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Time-Resolved Fluorescence Studies on Charge Transfer Interactions in 1,2,4,5-Tetracyanobenzene-Toluene Complex[1]

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Time-resolved CT (charge transfer) fluorescence spectra and the fluorescence rise and decay curves at various wavelengths of the CT fluorescence band have been measured for the 1,2,4,5-tetracyanobenzene (TCNB)-toluene system at various temperatures. The results and detailed studies of the effect of solvent polarity on the fluorescene wavenumbers have demonstrated that the relaxation process is due to the change of structure including the surrounding solvent molecules from the Franck–Condon (F.C.) state to the equilibrium (e.q.) state of the excited complex. This relaxation process causes a large Stokes shift of the CT fluorescence.

Although there are numerous investigations on the electron donor-acceptor (EDA) complexes by the absorption spectral measurements, few studies have been carried out on the excited complexes by fluorescence spectral measurements, except for rigid solvents at lower temperatures, because of the fact that the fluorescence yield of the EDA complex in solution at room temperature is extremely small in general.[3] However, somewhat detailed fluorescence studies are possible in the case of TCNB-aromatic hydrocarbon EDA complexes since they are strongly fluorescent in solution at room temperature when the solvent dielectric constant is not large.

It has been observed for the TCNB-toluene EDA complex that the fluorescence lifetime at room temperature is more than 100 nsec which is much longer than the radiative lifetime (~50 nsec) calculated from the intensity of the CT absorption band.[4] Contrary to this, the fluorescence lifetime observed in a rigid state at 77°K is nearly equal to the calculated radiative lifetime.[4] This clearly indicates a considerable change in the structure of the complex during the fluorescence lifetime, where the molecular rearrangement motions including the surrounding solvent molecules occur easily at room temperature but with difficulty at 77°K. The rearrangement relaxation from the F. C. excited state to the e.q. fluorescent state, which can be ascribed to the strong interaction between the excited complex and the surrounding solvent molecules, brings out an extraordinary large Stokes shift of *ca.* 12000 cm^{-1} at room temperature.[4]

In order to elucidate the structure of the excited complex and the dynamical processes of its rearrangement motions we have carried out detailed studies on the effect of temperature and solvent polarity on the fluorescence wave-numbers. We have measured the time resolved fluorescence spectra and the fluorescence rise and decay curves at various fixed wavelengths of the CT fluorescence band of the complex at various temperatures. The results of the time-resolved fluorescence studies gave a direct demonstration of the extensive F.C.→e.q. relaxation process assumed previously.[4]

Experimental

A 337 nm light pulse of nitrogen gas laser was used for the excitation of the complex. The light pulse has a peak output power of 10 kW and duration of 3 nsec. Its repetition rate was *ca.* 50 Hz. Fluorescence emission was observed with a travelling wave-pulsed photomultiplier according to Bennett.[5] The outputs from the photomultiplier with delay line were displayed on an X-Y recorder. Thus, we obtained the time-resolved spectrum at a fixed delay time

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[1] A preliminary note has been published in *Chem. Phys. Letters*. **8**, 108 (1971).

[2] To whom all correspondences should be addressed.

[3] a) G.Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1962); b) N.Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel-Dekker Inc., New York (1970).

[4] N.Mataga and Y.Murata, *J. Amer. Chem. Soc.*, **91**, 3144 (1969).

or the time variation of luminescence intensity at a fixed wavelength. Our apparatus was calibrated to obtain correct luminescence quantum spectrum. For the measurement of ordinary luminescence spectrum, an Aminco-Bowman spectrophotofluorometer calibrated to obtain the correct luminescence quantum spectrum was used. The measurement of temperature effect on the fluorescence was conducted by using a metal dewar with quartz windows. The temperature of the solution in a quartz cuvette placed in the dewar was controlled by a constant flow of cold nitrogen gas. The flow of the gas was controlled by heating liquid nitrogen and the temperature of the solution was measured with a thermocouple. The measurement at 77°K was carried out with a quartz dewar containing a solution in a cuvette immersed in liquid nitrogen. Differential thermal analysis on the phase transition of toluene was made with an apparatus constructed by Prof. S. Seki and his coworkers of this university.

