 3-methyl-2-aminopyridine in methylcyclohexane indicates that S_2 emits at room temperature, while at 77 K S_1 and S_2 fluoresce. An out-of-plane vibrational mode (about 504 cm^{-1}) in the low temperature emission spectrum indicates that vibronic coupling of ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states is occurring. Interpretation of the behavior is supported by complete neglect of differential overlap-configuration interaction calculations, lifetime measurements and excitation spectra. The observed effect, which is due to close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states, is shown to be absent in alcohol where the two states are sufficiently separated in energy.

1. Introduction

Electronic states of different orbital symmetry, when they are close lying, can lead to the appearance of a symmetrically displaced double minimum in the lower state while the upper state narrows its potential surface. This pseudo-Jahn-Teller effect has been discussed by Hochstrasser and Marzocco [1] and its implication was elegantly demonstrated in a luminescence study of pyrazine. In aromatic nitrogen heterocyclics the two interacting electronic states are n,π^* and π,π^* , and generally an out-of-plane vibrational mode is expected in the emission spectrum of these molecules. Similar effects of vibronic coupling in phosphorescence spectra have also been reported by Lim [2, 3] and Duben *et al.* [4]. Theoretical calculations of vibronic coupling integrals of pyrazine have been reported by Orlandi and Marconi [5]. When n,π^* and π,π^* are strongly mixed via vibronic coupling the Born-Oppenheimer approximation is no longer valid and the two new states arising from this interaction can be described by $\psi = C_1 f_1({}^1n,\pi^*) + C_2 f_2({}^1\pi,\pi^*)$. The parameters that can be used to probe vibronic coupling in aromatic molecules include solvent, temperature and substitution. For example, methyl substitution in aromatics shifts the ${}^1n,\pi^*$ states to higher energies while lowering the energy of the ${}^1\pi,\pi^*$ states [6]. Lai and Lim [7] have reported that the fluorescence and triplet yields of quinoline and isoquinoline in ethyl alcohol decrease with increasing temperature.

The interaction of close-lying n,π^* and π,π^* states in aromatic nitrogen heterocyclics has remained a subject of fundamental interest to photochemists and spectroscopists with the aim of understanding the radiationless processes of pyridine relative to those of benzene. In a previous study performed in this laboratory on the fluorescence of 2-aminopyridine we demonstrated the existence of close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states which can be inverted in going from a hydrocarbon to an alcoholic solvent [8]. Although complete neglect of differential overlap-configuration interaction (CNDO-CI) calculations indicate that the ${}^1n,\pi^*$ state is lower [9], the overall effect of a polar solvent in this molecule is to place the ${}^1\pi,\pi^*$ state lower, *i.e.*



There would be no inversion if the lowest excited singlet were already ${}^1\pi,\pi^*$ in a non-polar solvent, as is shown for the ordering of states on the right-hand side. Thus in the polar solvent vibronic coupling would be significantly diminished if the two lowest states were close lying. With the possibility of affecting the spacing of these two singlet states by substitution we have undertaken a variable-temperature study in various solvents of the fluorescence of 3-methyl-2-aminopyridine, which CNDO-CI calculations predict has a ${}^1n,\pi^* - {}^1\pi,\pi^*$ separation of only about 800 cm^{-1} with the ${}^1\pi,\pi^*$ state lying lowest.

With regard to the interaction between the two close-lying molecular energy levels, an interesting effect also exists whereby the two states, each with a different lifetime, may emit, for example, ${}^3n,\pi^*$ and ${}^3\pi,\pi^*$ phosphorescence from some aromatic aldehydes and ketones [3, 4]. It would appear interesting to observe the fluorescence from two close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states which are vibronically coupled through some out-of-plane vibrational mode. In view of the predicted close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states in 3-methyl-2-aminopyridine a variable-temperature and solvent fluorescence study of this molecule was undertaken to test its possible conformity with the pseudo-Jahn-Teller effect.

2. Experimental details

2.1. Materials

3-methyl-2-aminopyridine was purified by vacuum sublimation at 7×10^{-4} Torr to yield colorless crystals. Fluorometric grade methylcyclohexane

and ethyl alcohol were used as received, after verifying that they contributed no impurity fluorescence. The concentration of the solutions was generally 1×10^{-4} M and the fluorescence measurements were made in 4 mm Suprasil tubes with a graded seal to Pyrex which were vacuum degassed at 7×10^{-4} Torr prior to sealing off from the vacuum line.

