Re-absorption Effect of Charge-Transfer Fluorescence by the Excited Electron Donor-Acceptor Complex

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It has been shown that excited electron donor-acceptor (EDA) complexes of *s*-tetracyanobenzene (TCNB) with benzene or toluene can be produced quite densely when excited with a giant pulse laser and that there arises a remarkable re-absorption of the charge-transfer (CT) fluorescence by the excited EDA complexes. We have investigated in detail the re-absorption effect by examining the dependence of the CT fluorescence spectra on the direction of observation, the decay function of the fluorescence, the effect of the concentration of solution as well as the effect of the exciting light intensity on it. The excited singlet-singlet ($S_n \leftarrow S_1$) absorption spectra have been obtained by analyzing the re-absorption effect. Since the CT fluorescence spectra are broad and have no structure, the fluorescence can work as a good light source for the absorption spectral measurement.

The nsec flash photolysis has been made possible by using a giant pulse laser as an exciting light source. The absorption spectra of short-lived transient species such as excited singlet state of aromatic molecules produced by excitation with the laser in solution have been determined with some intense flash lamps of short duration. Novak and Windsor used laser-induced sparks in O_2 and Xe gases as spectroflashes and an image-converter camera as a detection apparatus.$^{1)}$ Porter and Topp used some scintillators as a spectroflash.$^{2)}$ On the other hand, there are some difficulties in the kinetic analysis of processes in nsec time region. As an example, strong fluorescence spectra caused by the laser excitation often overlap the absorption bands of excited singlet states and the signal to noise ratio in the photoelectric measurement is rather large. Such difficulties have been removed to some extent by applying a Xe flash lamp$^{2)}$ or a pulsed Xe lamp as a monitoring light source.$^{3,4)}$

Recently, we have found a characteristic hollow in time-resolved fluorescence spectra of EDA complexes of TCNB, which is due to the re-absorption of CT fluorescence by excited complex. The $S_n \leftarrow S_1$ absorption spectra of TCNB-benzene and TCNB-toluene complexes have been obtained by analyzing the re-absorption.$^{5)}$ Since the CT fluorescence spectra of TCNB complexes are rather broad and have no structure, the fluorescence can work as a good light source for the absorption spectral measurement. In the present paper, results of investigations concerning the dependence of the CT fluorescence on the direction of observation, fluorescence decay function, effect of the solute concentration as well as the effect of exciting light intensity on the re-absorption of CT fluorescence, will be reported and a theoretical estimation of the re-absorption effect will be given.

Experimental

We used a Q-switched ruby laser (Japan Electron Optics, JLR-02A) with an output of *ca.* 1.5 J. An exciting light pulse of 347 nm was produced through the ADP frequency doubler with conversion efficiency of *ca.* 8%. The output of a 347 nm pulse was measured with a ballistic thermopile TRG model 100 (HADRON). Fluorescence spectra and fluorescence decay curves were observed with a Nalumi R21 spectrograph and an RCA 1P28 photomultiplier. A Tektronix 585 A synchroscope was triggered by a signal from a Hewlett-Packard 5082-4220 photodiode which receives a scattered laser pulse. Fluorescence was observed from the side of the cuvett opposite the laser excitation (rear observation) as well as from a direction perpendicular to the excitation (side observation). The ordinary fluorescence measurement was made with an Aminco-Bowman spectrophotofluorometer. All the chemicals were the same as used before.$^{5)}$ Solutions were degassed carefully by the usual method.

Results and Discussion

Since the population of the excited EDA complex in the case of laser excitation is much larger than that in ordinary spectrophotometric measurement, there arises strong re-absorption of the CT fluorescence by the excited complex. The following features of the CT fluorescence were found in the case of TCNB-benzene and TCNB-toluene complexes.$^{5,6)}$ (1) A characteristic hollow appears at about 460 nm in the time-resolved fluorescence spectra at an earlier stage of decay (0—50 nsec). It can be obtained by plotting the fluorescence intensities at various stages of decay. (2) At about 460 nm, the decay curve of the fluorescence is not exponential but has a peculiar shape, while the decay curves are nearly exponential at other wavelengths. Time-resolved fluorescence spectra and typical decay curves are shown in Figs. 1 and 2. They can be ascribed to re-absorption of CT fluorescence by the high density excited state produced by the laser excitation. We have carried out a quantitative estimation of the re-absorption effect as follows.$^{7)}$

Spatial Distribution of Excited EDA Complexes. The

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1) J. R. Novak and M. W. Windsor, *Proc. Roy. Soc. A*, **308**, 95 (1968).

