Polarization Study of the Fluorescent State of the Hydrogen Bonded α-Naphthol

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In molecular emission spectroscopy it has been established that fluorescence of a molecule in a condensed phase is associated with the electronic transition from the lowest singlet excited state to the ground state. The situation becomes somewhat complicated, however, when there exists another singlet excited state close to the lowest one. Mataga *et al.*[1,2] created such a condition for α-naphthylamine and indole by the aid of the solvent perturbation and they concluded that the fluorescent state of these molecules changes from the ^1L_b to the ^1L_a state with the increase of the polarity of the solvent. Lippert *et al.*[3] also found a similar phenomenon for *p*-cyanodimethylaniline. Zimmermann *et al.*[4,5] applied the photoselection technique to the assignment of closely situated singlet excited states in some organic molecules. In the present study the same problem has been treated for α-naphthol from the viewpoint of polarization of electronic transitions.

The degree of polarization (P) of fluorescence excitation spectra was measured by the method of photoselection[6-8] at liquid-nitrogen temperature with 4 : 1 isopentane and methylcyclohexane mixture (PM) as a glass-forming solvent. Ether or triethylamine was added to increase the solubility of α-naphthol. It was expected that these proton-accepting substances would produce an effect on the electronic levels of the naphthol

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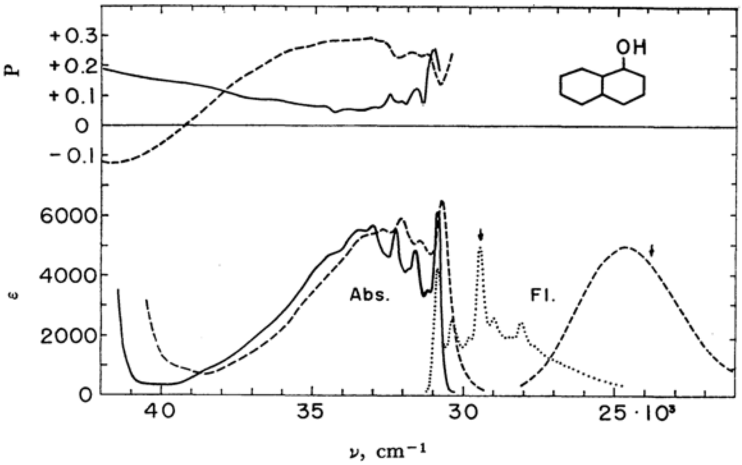

Fig. 1. Upper: Polarization of fluorescence excitation spectra of α-naphthol; Lower: Absorption and fluorescence spectra of α-naphthol. Solid and dotted curves: Spectra in 4 : 1 PM with 1.0 M ether; Dashed curves: Spectra in 4 : 1 PM with 0.2 M triethylamine. Arrows indicate the frequency at which the observation of the fluorescence was made.

through hydrogen bond formation. The results of the polarization measurements are shown in Fig. 1, together with the absorption and fluorescence spectra.

Of the four absorption bands of α-naphthol in the near ultraviolet region, the lowest frequency band with a sharp fine structure is assigned to the ^1L_b transition, the broad band near 34000 cm^{-1} which overlaps the ^1L_b to the ^1L_a transition, and the strong band at higher frequencies than 40000 cm^{-1} is assigned to the ^1B_b transition.[9,10] It is known that the moments of the ^1L_b and ^1B_b transitions lie nearly along the direction of the long axis of the molecule, while the moment of the ^1L_a transition along the short axis.[11,12]

The polarization spectrum in PM with ether as the proton acceptor exhibits positive peaks at the frequencies corresponding to the vibrational peaks of the ^1L_b absorption band. The degree of polarization is only slightly positive in the region of the ^1L_a band, whereas it has large positive values in the ^1B_b absorption region. These observations indicate that the polarization of the fluorescence transition is parallel to that of the ^1L_b absorption, and therefore the fluorescent state is the ^1L_b state. Also, the ^1L_b and ^1B_b transitions are seen to be polarized in almost the same direction. This is consistent with the results of theoretical studies by Nishimoto *et al.* for the free α-naphthol.[11,12]

In the presence of triethylamine which is a strong proton acceptor, the fluorescence spectrum of α-naphthol in PM shifts considerably to the red, and coincides with its fluorescence spectrum in alkaline solution. Inspection of absorption and fluorescence data shows that the proton of the hydroxyl group of the naphthol is transferred to the amine in the excited state and the resulting ion pair is responsible for the fluorescence, while the absorbing species is the hydrogen-bonded naphthol. It is seen in Fig. 1 that the polarization spectrum undergoes essential changes on changing the proton acceptor from ether to triethylamine. Thus, in the case of triethylamine, the peaks of the ^1L_b absorption band correspond to polarization minima which lie on a plateau of the polarization curve having highly positive P values, the plateau being assigned to the ^1L_a absorption. Further, the degree of polarization is negative in the region of the ^1B_b transition. The behavior of the polarization spectrum shows in every respect that the fluorescence is polarized parallel to the ^1L_a absorption. One is thus led to the conclusion that in the system of α-naphthol and triethylamine the fluorescent state is the ^1L_a, which should correspond to the lowest singlet excited state for the ion pair mentioned above.

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