2.2. Instrumentation

Fluorescence measurements were made, with front surface illumination and 1 nm band excitation, using a photon counting system which has been described previously [10]. Variable-temperature fluorescence measurements were made using an Oxford Instruments Dewar. A pulsed frequency-doubled argon ion laser was used to measure the fluorescence lifetimes.

The CNDO-CI calculations were performed according to the CNDUV99 method [11] and consistent force field calculations were performed according to the quantum consistent force field (π electron approximation) (QCFF/PI) method [12].

3. Results

The lowest UV absorption band of 3-methyl-2-aminopyridine in methylcyclohexane is unstructured and exhibits a maximum at 289 nm which suggests that the ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states may be close lying. The fluorescence spectra of this molecule in methylcyclohexane at room temperature and 77 K are shown in Fig. 1, where it is apparent that, although the room temperature fluorescence with the wavelength maximum at 332 nm is unstructured, cooling shifts the fluorescence so as to have a maximum at about 355 nm and increases vibrational structure. At room temperature the fluorescence yield of 3-methyl-2-aminopyridine is 0.047 when excited at 285 nm. This fluorescence spectrum is independent of the excitation wavelengths 285, 295 and 305 nm and is marked as curves 1 and 2 in Fig. 1. In fact, at room temperature the absorption and fluorescence spectra indicate a normal mirror image relationship. When 285 nm excitation is employed, variable-temperature fluorescence intensity measurements at 335 nm indicate that a thermally activated route is removed upon cooling. It is noteworthy that the observed low temperature emission spectrum is shifted to lower energies and exhibits an out-of-plane vibrational mode (about 504 cm^{-1}) that is evident in Fig. 1, curve 3. A vibrational analysis of the fluorescence envelope is given in Table 1 and supports the presence of vibronic coupling. The presence of this out-of-plane band strongly implies interaction between the two close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states. It was found that the first peak at $32\,123 \text{ cm}^{-1}$ is a Raman peak of the solvent and that the 0-0 band is at $31\,696 \text{ cm}^{-1}$. Excitation at 295 and 300 nm (Fig. 1, curve 4) at 77 K, however, generates a spectrum similar to that obtained with 285 nm excitation but without any vibrational structure.

Excitation spectra were measured at room temperature and at low temperature with the aim of determining the relationship between the