2) G. Porter and M. R. Topp, *ibid.*, **315**, 163 (1970).

3) R. Mcneil, J. T. Richards, and J. K. Thomas, *J. Phys. Chem.*, **74**, 2290 (1970).

4) C. R. Goldschmidt, M. Ottolenghi, and G. Stein, *Israel J. Chem.*, **8**, 29 (1970).

5) H. Masuhara and N. Mataga, *Chem. Phys. Letters*, **6**, 608 (1970).

6) H. Masuhara and N. Mataga, "The Electronic Structure of the Electron Donor-Acceptor Complex in its Lowest Excited Singlet State," *Z. Physik. Chem. N. F.*, in press.; The 24 th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

7) In relation to the $S_n \leftarrow S_1$ absorption spectra of TCNB complexes, only the final Eqs. (5), (6), (9), (10) were given without any detailed account in Ref. 5.

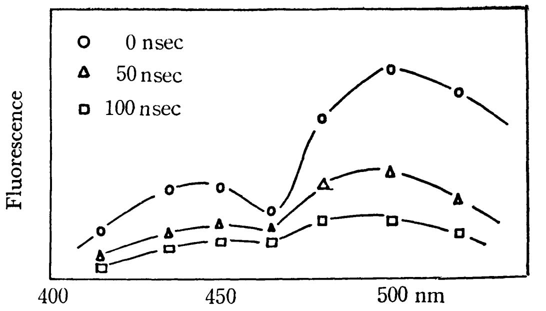

Fig. 1. The time-resolved fluorescence spectra of TCNB-benzene complex in the case of rear observation. $\varepsilon_{g\lambda}c_g=0.8$. In the present paper (Figs. 1, 5, and 7), 0 nsec is used to indicate the time when the concentration of excited complex is the maximum (taken from Ref. 6).

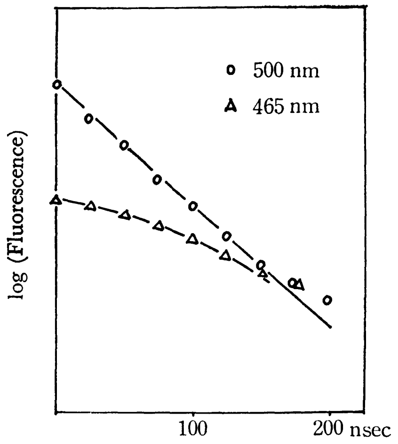

Fig. 2. Observed (○, △) and calculated (——) fluorescence decay curves of TCNB-benzene complex in the case of rear observation. $\varepsilon_{g\lambda}c_g=0.8$ (taken from Ref. 6).

distribution of fluorescent EDA complexes is expected to be proportional to $\Phi_{\lambda0}10^{-\varepsilon_{g\lambda}c_g x}$, where $\Phi_{\lambda0}$ is the intensity of 347 nm pulse which is exciting exclusively the CT band of TCNB complexes; x is the distance from the front face of the cell in cm; $\varepsilon_{g\lambda}$ and c_g are the molar extinction coefficient at 347 nm and the concentration of EDA complex in the ground state, respectively. In the present work $\varepsilon_{g\lambda}c_g$ is *ca.* 1.0. However, a deviation of distribution from $\Phi_{\lambda0}10^{-\varepsilon_g c_{g\lambda} x}$ can be expected, since the high intensity excitation often leads to saturation of absorption in the front part of the sample. We have examined this question by photographing the fluorescing sample cell from a direction perpendicular to the excitation.[8] The obtained film blackening is given in Fig. 3, which shows an approximate linear relation between log I (flourescence intensity) and x. Consequently, it is appropriate to assume that the distribution of the excited EDA complex is proportional to $\Phi_{\lambda0}10^{-\varepsilon_{g\lambda}c_g x}$.