TCNB sample was the same as used before.[4] It was recrystallized from ethanol before use. Benzene and toluene were shaken with sulfuric acid, dried over calcium chloride and after passing through a column of activated alumina, distilled fractionally. *o*- and *m*-xylene were distilled. Cyclohexane and *n*-hexane were passed through a column of activated silica gel, dried over sodium metal and distilled. *o*-Dichlorobenzene and monochlorobenzene were dried over calcium chloride and distilled. Trichloroethylene was distilled. Merck spectrograde tetrachloroethylene was used without further purification. All solutions were deaerated by freeze-pump-thaw cycles.

Results and Discussion

The luminescence spectra of TCNB-toluene system at several temperatures are given in Fig. 1.

When the temperature of the solution is lowered from room temperature to 193°K, the wavelength of the fluorescence band maximum ($\lambda_F{}^m$) shifts from 510 nm to 530 nm. A slight decrease of fluorescence intensity as well as decay time occurs. In the temperature range 183—153°K, where the system is in a supercooled liquid state, the $\lambda_F{}^m$ value is approximately constant (~530 nm). A remarkable spectral shift from 530 nm to 450 nm occurs in the temperature range 150—138°K, as indicated partly in Fig. 2. At *ca.* 138°K, the phosphorescence band appears at about 500 nm. It seems probable that, at some temperature around 138°K, the phase transition from the supercooled liquid to the glassy state occurs when the temperature is lowered. At about 146—148°K, the solution is in a quite viscous supercooled liquid state and the fluorescence band with maximum at 490 nm is very broad (with half-value width of *ca.* 6000 cm^{-1}). At lower temperatures (136—77°K) fluorescence band shows further blue shift ($\lambda_F{}^m$=435 nm at 133°K and 420 nm at 77°K).

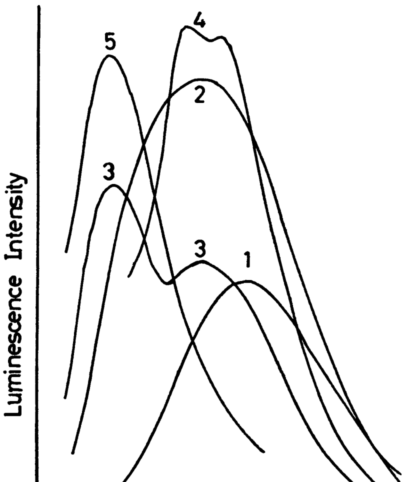

Fig. 1. Luminescence spectra of TCNB-toluene system at various temperatures. [TCNB]=10^{-3} M
1. 260°K (liquid state), 2. 146°K (supercooled liquid state), 3. 113°K (glassy state), 4. 156°K (crystalline state) 5. 189°K (liquid state)

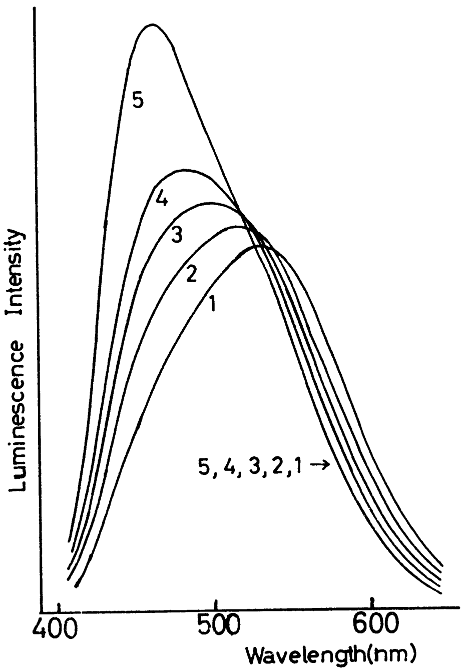

Fig. 2. Spectral change in the temperature range 150—145°K.
1—4: 150—147°K, 5: 145°K.