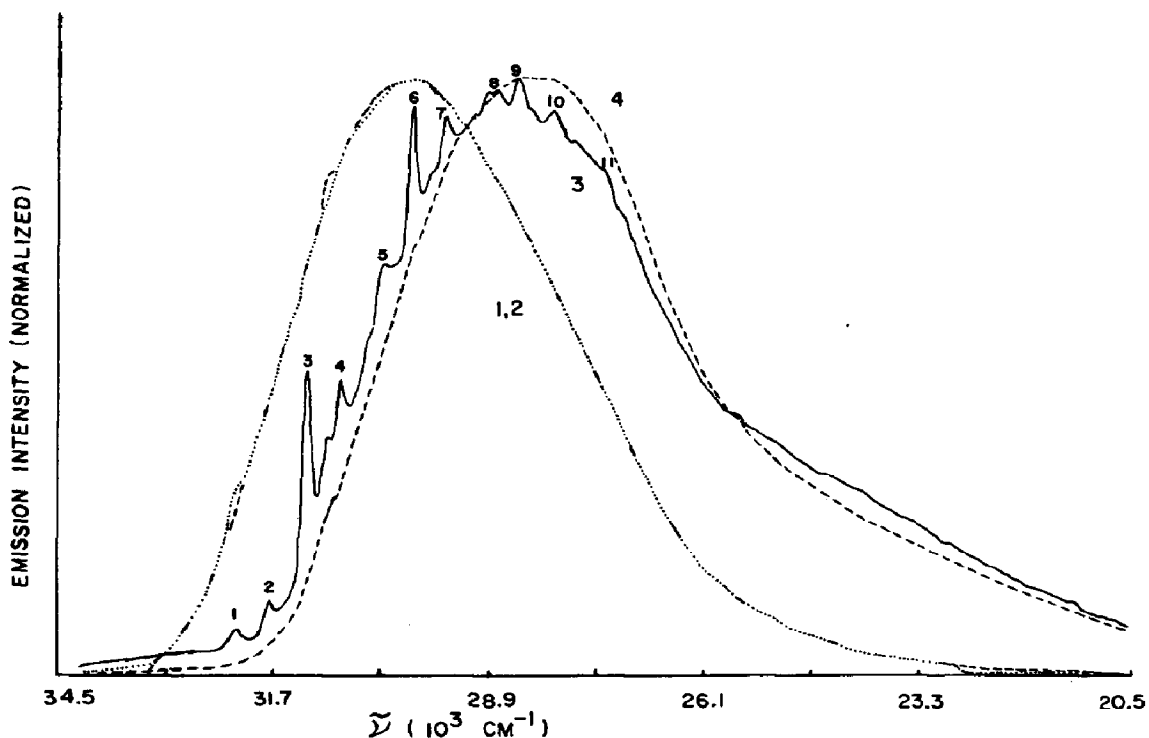


Fig. 1. Fluorescence spectrum of degassed 3-methyl-2-aminopyridine in methylenecyclohexane at different temperatures: curves 1 and 2, room temperature fluorescence spectrum when excited at 285 and 295 nm; curve 3, total emission spectrum at 77 K when excited at 285 nm; curve 4, total emission spectrum at 77 K when excited at 295 nm.

TABLE 1

Vibrational analysis of the fluorescence envelope of 3-methyl-2-aminopyridine in methylenecyclohexane at 81.7 K (285 nm excitation; vacuum degassed)

Peak	λ (fluor) (nm)	$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	Multiples of 504 cm^{-1}
1	311.3 (Raman)			
2	315.5	31696	0	
3	320.6 (intense)	31192	504	504
4	325.5	30722	974	1008
5	331.5	30166	1530	1512
6	336.1 (intense)	29753	1943	2016
7	340.9	29334	2362	2520
8	348.8	28670	3026	3024
9	352.3	28385	3311	3528
10	358.2	27917	3779	4032
11	366.8	27263	4433	4536

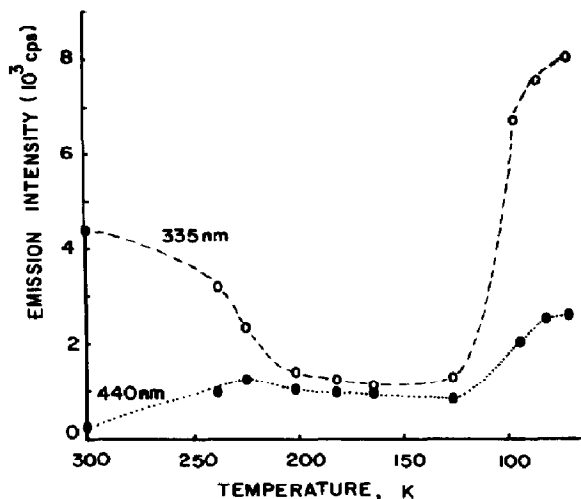


Fig. 2. Temperature dependence of the emission intensity at 335 and 440 nm for vacuum-degassed 3-methyl-2-aminopyridine in methylcyclohexane excited at 285 nm.

absorbing and the emitting species. At room temperature the excitation spectra measured with the emission monochromator at 335 nm and at 360 nm correlated with only one state with a maximum absorption in the vicinity of 296 nm; however, at 77 K there is clear evidence from excitation spectra run at different emission wavelengths in the range 325 - 360 nm that two overlapping states are present: one unstructured peak at about 300 nm and another peak at approximately 313 nm. The low temperature excitation spectrum with the emission monochromator at 320.5 nm shows a vibronic mode of about 500 cm^{-1} .

In view of the shifted fluorescence spectrum observed at low temperatures relative to room temperature, the fluorescence temperature dependence was measured with the emission monochromator at 335 and 440 nm. These results, summarized in Fig. 2, indicate that at 335 nm the fluorescence initially decreases with temperature, levels off and then increases dramatically below 130 K. Clearly, the fluorescence intensity is significantly higher at lower temperatures. At 440 nm there is only a small increase in the emission contribution upon cooling which corresponds to the lower energy region of the fluorescence spectrum and the phosphorescence region of 2-aminopyridine. However, amino pyridines do not phosphoresce in hydrocarbon solvents [13].