The distribution of the re-absorbing EDA complex is of course the same as that of the fluorescent EDA complex. The concentration of the excited complex in M, c_e, is given by

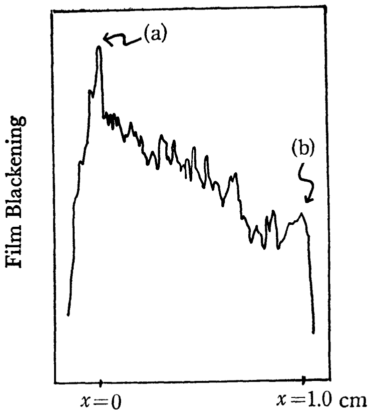

Fig. 3. Film blackening due to the fluorescing sample cell. TCNB-toluene system. $\varepsilon_{g\lambda}c_g=1.67$.
(a) Front. (b) Back.

$$c_e(x) = s\Phi_{\lambda0}10^{-\varepsilon_{g\lambda}c_g x} \qquad (1)$$

where s is a proportionality constant.

Dependence of Fluorescence on the Direction of Observation. In the case of rear observation, since differential fluorescence intensity I_x emitted from the thin layer between x and $x+dx$ can be re-absorbed by the thin layer between y and $y+dy$, the following equation can be obtained.

$$dI_x = -\mu(y)I_x dy \qquad (2)$$

where y is the distance from x to the back of the cell in cm and μ (y) is the absorption coefficient at y. A schematic model for the present analysis is shown in Fig. 4. Although μ is independent of y in the usual treatment, it is a function of y in the present case and can be written as

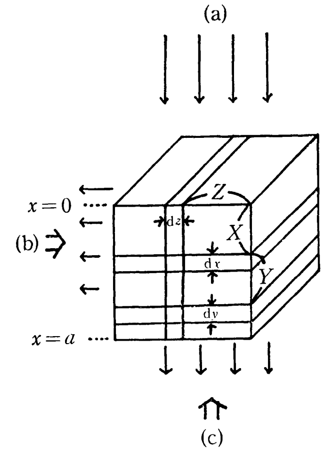

Fig. 4. A schematic model for analysis of the re-absorption of CT fluorescence by excited complex itself.
(a) excitation (b) side observation (c) rear observation.

$$\mu(y) = \varepsilon_{e\lambda'}c_e(x+y) = \varepsilon_{e\lambda'}s\Phi_{\lambda0}10^{-\varepsilon_{g\lambda}c_g x}10^{-\varepsilon_{g\lambda}c_g y} \qquad (3)$$

where $\varepsilon_{e\lambda'}$ is the molar extinction coefficient of the $S_n \leftarrow S_1$ band at λ' (the wavelength at which the fluorescence is observed). Putting Eq. (3) into Eq. (2) and integrating Eq. (2) with respect to y, the differential fluorescence intensity I_x observed at the back of the cell is given as follows.

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[8] The authors wish to express their thanks to Prof. Shunji Kato of Osaka University for his helpful discussion on this problem.

$$I_x(y=a-x) =$$

$$10^{-\varepsilon_{g\lambda}c_g x}10^{\log Q}10^{\varepsilon_{e\lambda'}s\Phi_{\lambda 0}(10^{-\varepsilon_{g\lambda}c_g a}-10^{-\varepsilon_{g\lambda}c_g x})/\varepsilon_{g\lambda}c_g} \quad (4)$$

$$Q = \rho\Omega\Phi_{\lambda 0}F_\lambda(\lambda')\varepsilon_{g\lambda}c_g/4\pi n^2$$

where ρ, Ω, $F_\lambda(\lambda')$, and n represent reflective index on the surface of the cell, solid angle in which the fluorescence is observed, fluorescence quantum yield observed in the wavelength range $\lambda' \sim \lambda' + d\lambda'$, and refractive index of solvent, respectively. Since we are observing the sum of the differential fluorescence intensities, I_x must be integrated with respect to x from 0 to a. Consequently the fluorescence intensity at λ' in the side opposite the excitation is given as follows.

$$\begin{aligned} d\Phi'(\lambda') &= \int_0^a I_x dx d\lambda' \\ &= \rho\Omega F_\lambda(\lambda')\varepsilon_{g\lambda}c_g(1-10^{\varepsilon_{e\lambda'}s\Phi_{\lambda 0}(10^{-\varepsilon_{g\lambda}c_g a}-1)/\varepsilon_{g\lambda}c_g}) \\ &\quad \times d\lambda'/4\pi n^2\varepsilon_{e\lambda'}s \end{aligned} \quad (5)$$

For notation in these equations, we refer to Förster's treatment.[9] When the excitation intensity $\Phi_{\lambda 0}$ is weak, Eq. (5) is reduced to the usual Eq. (6).[9]

$$d\Phi'(\lambda') = \rho\Omega\Phi_{\lambda 0}F_\lambda(\lambda')(1-10^{-\varepsilon_{g\lambda}c_g a})d\lambda'/4\pi n^2 \quad (6)$$