When the temperature is raised from 77°K, the fluorescence band maximum shows a red shift. An abrupt change in the spectrum as well as in the temperature of the system occurs at 137°K where the phosphorescence intensity becomes much stronger than the fluorescence intensity. We have confirmed by means of differential thermal analysis that this spectral change can be ascribed to the phase change of solution from glassy to crystalline states. The luminescence spectrum of the complex in the crystalline state is shown in Fig. 1. We have confirmed that this luminescence band can be ascribed to the phosphorescence of the complex by means of phosphorescence measurement. The observed phosphorescence decay time was about 2 sec. Thus, the spectra in the crystalline state differ from those in the glassy

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5) R G. Bennett, *Rev. Sci. Instr.*, **31**, 1275 (1960).

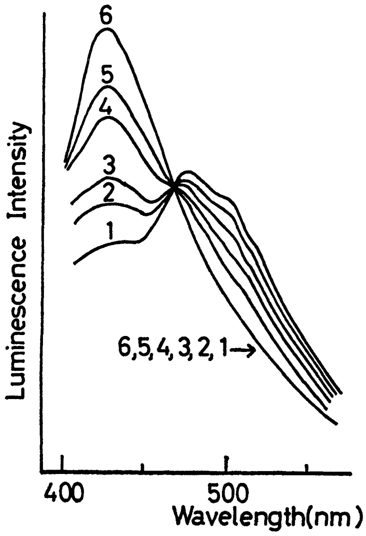

Fig. 3. Spectral change corresponding to the melting of the crystal.
1—3: 182—183°K, 4: 184°K, 5: 185°K, 6: 186°K.

state. In the temperature range 182—188°K, the phosphorescence band with peaks at 475 nm and 500 nm disappears and the fluorescence band appears at 425 nm as shown in Fig. 3. This change corresponds to the melting of the crystal. It should be noted that we can recognize an iso-emissive point at *ca.* 470 nm. At higher temperatures the fluorescence band shows a red shift and $\lambda_F{}^m$ value at 243°K is *ca.* 530 nm. When the temperature is raised further, the spectrum shows a blue shift to $\lambda_F{}^m$ value of 510 nm at room temperature.

At room temperature, the fluorescence spectra at various delay times from the exciting laser pulse were practically the same, and the fluorescence decay times at various wavelengths of the band were all equal to *ca.* 100 nsec. Analogous results can be observed also in the case of the glassy state at low temperatures (137°—77°K), where the fluorescence decay times at various wavelengths were all equal to *ca.* 50 nsec.

The results indicate that the excited F.C.→e.q. relaxation process of the complex including the surrounding solvent molecules at room temperature is much faster than the time resolving ability (a few nsec) of the apparatus. In the case of the glassy state at low temperatures, however, the observed results seem to indicate that it is impossible for the above relaxation process to occur during the fluorescence lifetime in the rigid state.

If the excited F.C.→e.q. relaxation time becomes comparable to the fluorescence lifetime somewhere between room temperature and the temperature of the glassy state, the fluorescence of the complex should show a time-dependent spectral shift and wavelength-dependent fluorescence rise and decay times. We have actually observed such results in the case of the supercooled liquid state at about 147°K.

