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The Temperature Dependence of the Fluorescence and Polarization Spectra of 1-Naphthol

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In general, the fluorescence of an organic compound in a condensed medium originates from the lowest excited singlet state, because the internal conversion between excited singlet states is fast compared with the fluorescence emission. If two excited singlet levels are closely situated in the region of the lowest absorption band, a dual emission is expected to be observed.[1-5] On the other hand, it is well accepted that a molecule in a fluid solution is first excited to the Franck-Condon excited state, and that it then passes into the equilibrium excited state from which the fluorescence emission occurs. At sufficiently low temperatures, such a relaxation process cannot take place during the fluorescence lifetime because of the high viscosity of a solvent. As a result of this phenomenon, the fluorescence emission originates from the Franck-Condon excited state and, hence, shifts to the blue. This note will report the inversion of the fluorescent state in 1-naphthol caused by a lowering of the temperature.

Experimental

1-Naphthol was recrystallized three times from water and then sublimed *in vacuo*. Glycerin (Wako Pure Chemical Industiries, Inc., JIS S grade) was used without further purification.

The absorption spectra were recorded on a Hitachi EPS-2 recording spectrophotometer. The fluorescence and excitation spectra were obtained by means of a Hitachi MPF-2A fluorescence spectrophotometer. The temperatures of the solutions were controlled by using a cryostat (Torisha Laboratory, Ltd.) with an accuracy of about ±1 K. The degree of polarization, P, was measured by the method of photoselection.[6-8]

Results and Discussion

The temperature dependence of the fluorescence spectra for 1-naphthol in a glycerin solution is shown in Fig. 1, together with the absorption and polarization spectra.

1-Naphthol has four absorption bands 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 3.4 kK which overlaps the ^1L_b, to the ^1L_a transition, and the other two strong bands at higher frequencies than 4 kK, to the ^1B_b transition.[9-11] 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 is nearly along the short axis.[11-13]

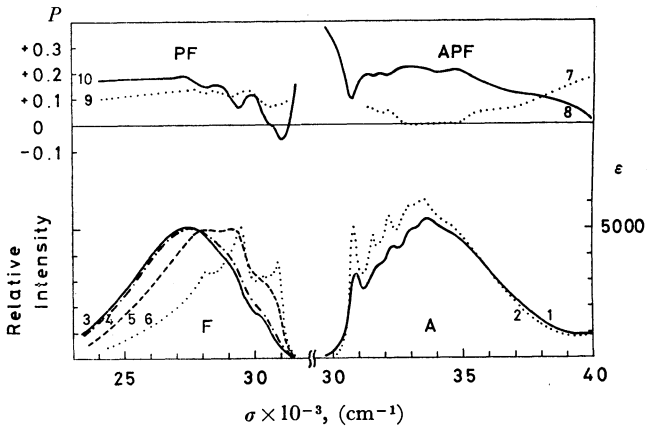

Fig. 1. Temperature dependence of the absorption, fluorescence, and polarization spectra of 1-naphthol in glycerin. a) Absorption spectra(A) 1: 299 K; 2: 135 K. b) Fluorescence spectra(F) Excitation wavelength: 297 nm; 3: 329 K; 4: 261 K; 5: 242 K; 6: 168 K. c) Fluorescence excitation polarizarion spectra(APF) 7: 200 K, observed at 325 nm; 8: 200 K, observed at 360 nm. d) Fluorescence polarization spectra (PF) Excitation wavelength: 297 nm; 9: 283 K; 10: 195 K.

At room temperatures, 1-naphthol has a broad, structureless fluorescence band. In the excitation polarization spectrum at 200 K, obtained by monitoring the fluorescence at the wavelength of 360 nm, which corresponds to the maximum of the broad fluorescence band, the peaks of the ^1L_b-absorption band correspond to the polarization minima, whereas the polarization spectrum has large positive P values in the ^1L_a-band region. Further, the degree of polarization is negative in the region of the ^1B_b transition. Such behavior in the excitation polarization spectrum is very similar to that observed in the system of 1-naphthol and triethylamine.[4] The fluorescence polarization curve obtained with excitation at the ^1L_a band has nearly the same positive P values over the whole region of the fluorescence band. These observations indicate that the polari-

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zation of the broad fluorescence transition is parallel to that of the ^1L_a and that, hence, the fiuorescent state is the ^1L_a state.

As the temperature is lowered, the fluorescence spectrum shifts to the blue and changes to a structured band, the peaks of which lie in mirror-symmetry positions with respect to the ^1L_b absorption peaks.

At a low temperature, the excitation polarization spectrum obtained by monitoring the highest-frequency peak of the fluorescence band exhibits minima at the wavelengths corresponding to the region of the ^1L_a-absorption band. The degree of polarization is positive in the region of the ^1B_b-absorption band. The degree of polarization of the fluorescence emission obtained with an excitation wavelength of 297 nm shows a considerable decrease in the short-wavelength region. The wavelengths at which the minima of the polarization curve occur coincide with the peaks of the fluorescence band. The behavior of the polarization spectra confirms that the fluorescence emission from 1-naphthol in glycerin at sufficiently low temperatures is predominantly from the ^1L_b state. The same temperature dependence of fluorescence and polarization spectra was observed in both propylene glycol and ethanol solvents.

The results may be interpreted as follows. In the equilibrium excited state, the interaction of a solute molecule with solvent molecules lowers the ^1L_a energy below the ^1L_b, so that the broad ^1L_a fluorescence is observed. At a sufficiently low temperature, where the solute and solvent molecules do not have enough time to relax to the equilibrium configuration, the ^1L_a state lie above the ^1L_b, therefore, the blue-shifted ^1L_b fluorescence is observed. This interpretation is consistent with the finding of the theoretical calculation that the π-moment of the ^1L_a state is larger than that of the ^1L_b.[12]

The degree of polarization in glycerin increases to a maximum value at 10°C. This means that 1-naphthol cannot re-orient itself during its fluorescence lifetime at a temperature below 10°C. It should be noted that the temperature at which the fluorescence from the ^1L_b state becomes appreciable is lower by about 30 degrees than that at which the re-orientation of the solute ceases. The effects of molecular motions on the fluorescent state will be discussed later.