In the present case, the excitation intensity $\Phi_{\lambda 0}$ is determined to be *ca.* 1.7×10^{17} photons,[10] $\varepsilon_{g\lambda}c_g$ is adjusted to be 1.0, a is 1 cm, and s is calculated to be 2×10^{-21}, assuming the re-absorption extinction coefficient of $S_n \leftarrow S_1$ band at 462 nm $\varepsilon_{e\lambda'}$ to be 10^4. The re-absorption of several tens % of the fluorescence at 460 nm is expected from the estimation by Eqs. (5) and (6) with these values. It is in good agreement with our result.

In the case of side observation, the differential fluorescence intensity I_x can be re-absorbed in the layer between z and $z+dz$. Thus, we have

$$dI_x = -\varepsilon_{e\lambda'}c_e(x)I_x dz \quad (7)$$

The equation is in the same form as the usual Lambert-Beer equation. The fluorescence intensity in the case of side observation is given as follows.

$$d\Phi'(\lambda', x) =$$

$$\rho\Omega F_\lambda(\lambda')\varepsilon_{g\lambda}c_g(1-10^{-a\varepsilon_{e\lambda'}s\Phi_{\lambda 0}10^{-\varepsilon_{g\lambda}c_g x}})d\lambda'/4\pi n^2\varepsilon_{e\lambda'}s \quad (8)$$

where one should note the x-dependence of the fluorescence intensity. Numerical estimation by means of Eq. (8) indicates that at $x\sim 0$ cm a re-absorption of several tens % of fluorescence arises as in the case of rear observation, while no appreciable re-absorption effect will be observed at $x\sim 1.0$ cm. The results shown in Fig. 5 are in good agreement with this numerical estimation.

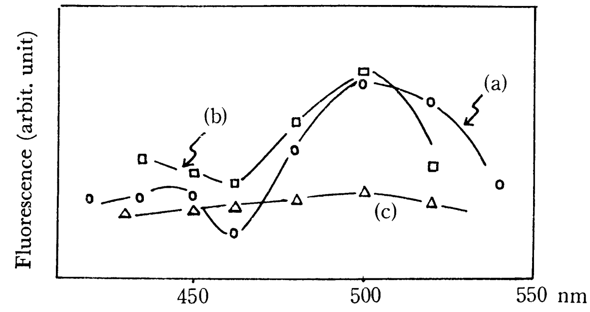

Fig. 5. The fluorescence spectra of TCNB-benzene system (t~0 nsec) obtained in the case of side observation. $\varepsilon_{g\lambda}c_g=0.8$.
(a) $x\sim 0$ cm (b) $x\sim 0.5$ cm (c) $x\sim 1.0$ cm

Fluorescence Decay Function.[11] Since the coefficients of re-absorption as well as fluorescence follow the exponential decay, the following can be easily derived in the case of rear observation:

$$\begin{aligned} &d\Phi'(\lambda', t) = \\ &\rho\Omega F_{\lambda 0}(\lambda')\varepsilon_{g\lambda}c_g(1-10^{\varepsilon_{e\lambda'}s_0\Phi_{\lambda 0}e^{-t/\tau}(10^{-\varepsilon_{g\lambda}c_g a}-1)/\varepsilon_{g\lambda}c_g}) \\ &\times d\lambda'/4\pi n^2\varepsilon_{e\lambda'}s_0 \end{aligned} \quad (9)$$

where τ is fluorescence lifetime, and $F_{\lambda 0}$ and s_0 satisfy the following equations, respectively.

$$\begin{aligned} F_\lambda &= F_{\lambda 0}e^{-t/\tau} \\ s &= s_0 e^{-t/\tau} \end{aligned} \quad (10)$$

The simulated curves obtained by means of Eq. (9), using the value of lifetime obtained from the fluorescence decay at 500 nm, are given in Fig. 2. One can see a good agreement between experimental and simulated curves. In the case of side observation at $x\sim 0$ cm the same nonexponential decay of the fluorescence at λ' as indicated by Eq. (9) is expected, while little deviation of fluorescence decay from the exponential function will occur at $x\sim 1.0$ cm. As shown in Fig. 6, the simulated curves can reproduce the experimental ones satisfactorily.