As indicated in Fig. 4, the fluorescence decay times at 147°K and at 145°K show remarkable wavelength-dependences and the decay times at long wavelength part of the fluorescence band are much longer than those at short wavelength part of the band. In Fig. 5, we show fluorescence rise and decay curves at 147°K for several different wavelengths. We see

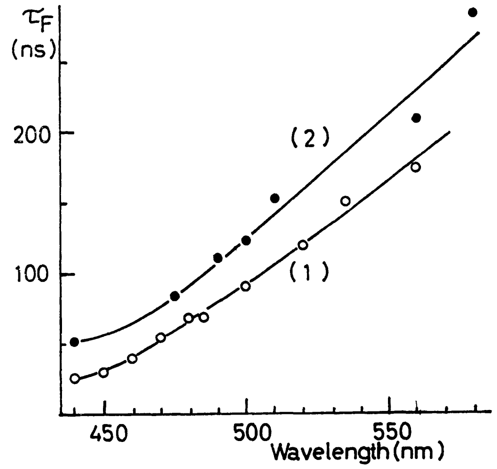

Fig. 4. Wavelength-dependence of the fluorescence decay time in the supercooled liquid state.
1: 147°K, 2: 145°K

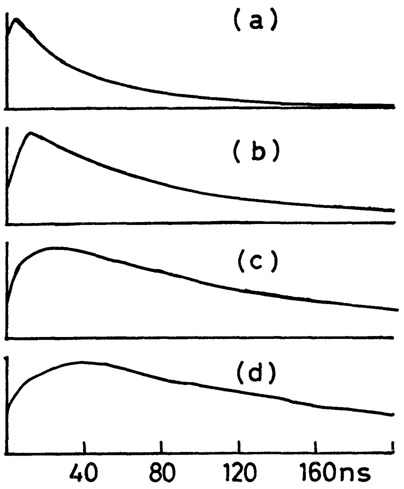

Fig. 5. Rise and decay curves at several wavelengths of the fluorescence band at 147°K.
(a) 460 nm, (b) 500 nm, (c) 540 nm, (d) 580 nm

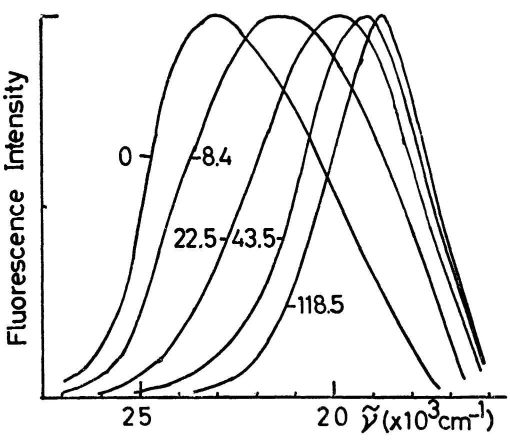

Fig. 6. Time-resolved CT fluorescence spectra of TCNB-toluene system in the supercooled liquid state at 147°K. Times indicated are in nsec after the rise of the laser pulse.

that both the fluorescence rise and decay times are longer at longer wavelengths. Furthermore, as shown in Fig. 6, time-resolved spectra (different spectra at delay times differing from the exciting pulse) have been clearly observed at 147°K.

The above results clearly show that the excited F.C.→e.q. relaxation process in the highly viscous environment at 147°K is much slower than that at room temperature. At 147°K, the relaxation time can be comparable to the decay time of the excited state. Thus, the relaxation process involving the surrounding solvent molecules has been demonstrated.

In Fig. 6, the band shape at the early stage of the fluorescence emission appears to differ considerably from that at the later stage of emission. This might be ascribed to the change in the structure of the complex during the relaxation process. However, it does not seem conclusive since the experimental error is larger at smaller delay times because of the time jitter ($\leq$2 nsec) due to the discharge trigger of the laser tube and smaller emission intensities. At any rate, the change of the structure of the complex should occur somewhere in the course of the excited F.C.→ e.q. relaxation since the radiative lifetime calculated from the absorption intensity is much smaller than the observed decay time.