The fluorescence of 3-methyl-2-aminopyridine measured at room temperature and at 77 K in ethyl alcohol is given in Fig. 3 where it is evident that no wavelength shift in fluorescence occurs and that there is no marked increase in intensity upon lowering the temperature to 77 K. The fluorescence intensity at 356 nm in ethyl alcohol only increases by about 25% in the temperature range from 300 down to 80 K. A significant difference in the fluorescence behavior of this molecule in ethyl alcohol relative to that in cyclohexane is evident.

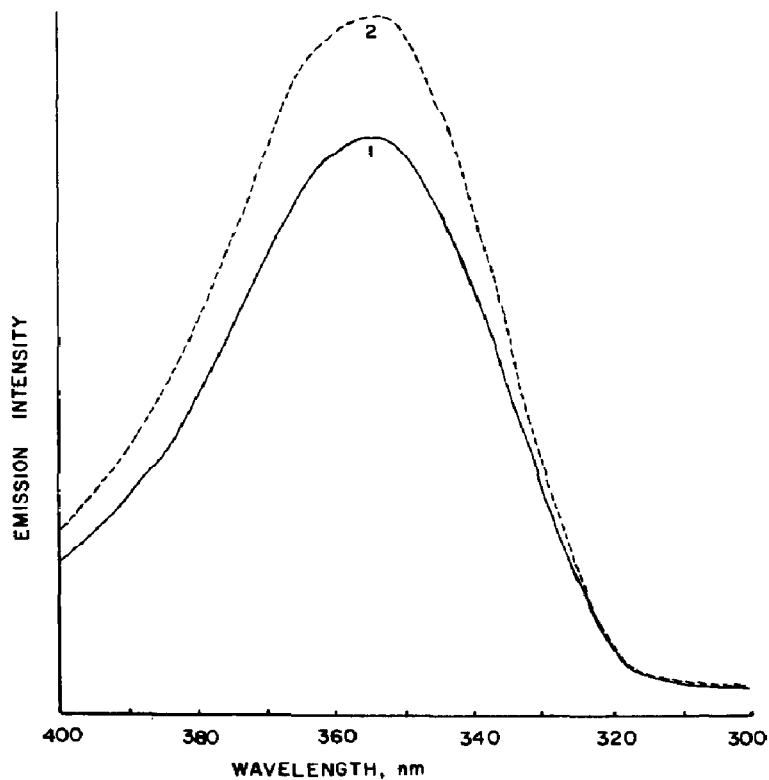


Fig. 3. Emission spectrum for degassed 3-methyl-2-aminopyridine in ethyl alcohol excited at 285 nm: curve 1, room temperature fluorescence; curve 2, total emission at 77 K.

Fluorescence lifetimes were measured in methylcyclohexane at three wavelengths at 77 K with the aim of corroborating the presence of two emitting states. On excitation at 257 nm from a pulsed frequency-doubled argon ion laser, the sharp peak in the emission spectrum at 320 nm (band 3) was determined to have a lifetime of 12.1 ns, while the emissions at 350 nm and 390 nm have lifetimes of 4.9 ns and 5.3 ns respectively.

4. Discussion

From the results presented above it appears that for 3-methyl-2-aminopyridine in methylcyclohexane there are ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states which are strongly coupled and, depending upon the temperature, both states can emit. The variable-temperature behavior of the fluorescence at 335 nm indicates that a thermally activated route to radiationless decay is important at room temperature. The out-of-plane vibrational mode observed in the low temperature fluorescence spectrum (Fig. 1) provides convincing evidence that the two states are vibronically coupled and that the potential energy curve along that coordinate is distorted. The loss of structure at low temperature in the fluorescence spectra excited at 295 and 300 nm simply reflects a larger con-