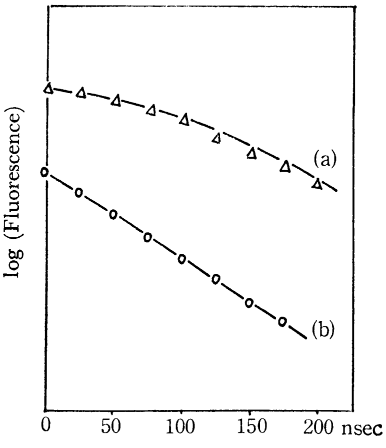

Fig. 6. Observed (○, △) and calculated (——) fluorescence decay curves of TCNB-benzene system at 465 nm in the case of side observation. $\varepsilon_{g\lambda}c_g=0.8$.
(a) $x\sim 0$ cm (b) $x\sim 1.0$ cm

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[9] Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhaeck und Ruprecht, Götingen, 1951. p. 35.

[10] In Ref. 5 effective excitation intensity $\Phi_{\lambda 0}$ was assumed to be 10^{16} photons per pulse. However, no change of the results in Ref. 5 is required since there was a numerical mistake in calculating s, which cancelled out an error in value. There arises some ambiguity in estimating effective concentration of the excited EDA complex, which is required for calculating s, since the distribution of the excited complex is not uniform. In the present work s was obtained assuming the concentration of the excited complex as $(1.7\times 10^{17}/\pi r^2 \times a \times 6.03 \times 10^{23}) \times 10^{-x}$M, where r is an effective diameter of a 347 nm pulse.

[11] The effect of absorption by excited singlet state as well as triplet state on fluorescence decay function was mentioned in Ref. 2.

Effect of the Concentration of Solution on Re-absorption. Since the CT fluorescence is re-absorbed by the excited EDA complex the characteristic hollow in the fluorescence spectra as well as the nonexponential decay of fluorescence might not be observable under low concentration of the excited complex. The excitation of a low concentration solution of the EDA complex with a laser pulse of moderate intensity as well as low intensity excitation of a solution of mederate concentration will produce excited EDA complexes of rather low concentration. A comparison of the time-resolved fluorescence spectra between solutions of moderate and low concentrations is given in Fig. 7, where the excitation light intensity was moderate and side observation was performed. A characteristic hollow is observed only in the case of rather high concentration solution.

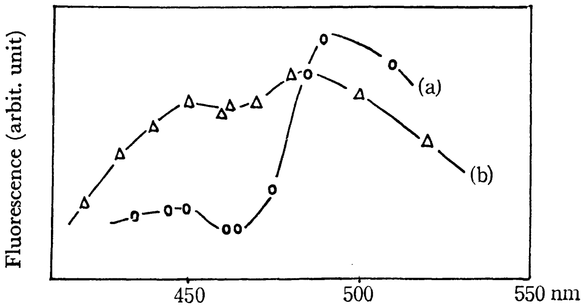

Fig. 7. Concentration dependence of the re-absorption effect in the case of the TCNB-toluene complex. ($t \sim 0$ nsec)
(a) $\varepsilon_{g\lambda} c_g = 1.67$. (b) $\varepsilon_{g\lambda} c_g = 0.16$.

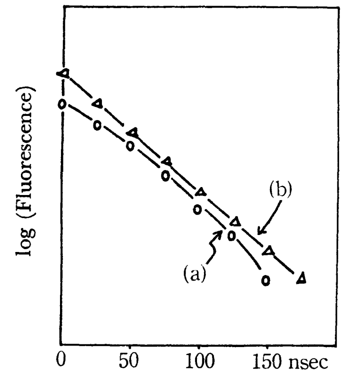

Fig. 8. Effect of the excitation light intensity on the re-absorption. TCNB-benzene system, $\varepsilon_{g\lambda} c_g = 0.8$.
Intensity; (a) normal laser excitation (b) 0.3% of the normal value.

Effect of Exciting Light Intensity on Re-absorption. The excitation intensity was varied by neutral filters composed of wire gauzes. The dependence of decay function at 462 nm on the exciting light intensity is given in Fig. 8. When the exciting light intensity was reduced to 0.3% of the normal value (1.7×10^{17} photons/pulse), the observed fluorescence decay was almost exponential.