Recently, the excited singlet-singlet (S_n-S_1) absorption spectra of TCN-Bbenzene and TCNB-toluene complexes have been measured by laser photolysis and by analyzing the reabsorption effect of the CT fluorescence by the excited singlet complexes.[6,7] Since the observed S_n-S_1 absorption spectra are very similar to those of TCNB anion, the electronic structure of the complex in the fluorescent e.q. state has been concluded to be a contact ion-pair.[6,7] Quantum chemical calculations on the TCNB-toluene complex show that the local excitation of TCNB and CT configuration contribute equally to the excited F.C. state while the fluorescent e.q. state has been found to have 99% CT character.[6b] Theoretical calculations have indicated clearly that the complex has the structure given in Fig. 7a in the ground e.q. as well as the excited F.C. states where the intermolecular overlap integral is considerable, while it has a symmetrical overlapping structure (Fig. 7b) in the excited e.q. and ground F.C. states where the intermolecular overlap integral is very small.[6b] Thus the F.C.→e.q. relaxation observed directly in the present work presumably involves a considerable structural change of complex in addition to rearrangements of the surrounding solvent molecules, and the contact ion-pair state seems to have a much longer radiative lifetime than that calculated from absorption intensity.

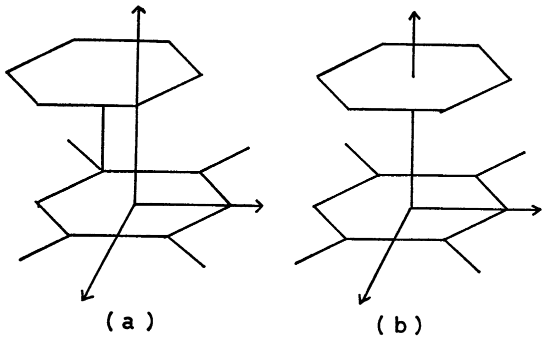

Fig. 7. Possible geometrical configurations of the complex.
a. Ground e. q. and excited F. C. states.
b. Fluorescence e. q. and ground F. C. state.

Since the structural change in the course of the excited F.C.→e.q. relaxation is quite large and the dipole moment of the excited e.q. state seems to be much larger than those in the excited F.C. and ground states, the effect of the solvent polarity on the wavenumbers of the fluorescence band maxima of the complex may be similar to the case of heteroexcimers. Using the theory of dielectric polarization, we can easily show that the wavenumber difference between the absorption and fluorescence band maxima can be given by[8]

$$\boldsymbol{hc}(\tilde{\nu}_a-\tilde{\nu}_f) \cong 2(\Delta f/a^3)(\vec{\mu}_a{}^2-\vec{\mu}_a\cdot\vec{\mu}_g{}^{\mathrm{FC}}-\vec{\mu}_g\cdot\vec{\mu}_a{}^{\mathrm{FC}}+\vec{\mu}_g{}^2)$$

$$-(\Delta f_n/a^3)(\vec{\mu}_a^{\,2}-\vec{\mu}_g^{\,2\,\mathrm{FC}}-\vec{\mu}_a^{\,2\,\mathrm{FC}}+\vec{\mu}_g{}^2), \qquad (1)$$

$$\Delta f=\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1},\quad \Delta f_n=\frac{n^2-1}{2n^2-1}$$

where a is the cavity radius in Onsager's theory of reaction field, ε and n are the solvent dielectric constant and refractive index, respectively, $\vec{\mu}_a$ and $\vec{\mu}_g$ represent dipole-moments in the excited e.q. and ground e.q. states, respectively, $\vec{\mu}_a{}^{\mathrm{FC}}$ and $\vec{\mu}_g{}^{\mathrm{FC}}$ are dipolemoments in the excited F.C. and ground F.C. states. In the present, the terms with $\vec{\mu}_a{}^2$ might be much larger than the others in the rhs of Eq. (1). Thus, we have

$$\boldsymbol{hc}(\tilde{\nu}_a-\tilde{\nu}_f) \approx 2(\vec{\mu}_a{}^2/a^3)\left(\Delta f+\frac{1}{2}\Delta f_n\right). \qquad (2)$$

As shown in Fig. 8, Eq. (2) can reproduce experimental results of TCNB-toluene complex in various solvents very well. Since $\tilde{\nu}_a$ value is approximately constant in these systems, the following is valid.

$$\boldsymbol{hc}\tilde{\nu}_f \approx -2(\vec{\mu}_a{}^2/a^3)\left(\Delta f+\frac{1}{2}\Delta f_n\right) \qquad (3)$$

This is the same equation as that applied to the solvent shift of the heteroexcimer fluorescence.