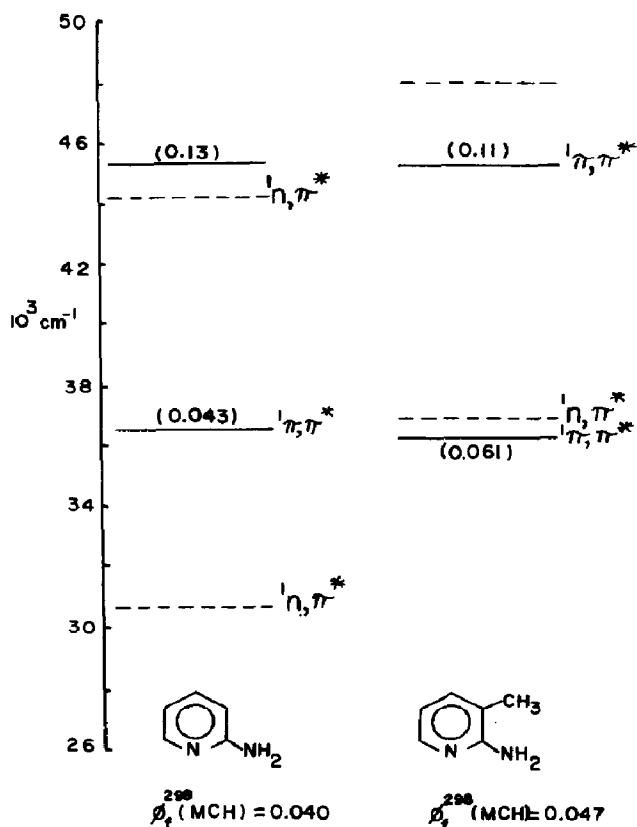
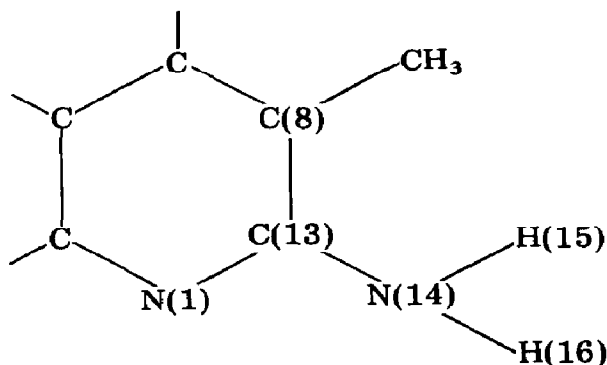


Fig. 4. Summary of excited singlet state energies from the CNDUV99 calculations for 2-aminopyridine and 3-methyl-2-aminopyridine.

tribution from S_1 which is unstructured. The absence of structure in the low temperature fluorescence spectrum measured in ethyl alcohol, together with the absence of significant temperature-dependent effects, is readily accounted for by the increased separation of these states, *i.e.* $^1n,\pi^*$ moves to higher energies while $^1\pi,\pi^*$ moves to a lower energy.

Figure 4 shows the results of a CNDUV99 calculation which we have performed for the singlet states of 3-methyl-2-aminopyridine together with those for 2-aminopyridine [9]. These calculations support the observation that the methyl substitution in the 3 position has inverted the two lowest excited singlets and more importantly has decreased the energy gap relative to 2-aminopyridine.

In an attempt to identify the out-of-plane vibrational mode (about 504 cm^{-1}) active in the fluorescence spectrum at 77 K in methylcyclohexane, we have performed a consistent force field calculation. The following out-of-plane mode theoretically predicted at 471 cm^{-1} , involving changes in the dihedral angle defined by the atoms below, is a torsional oscillation of NH_2 about the C–N bond and is attractive in accounting for vibronic coupling between the $^1n,\pi^*$ and $^1\pi,\pi^*$ states:



(out-of-plane vibration involving amino group; QCFF vibration predicted at 471 cm^{-1} ; N—C—N—H, atoms 1—13—14—15; N—C—N—H, atoms 1—13—14—16; C—C—N—H, atoms 8—13—14—15; C—C—N—H, atoms 8—13—14—16).

In order to account for the observed solvent and temperature effects on the fluorescence behavior of 3-methyl-2-aminopyridine we should like to suggest a modification to the symmetrical double minimum in the lower state predicted by the pseudo-Jahn-Teller effect. Specifically we should like to consider the influence of an asymmetrical molecular environment on the potential energy surface. In particular there are two possibilities that are in principle experimentally verifiable, and these are shown in Fig. 5. In case I we have the situation whereby excitation into S_1 at room temperature would, via thermal activation, result in channeling to the lower side of the double minimum and efficient radiationless decay to the ground state would occur. Excitation into S_2 at room temperature, however, could result in fluorescence emission. Upon lowering the temperature the thermally activated process leading to the lower half of the double minimum is prevented and the possibility exists for both S_1 and S_2 to emit. Case II involves another interesting case whereby a double minimum appears in S_2 and at room temperature only S_1 fluoresces, while thermal activation in S_2 may result in photochemistry. At low temperatures, when the thermally activated route is removed, fluorescence may be observed from both S_1 and S_2 . The major difference in these two cases is that in case I the fluorescence shifts to lower energies with decreasing temperature, while in case II the fluorescence shifts to higher energies. We believe that an asymmetrical pseudo-Jahn-Teller effect (case I) provides a reasonable interpretation for the results presented in this study. This explanation is supported by (a) the clear evidence of out-of-plane vibrational activity, (b) solvent and temperature effects, (c) excitation spectra, (d) fluorescence lifetime measurements and (e) CNDO-CI calculations.