The $S_n \leftarrow S_1$ Absorption Spectra. From the above results, it is confirmed that a characteristic hollow in the fluorescence spectra of earlier stage of decay and the nonexponential decay at about 460 nm are due to the re-absorption of the fluorescence by the excited singlet state of the EDA complex. Consequently, we can obtain the $S_n \leftarrow S_1$ absorption spectra by comparing the fluorescence spectra observed by an Aminco-Bowman spectrophotofluorometer and those observed by laser excitation. The result in the case of TCNB-benzene complex is given in Fig. 9. For the absorption spectral measurement of the excited complex, the fluorescent light can work as a good light source, the duration of which is the same as the lifetime of the objective transient. Thus, it is concluded that this method is useful for obtaining $S_n \leftarrow S_1$ absorption spectra.

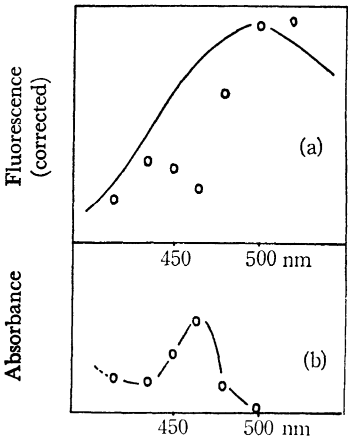

Fig. 9. Fluorescence spectra and $S_n \leftarrow S_1$ absorption spectra of TCNB-benzene complex. $\varepsilon_{g\lambda} c_g = 0.8$ (taken from Ref. 6).
(a) Fluorescence spectra measured by laser excitation (○) and by Aminco-Bowman spectrophotofluorometer (—).
(b) $S_n \leftarrow S_1$ absorption spectra.

The conditions necessary for the absorption spectral measurement by this method might be as follows; (1) The optical density at λ can be adjusted to be *ca.* 1.0. (2) The fluorescence and the $S_n \leftarrow S_1$ absorption spectra overlap each other to some extent. (3) The fluorescence lifetime is in the same order as the duration of an exciting pulse, although in order to identify the lifetime of the re-absorbing species with that of the fluorescent one the lifetime of fluorescence must be longer than the duration of the 347 nm pulse. We have a few critical experimental results concerning the above conditions. We have studied the $S_n \leftarrow S_1$ spectra of TCNB-mesitylene complex by the present re-absorption method. However, no appreciable re-absorption was observed, but we were able to measure the $S_n \leftarrow S_1$ spectra of this complex by the nsec flash photolysis method.[6,12] Since the fluorescence lifetime is 43 nsec,[13] which satisfies the condition (3), no observation by the present re-absorption method can be ascribed to the poor overlapping between fluroescence and the $S_n \leftarrow S_1$ absorption spectra. Concerning condition (3), the fluorescence lifetime of TCNB-benzene complex was adjusted by saturating the solution with air. The re-absorption of CT fluorescence was observed in the case

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12) H. Masuhara and N. Mataga, The Symposium on Molecular Structures, Kyoto, 1971.

13) T. Kobayashi, K. Yoshihara, and S. Nagakura, The Symposium on EDA Complexes, Osaka, 1970, Preprint.

of this complex, where the shape of the fluorescence light pulse was almost the same as that of the exciting pulse and the apparent lifetime was several nsec. Thus, condition (3) is valid.[14)]

Related Problems. When the re-absorption of CT fluorescence by the excited complex itself occurs, higher excited states of the complex will be produced. The rate equation for these processes can be written as

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -aE - fE + \beta cE^* \qquad (11)$$

$$\frac{\mathrm{d}E^*}{\mathrm{d}t} = \alpha fE - cE^* \qquad (12)$$

where E and E^* are concentrations of fluorescent and higher excited states, a and c represent the rate constants of the unimolecular decay of E and E^*, respectively, and f is the rate constant of the re-absorption of CT fluorescence. The notations α and β are the yields of corresponding processes. Since f is proportincal to E, these equations are similar to those used in analyzing the lifetime shortening of exciplexes through bimolecular interaction.[15)] In this paper the higher excited state is assumed to return to the fluorescent state through radiationless degradation. Problems on the higher excited states of TCNB complexes as well as those on the interactions of excited complexes through re-absorption of CT fluorescence by the excited complex will be solved with progress of laser experiments.

The authors thank Mr. N. Tsujino for his assistance in the experimental work.

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14) The $S_n \leftarrow S_1$ spectra of 1,12-benzperylene-*N*,*N*-dimethylaniline heteroexcimer have been observed in this laboratory. This heteroexcimer is an another good example which satisfies conditions (1)—(3).

15) H. Masuhara and N. Mataga, *Chem. Phys. Letters*, **7**, 417 (1970).