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Excited State Dynamics of Microcrystalline Acridine by Femtosecond Diffuse Reflectance Spectroscopy

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The electronic structure of the excited states and triplet formation dynamics in the acridine microcrystal have been studied by femtosecond diffuse reflectance absorption spectroscopy and picosecond fluorescence spectroscopy. It was confirmed that an excimer was formed in the microcrystal within a few picoseconds after excitation. The time constant of triplet formation from the lowest excited singlet (S_1) state was obtained to be about 900 ps at room temperature, which is about ten times slower than that in an aprotic solvent. Also, triplet formation was not observed up to 6 ns at 77 K. Slow intersystem crossing in the crystal was explained in terms of a selective stabilization of the $^1\pi\pi^*$ electronic configuration due to excimer formation. An important role of intermolecular interactions on the intersystem crossing process of the crystal is discussed.

Intersystem crossing is one of the fundamental relaxation channels of excited singlet state molecules, and the generated triplet state often plays a key role as an important intermediate in various photochemical reactions in solution and also probably in the solid phase. Although the dynamics and mechanism have been studied for a number of molecules in various solvents, few cases have been reported concerning their crystalline phase.[1—3] Organic molecular crystals are usually formed based on van der Waals forces; hence, the molecules will preserve their individuality as a first approximation. In this sense, the intersystem crossing yield and its rate constant in the crystalline phase can be well characterized by the nature of the component molecules. Although this simple consideration can be applicable to many cases, of course it does not hold in general.

First, electronic interactions, mainly a dipole–dipole interaction, between an excited molecule and the neighboring ground state one would be an important factor for characterizing the intersystem crossing process. The interactions do not only modify the energy level of the excited state from that of the individual molecules, but also strongly affect the relaxation dynamics. One typical example for such interactions is excimer formation. Intersystem crossing takes place also from the excimer, and it should be very much changed from that of the monomer. Second, strong restrictions of conformational relaxations affect the intersystem crossing process. We have recently demonstrated this for microcrystalline benzil by picosecond transient diffuse reflectance spectroscopy.[3] The intersystem crossing rate in the microcrystal is one order of magnitude faster than in a cyclohexane solution, which was interpreted as being a geometrical difference of the relaxed excited state and the resultant changes in the electronic structure of the singlet and triplet excited states from the solution phase to the crystalline phase. The geometry of the relaxed excited state in the crystal is skewed, but trans planner in solution, which is realized by a conformational change in the excited state. The terms "skewed" and "trans-planar" refer to the dihedral angle between the planes containing two benzoyl groups. Third, since the dielectric properties of the surrounding molecules in the crystal is different from those of the solvent, the intersystem crossing may be influenced. For example, the energy levels of the $n\pi^*$ and $\pi\pi^*$ singlet and triplet states are determined by the solvent polarity and/or hydrogen bonding formation, which may be rather rare in a crystal.

Many of the previous studies on the excited state dynamics of molecular crystals were performed using luminescence (fluorescence) spectroscopic techniques. Hence, much attention has been paid mainly to the electronic structure of the singlet excited state and to its dynamics, such as energy migration and trapping processes.[4—6] However, the crystal effects on intersystem crossing have not been well elucidated as far as we know. This is because the nonluminescent triplet state has not been identified and its rise and decay kinetics have not been analysed. In order to do so, it would be powerful to examine the transient absorption spectra of crystals over a wide wavelength region, for which time-resolved diffuse reflectance spectroscopy is a very useful method, because it does not require a large and transparent sample.

In the present work, we dealt with acridine from the following viewpoints. First, because acridine has a rigid molecular structure, the effects of a structural difference between the solution and crystalline phases should be neglected. Second, the molecule is well known as a compound showing ultra-fast intersystem crossing through a strong spin-orbit coupling between the $^1n\pi^*$ and $^3\pi\pi^*$ (T_3) states; also, the mechanism and dynamics in the solution and gas phases have been studied in detail.[7—11] The energy levels of the lowest $^1\pi\pi^*$ and the lowest $^1n\pi^*$ configurations of acridine are close to each other. Since they are very sensitive to the environmental conditions, the rate of intersystem crossing from the S_1 state strongly depends on the nature of the solvent.[7—11] Indeed, the present transient absorption experiments show a clear discrepancy of the intersystem crossing rate constant between the crystal and a nonpolar solution. The electronic structure of the excited state and the mechanism of triplet formation from the excited singlet state in the crystalline phase are discussed, compared with those in solution.

Experimental

Sample. Acridine (zone refined, 500 pass, Tokyo Kasei) was used as received. Microcrystalline powder samples prepared by grinding the crystal in a mortar was used for spectroscopic measurements. The particle size ranged over a few to several tens of microns, as estimated with an optical microscope. The sample powder was contained in a quartz cell of 2 mm thickness, and spectroscopic measurements were performed under deaerated conditions.