It should be noted that the ($\tilde{\nu}_a$-$\tilde{\nu}_f$) value in toluene *i.e.* the value for the TCNB-toluene two component system is included in Fig. 8. We have discussed the possibility of 1 : n ($n\geq 2$) complex formation during the lifetime of the fluorescent state in the case of TCNB-benzene and TCNB-toluene systems, in view of the very large Stokes shift.[4] The results in Fig. 8, show that the 1 : n ($n\geq 2$) complex formation is improbable, since the observed shift of the fluorescence band can be well explained as due to the electrostatic interaction between the 1 : 1 complex and the solvent molecules.

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6) H. Masuhara and N. Mataga, a) *Chem. Phys. Lett.*, **6**, 608 (1970); b) to be published.

7) R. Potashnik and M. Ottolenghi, *Chem. Phys. Letters*, **6**, 525 (1970).

8) See for example, N. Mataga, Y. Kaifu, and M. Koizumi, This Bulletin, **29**, 465 (1956); E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **61**, 962 (1957).

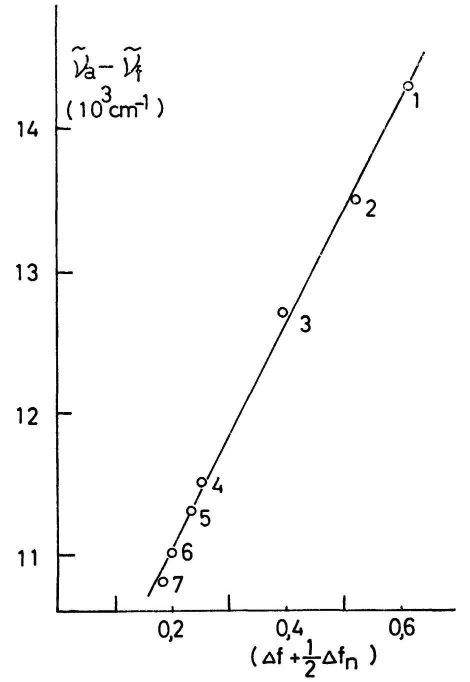

Fig. 8. $(\tilde{\nu}_a - \tilde{\nu}_f)$ vs. $(\Delta f + \frac{1}{2}\Delta f_n)$ relation observed for TCNB-toluene complex.
Solvent: 1, *o*-dichlorobenzene; 2, monochlorobenzene; 3, trichloroethylene; 4, toluene; 5, tetrachloroethylene; 6, cyclohexane; 7, *n*-hexane

TABLE 1. OBSERVED AND CALCULATED FLUORESCENCE DECAY TIMES FOR TCNB-TOLUENE SYSTEM AT 147°K

Wavelength (nm)	$\tau_{F,obs}$(nsec)	$\tau_{F,calc}$(nsec)
440	25	30
460	40	50
480	60	60
500	90	90
520	120	105
535	140	130
560	170	135

The results in Fig. 6 can be further analyzed by means of Bakhshiev's equation.[9] The fluorescence intensity at the wavenumber ν and at the delay time t can be written as

$$I(\tilde{\nu}, t) = n(0)B(t) \exp\left[-\int_0^t B(t)dt\right] \cdot \gamma(t) f(\tilde{\nu}, t) \tag{4}$$

where $n(0)$ is the number of excited molecules at $t = 0$, $B(t)$ is the sum of radiative and radiationless transition probabilities, and $\gamma(t)$ is the fluorescence quantum yield. $B(t)$ and $\gamma(t)$ are functions of t in general because of time-dependent structural changes of the system. $f(\tilde{\nu}, t)$ represents the effect of the time-dependent spectral shift on the observed fluorescence rise and decay processes.