An alternative explanation for the two emissions (sharp and broad fluorescence) observed at low temperature in methylcyclohexane, each having its own lifetime and excitation spectrum, is that it originates from two conformers rather than two states, *i.e.* two preferred orientations of the lone electron pair of the amino group relative to the aromatic ring. However,

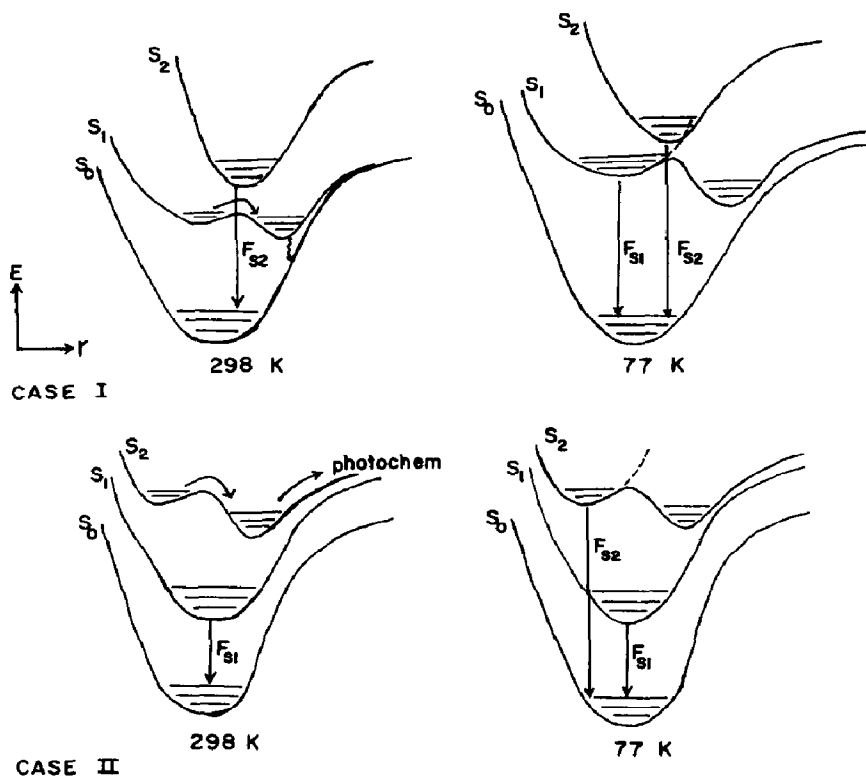


Fig. 5. Potential energy model which gives rise to two emitting species depending upon temperature. In case I the lowest excited singlet exhibits a double minimum and S_2 fluorescence is observed at room temperature. At low temperatures S_1 and S_2 emit.

the absence of dual emission in ethanol at low temperature and the room temperature correlation of the fluorescence and excitation spectrum with one state make this possibility very unlikely. Thus, since excitation spectral measurements conducted at room temperature indicate the presence of only one state and only one emission is observed in ethyl alcohol at low temperatures, we conclude that the two emissions originate from two states of the same molecule rather than from two conformers.

In summary, we have observed the fluorescence of two close-lying ${}^1n,\pi^*$ and ${}^1\pi,\pi^*$ states which are intimately mixed by vibronic coupling. Upon lowering the temperature a thermally activated radiationless route is removed, facilitating dual fluorescence. The change of solvent from methylcyclohexane to ethyl alcohol, however, removes vibronic coupling by increasing the separation between the close-lying states and gives the same fluorescence spectrum down to 80 K. Finally, the above behavior is satisfactorily explained in terms of an asymmetrical pseudo-Jahn-Teller effect (case I) which predicts a change from a single emission from S_2 at room temperature to dual emission in a non-polar solvent as the temperature is lowered.

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