Time-Resolved Fluorescence Studies on the Dual Fluorescence Process of *p*-(Dimethylamino)benzonitrile

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Time-resolved fluorescence spectra and the fluorescence rise and decay curves have been measured for *p*-(*N*,*N*-dimethylamino)-benzonitrile. The results demonstrate the relaxation process to be due to the interaction between the solvent and the ^1L_a state of the solute, leading to dual fluorescence.

In some molecules such as *p*-(dimethylamine)benzonitrile (DMABN)[1] and indole[2] the lowest excited singlet state is a slightly polar state of the ^1L_b type, and the highly polar ^1L_a state is not far from it. In such a case, there is a possibility that the solvent effect causes the inversion of two different energy states since the solvent effect on these two excited states seems to differ considerably. In relation to such a solvent effect, the fluorescence of DMABN has been studied in detail.[1]

In a nonpolar solvent such as cyclohexane, DMABN shows only one fluorescence band due to the transition from the ^1L_b state. However, in a polar solvent, fluorescence spectra have two peaks, since the ^1L_a state can be strongly stabilized in the excited equilibrium state because of the large dipole-dipole interaction and turn out to be the lowest excited state. Actually, from the solvent shift of the fluorescence, the dipole moment of the ^1L_a state, $\vec{\mu}(^1L_a)$,has been evaluated to be 23 D.[1]

So far no direct confirmation of the above relaxation process has been made. We have undertaken to observe the process by means of ns time-resolved fluorescence spectroscopy.

Experimental

The fluorescence rise and decay curves as well as time-resolved fluorescence spectra were obtained by exciting the solution with a 337 nm light pulse of nitrogen gas laser. Details of the apparatus were described elsewhere.[3] For the measurement of ordinary luminescence spectra, calibrated Aminco-Bowman and Hitachi MPF-2A spectrophotofluorometers were used. The absorption spectra were measured with Cary 15 and Shimadzu MPS-50L spectrometers. The temperature of a solution was controlled by a constant flow of cold nitrogen gas in a metal Dewar with quartz windows.

DMABN was recrystallized several times from cyclohexane. 2-Methyltetrahydrofuran (MTHF) was refluxed over metallic sodium wire, fractionally distilled and finally distilled under vacuum in the presence of lithium aluminum hydride. Spectrograde benzonitrile and cyclohexane were used without further purification.

Results and Discussion

DMABN shows ^1L_b fluorescence (F_b) at 365 nm and ^1L_a fluorescence (F_a) at 425 nm in MTHF solution at room temperature. The fluorescence quantum spectra at several temperatures are given in Fig. 1.

When the temperature of the solution is lowered from room temperature to −110 °C, F_a shows a remarkable red shift while F_b shows no shift at all. The former can be ascribed to the very polar structure of the ^1L_a state and increase of solvent polarity by temperature lowering, and the latter to the nonpolar nature of the ^1L_b state.[1]

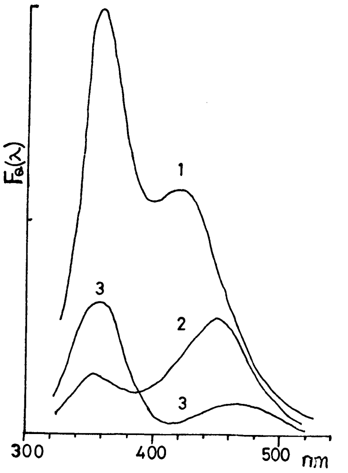

Fig. 1. Fluorescence quantum spectra of DMABN in MTHF at various temperatures.
1: room temperature (~20 °C), 2: −50 °C, 3: −110 °C

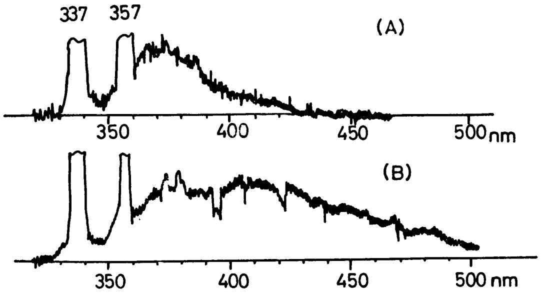

Fig. 2. Time-resolved fluorescence spectra of DMABN in MTHF at −115 °C.
(A) T_d=2.0 ns, (B) T_d=7.0 ns.
The spectra are not corrected, and the correction will shift the F_a band to the longer wavelength side. The lines at 337 and 357 nm are due to the scattered exciting pulse.

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[1] E. Lippert, W. Lüder, and H. Boos, "Advances in Molecular Spectroscopy," Pergamon Press, (1962), p. 443.

[2] N. Mataga, Y. Torihashi, and K. Ezumi, *Theoret. Chim. Acta* (Berl.) **2**, 158 (1964).

[3] N. Nakashima, N. Mataga, F. Usio, and C. Yamanaka, *Z. Phys. Chem. N. F.*, **79**, 150 (1972).

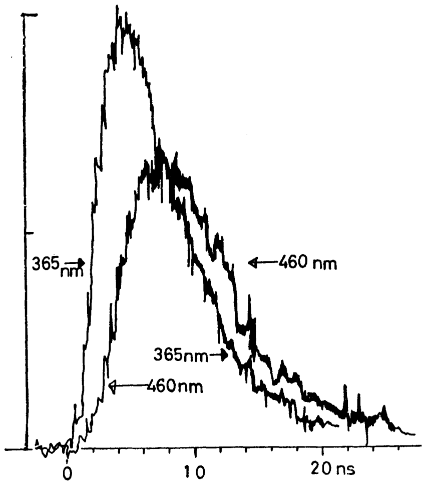

Fig. 3. Rise and decay curves of F_b and F_a bands.
(It has been confirmed that the intensity of the scattered exciting pulse can be neglected at 365 nm.)