If the transition probability and the fluorescence quantum yield is time-independent, *i.e.* the excited F.C.→e.q. relaxation process does not involve the structural change of the complex itself but is caused by the reorientation motions of the surrounding solvent molecules, Eq. (4) can be rewritten as,

$$\begin{aligned} I(\tilde{\nu}, t) &\approx n(0)\frac{1}{\tau_F} \cdot \gamma \exp\left[-t/\tau_F\right] \cdot f(\tilde{\nu}, t) \\ &= Const \cdot \exp\left(-t/\tau_F\right) \cdot f(\tilde{\nu}, t) \end{aligned} \tag{5}$$

If the change of the structure of the complex occurs at some time in the early stage of the excited F.C.→e.q. relaxation, the time variation of the fluorescence intensity after that time can be expressed by Eq. (5). $f(\tilde{\nu}, t)$ can be evaluated from the normalized time-resolved spectra as indicated in Fig. 6. The decay time associated with $I(\tilde{\nu}, t)$ can be calculated by means of Eq. (5) assuming an appropriate value for τ_F. In Table 1, the calculated values at various wavelengths taking $\tau_F = 120$ nsec are compared with the observed values. Agreement between the observed and calculated values is rather satisfactory. Almost all parts of the structural change might be completed immediately after the excitation.

No relaxation process occurs during the excited state lifetime in the case of the glassy state of TCNB-toluene system. However, we have found out that we can observe a slight time variation of fluorescence spectra in the case of the crystalline state. The crystalline state was formed at 137°K when temperature was raised from 77°K in the glassy state. After the phase transition occurred at 137°K, the temperature was lowered to 77°K or raised to 171°K and the wavelength dependence of the decay times as well as the time-resolved spectra were measured. The results are given in Figs. 9 and 10.

We see that the extent of the wavelength dependent variations of the decay time and the red shift in the time-resolved spectra at 171°K are larger compared to those at 77°K. In general, the extent and the rate of the time-dependent spectral changes in the crystalline state are much smaller than those in the supercooled liquid state at 147°K. This may be due to the fact that the molecular motions responsible for the excited F.C.→e.q. relaxation are much slower in the crystalline state than in the supercooled liquid state at 147°K.

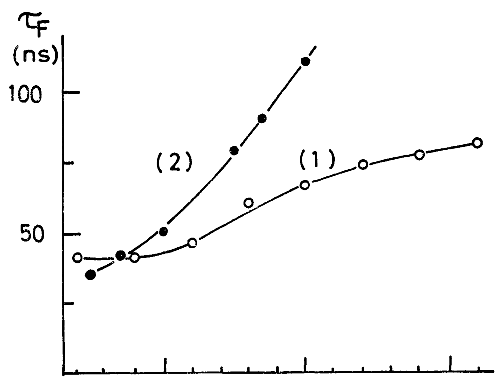

Fig. 9. Wavelength-dependence of the fluorescence decay time in the crystalline state.
1, 77°K; 2, 171°K

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[9] N. G. Bakhshiev, Y. T. Marurenko, and I. V. Piterskaya, *Opt. Spectry.* (USSR) (English translation) **21**, 307 (1966).