Transient Diffuse Reflectance Spectroscopy. The details of a femtosecond diffuse reflectance spectroscopic system have been reported elsewhere.[12,13] Briefly, an excitation light source consists of a cw self mode-locked Ti : sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar^+ laser (Innova 310, Coherent), and a Ti : sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched Nd : YAG laser (Surelight I, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3—4 mJ/pulse, 170 fs fwhm, 10 Hz) was frequency doubled (390 nm) and used for excitation. For an examination of the excitation intensity dependence of the transient absorption spectra and their temporal profiles, we changed the intensity from 0.05 to 0.65 mJ cm^{-2}, by using optical filters. The residual of the fundamental output was focused into a quartz cell (1 cm path length) containing H_2O in order to generate a white-light continuum as a probe beam.

The transient absorption intensity was displayed as percentage absorption (%absorption), given by %absorption $= 100\times(1-R/R_0)$, where R and R_0 represent the intensity of the diffuse reflected white-light continuum of a probe pulse with and without excitation, respectively. Typically, the spectral data were averaged over 300 measurements.

It is well known that %absorption is not always a linear function of the transient concentration, and that the linear relationship holds only for small values of %absorption.[13,14] Moreover, the range in which %absorption is proportional to the transient concentration depends on the optical properties of powder samples. We examined the excitation intensity dependence of the spectral shape of %absorption for an acridine powder sample at 4 ps after excitation. The shape was independent on the excitation intensity, and the %absorption linearly increased when the maximum %absorption was less than 20% (see Fig. 2). Hence, in this range of %absorption, the value is considered to be a linear function of the concentration of the transient species. We adjusted the excitation intensity so that the maximum %absorption was less than 20% in the measurement.

Transient Transmittance Absorption Spectroscopy. For a conventional transient absorption measurement of solution samples, the transmitted light of a probe pulse was used as an analyzing light.[15] In this case, the transient absorption was estimated from the equation, $\Delta A = \log(T_0/T)$, where T and T_0 are intensity of the transmitted light with excitation and without excitation, respectively.

Time-Resolved Fluorescence Spectra and Fluorescence Decay Curves. Fluorescence decay curves were measured using a ps 2-D streak camera (C4334, Hamamatsu).[15] Although the excitation light source was the same as that for the transient absorption measurement, the intensity was very weak; less than 0.1 μJ cm^{-2}.

Steady-State Absorption and Fluorescence Spectroscopy. The ground state absorption spectrum of a powder sample was estimated by the Kubelka–Munk function,[16)]

$$k/s = (1-r)^2/2r,$$

where k is the absorption coefficient, s the back scattering coefficient, and r the diffuse reflectance of the sample. The relative value of r against MgO powder, which has no absorption over 300 to 1000 nm, was measured as a function of the wavelength with two synchronously driven monochromators (a fluorometer F4500, Hitachi), on which the absorption spectra were estimated. Fluorescence spectra with steady-irradiation were measured by a fluorometer (F4500, Hitachi).

Results and Discussion

Transient Absorption Spectra of Acridine Microcrystalline Powder. As shown in Fig. 1, a broad transient absorption spectrum extending from 450 to 700 nm was obtained immediately after excitation of acridine microcrystalline powder with a 390 nm laser pulse. The long wavelength part decayed and a sharp band having a peak at 450 nm grew within a few nanoseconds. We examined the excitation intensity dependence of the spectral shape at 4 ps and 5 ns. The results at 4 ps is shown in Fig. 2. The absorption

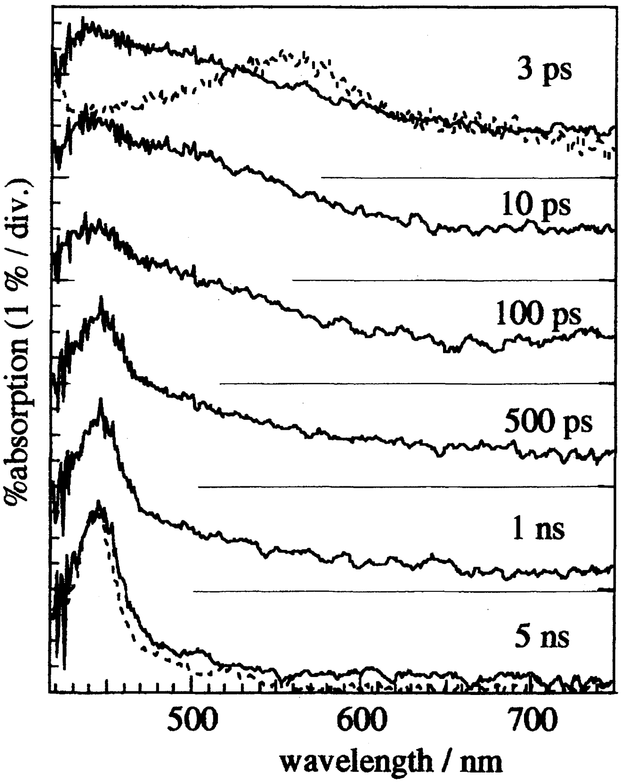


Fig. 1. Transient absorption spectra of acridine microcrystal (solid lines) excited with a femtosecond laser pulse (390 nm, 0.2 mJ cm^{-2}) at room temperature. The delay times are given in the figure. Dotted lines in 3 ps and 5 ns are the S_n–S_1 and T_n–T_1 absorption spectrum of acridine in benzene solution, respectively.