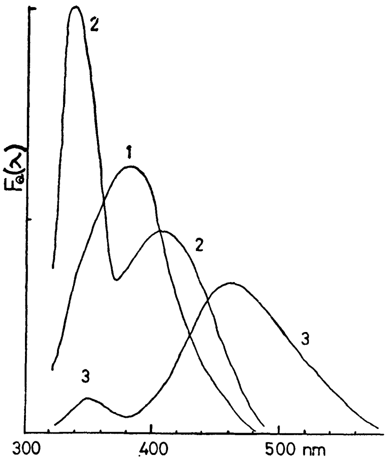

Fig. 4. Fluorescence quantum spectra of DMABN-benzonitrile system in cyclohexane at various temperatures. [DMABN] $=5.0\times10^{-4}$ M, [Benzonitrile] $=5.0\times10^{-3}$ M.
1: room temperature (~20°C) 2: 0°C, 3: −10°C.

In order to observe directly the solvent relaxation process leading to dual fluorescence, we have made the time-resolved fluorescence measurements as shown in Figs. 2 and 3. It can be seen that at the delay time (T_d) of 2 ns from the exciting pulse the F_b band is predominant and the intensity of the F_a band is very weak (Fig. 2). At $T_d=7$ ns, the intensity of the F_a band becomes comparable with that of the F_b band. The relaxation process can be demonstrated also by measuring the fluorescence rise and decay curves of the F_b and F_a bands. We see that the fluorescence rise time of the F_a band measured at 460 nm is longer than that of the F_b band, in agreement with the results in Fig. 2. The decay times of both bands are approximately the same, which seems to indicate the equilibrium or reaction between the two states, ^1L_b and ^1L_a. The results prove unambiguously the solvation process of the ^1L_a state which causes the dual fluorescence. The results given in Figs. 2 and 3 were obtained at −115 °C, but we have made measurements on the same system also at room temperature where the relaxation process is much faster than that at −115 °C. Thus even at small delay times, the intensity of the F_a band is fairly strong. Nevertheless, we observed that the intensity ratio $I(F_b)/I(F_a)$ at a small T_d value is larger than that at a large one.

In relation to the very polar nature of the ^1L_a state of DMABN, we have examined the possibility that the ^1L_a DMABN forms the complex with benzonitrile by electrostatic dipolar interaction. Such a possibility has already been examined by Chandross and Thomas[4] in the case of DMABN-propionitrile system in methylcyclohexane. They observed three fluorescence maxima upon successive additions of propionitrile to a methylcyclohexane solution. We studied the effect of temperature upon the fluorescence of the DMABN-benzonitrile system in cyclohexane, the results of which are shown in Fig. 4.

At 70 °C, we observed only one fluorescence band which may be ascribed to a free DMABN molecule. The spectra at room temperature seem to be a superposition of the band due to the free DMABN and that of the complex. At 0 °C as well as at −10 °C, we can clearly recognize two bands, the shorter being ascribable to the free DMABN and the longer to the complex. The fluorescence band due to the complex shows a remarkable red shift by temperature lowering. Presumably, the spectra of the complex at lower temperatures are not due to the 1 : 1 dipolar complex but can be attributed to a 1 : n complex or a 1 : 1 complex strongly solvated by benzonitrile.

We also examined temperature effect on the cyclohexane solution of DMABN itself. At low temperatures, this system shows a long wavelength fluorescence band with peaks at 390 and 460 nm together with the ^1L_b band of the free DMABN. Since the positions of the long wavelength fluorescence peaks and the ratio of their intensities do not change with temperature lowering or with the increase of DMABN concentration, the long wavelength band might be ascribed to the 1 : 1 dipolar complex (self-complex) of DMABN.

The fluorescence decay time at 390 and 460 nm was about 9 ns, while that measured at F_b band was shorter than 5 ns. A slightly longer lifetime of the long wavelength fluorescence may be explained based on the above dimer model. We assume the sandwich dimer configuration where the dimethylamino group comes over the cyano group, and take the excition type wavefunction $\Psi_\pm=(\Psi_1{}^a\Psi_2{}^o\pm\Psi_1{}^o\Psi_2{}^a)/\sqrt{2}$, assuming the perturbation Hamiltonian of the dipole-dipole interaction, where Ψ^a represents the ^1L_a state. Thus, the energies of these states may be written as $E_+=E_a-\{(|\vec{\mu}_e|\cdot|\vec{\mu}_g|+\mu_t{}^2)/R^3\}$, $E_-=E_a-\{(|\vec{\mu}_e|\cdot|\vec{\mu}_g|-\mu_t{}^2)/R^3\}$, where E_a is the energy of the ^1L_a state, $\vec{\mu}_e$ and $\vec{\mu}_g$ the dipole moments of the ^1L_a state and the ground state, respectively, and $\vec{\mu}_t$ the transition moment. Thus, $E_+<E_-$ and the transition between the ground state

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[4] E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971).

$\Psi_1^0 \cdot \Psi_2^0$ and Ψ_+ is forbidden. Presumably, this sort of exciton type interaction in addition to the permanent dipole-dipole interaction is responsible for making the lifetime of the long wavelength band a little longer.

In view of the above results of complex formation, short range dipolar interactions might be important even in the case of the interaction between ^1L_a DMABN and MTHF.