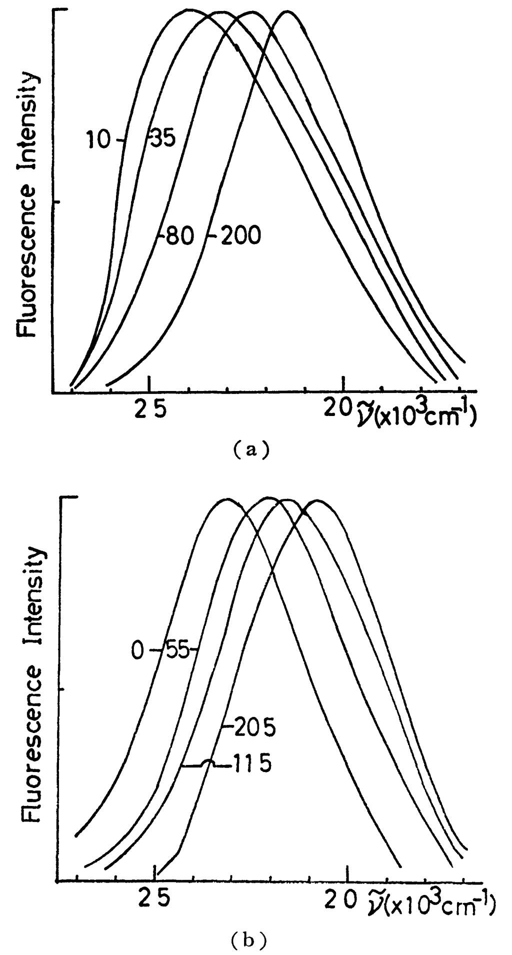

Fig. 10. Time-resolved fluorescence spectra of TCNB-toluene system in the crystalline state. Times indicated are in nsec after the rise of the laser pulse.
a, 77°K; b, 171°K

It seems rather peculiar that the time-dependent spectral changes were not observed in the glassy state, in contrast to the results of the crystalline state. However, since the crystalline state of the TCNB-toluene system was produced by the phase transition from the glassy state at a fairly high temperature, it might be rather soft and contain many defects, which would allow some molecular motions during the excited state lifetime. In the case of TCNB-benzene, TCNB-*o*-xylene and TCNB-*m*-xylene systems, the crystalline state is formed simply by the phase transition from the liquid state when the temperature is lowered. We were not able to observe any wavelength dependence of the fluorescence decay time for these systems in the crystalline state at 77°K. This seems to indicate that the crystals of these systems contain a much smaller amount of defects than the TCNB-toluene system, and it is very difficult for the molecular motions to rise during the excited state lifetime.

TABLE 2. OBSERVED AND CALCULATED FLUORESCENCE DECAY TIMES FOR TCNB-TOLUENE SYSTEM IN THE CRYSTALLINE STATE

(A) at 77°K taking $\tau_F=65$ nsec

Wavelength (nm)	$\tau_{F,obs}$(nsec)	$\tau_{F,calc}$(nsec)
420	40	40
440	40	50
450	45	55
480	60	65
500	65	65
540	75	70

(B) at 171°K taking $\tau_F=70$ nsec

Wavelength (nm)	$\tau_{F,obs}$(nsec)	$\tau_{F,calc}$(nsec)
425	35	50
450	55	60
475	80	75
500	110	100

We have analyzed the experimental results of Fig. 10 according to Eq. (5), and the results of calculations are shown in Table 2A and 2B. Agreement between the observed and calculated τ_F values is fairly satisfactory. Thus, the model assumed for Eq. (5) appears to be valid approximately in these cases as in the case of relaxation process at 147°K. Probably, a slight structural change in the complex occurs immediately after the excitation even in the crystalline state and only a slight reorientation relaxation of the surrounding solvent molecules occurs during the excited state lifetime.

Concluding Remarks

The extensive relaxation process of excited F.C.→ e.q. in the TCNB-toluene system including the surrounding solvent molecules has been demonstrated by the measurement of the time-resolved fluorescence spectra. The extensive relaxation seems to be initiated by the structural change of the complex due to excitation. Analysis of the time-resolved spectra has indicated that almost all parts of the structure change in the complex occurs immediately after the excitation even in the quite viscous medium at 147°K.

The authors are grateful to Professor S. Seki and his associates of this University for use of the apparatus for differential thermal analysis, and for their helpful discussions concerning the thermal analysis and phase transitions of toluene.