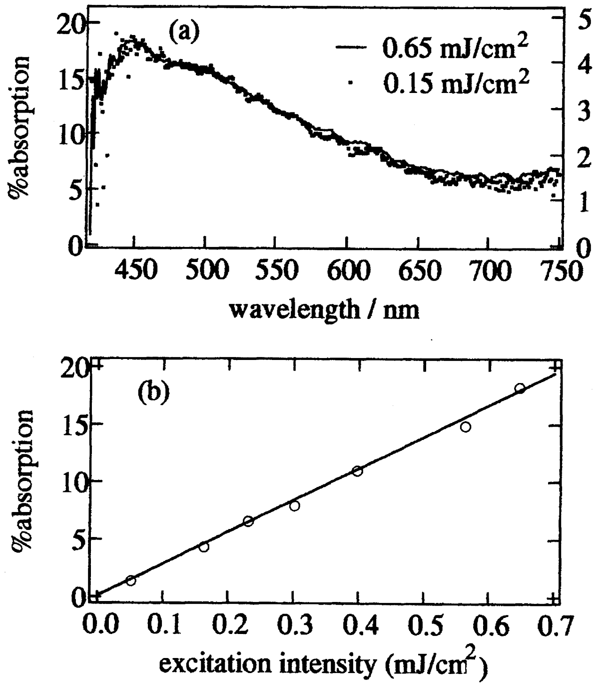


Fig. 2. An excitation intensity dependence of transient absorption spectrum of acridine microcrystal observed at 4 ps after excitation; (a) a comparison of the spectral shape of two excitation intensity, and (b) a plot of %absorption against excitation intensity.

spectra at both delay times were independent on the excitation intensity under the present experimental condition, and the %absorption at 4 ps linearly increased along with the excitation intensity. Hence, it is concluded that the transient species observed immediately after excitation is generated by a one photon excitation process.

Comparing these spectra to those in benzene solution, we can say that at 5 ns after excitation the same transient species was generated in a microcrystal and solution. The sharp spectrum in solution is safely assigned to a T_n–T_1 absorption band of acridine on the basis of a coincidence of the shape to the previously published spectrum taken at longer delay times.[10] The spectral similarity of the T_n–T_1 absorption band between the solution and crystalline phases has also been observed for other aromatic compounds,[1—3] which is consistent with the very weak electronic interactions between the triplet state and the neighboring ground state molecules.

On the other hand, the transient absorption spectra at early delay times are quite different from that of benzene solution at 1 ps, which indicates that the electronic structure of the S_1 state of the microcrystal differs from that of the monomer in benzene solution. This is consistent with the fact that the microcrystalline sample of acridine has a broad and Stokes-shifted fluorescence spectrum, which is quite different from that of monomer fluorescence with some vibrational structures (Fig. 3). Moreover, in a time-resolved fluorescence spectral measurement, it was confirmed that the broad spectrum increased within the temporal resolution of the apparatus (10 ps) and decayed with a lifetime of about 900 ps.

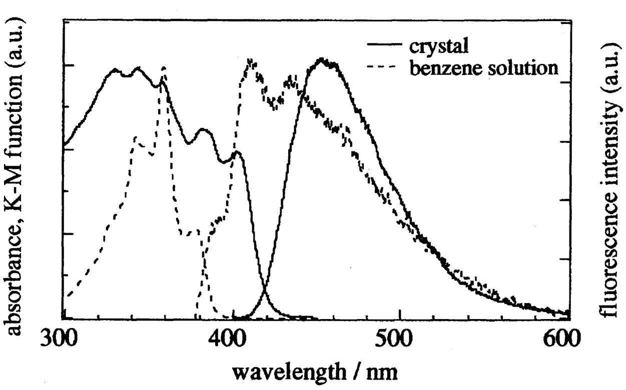


Fig. 3. Absorption and fluorescence spectrum of acridine crystalline powder and its benzene solution [ca. 10^{-4} M] at room temperature. Absorption spectrum of the powder was estimated by the Kubelka–Munk function.

The latter value is in good agreement with the decay time of the broad absorption band and with the rise time of the T_n–T_1 absorption band, although a detailed analysis is given later. Therefore, we assign the broad transient absorption spectrum at 4 ps in Fig. 1 to the absorption band of the S_1 state (fluorescence state) of the crystal.

A broad and Stokes-shifted fluorescence spectrum has been observed in several molecular crystals of aromatic hydrocarbons, such as pyrene, α-perylene, and β-9,10-dichloroanthracene (DCA) crystals, which have a structure composed of card-packed dimer units.[4,5,17,18] An electronic excitation in these crystals is coupled with the lattice vibration and relaxes on two molecules of a dimer unit, which leads to a closer approach of them to form an excimer.[19,20] The excimer formation of pyrene and α-perylene crystals takes place with a time constant of about 10 ps. Another form (β-perylene) of perylene crystal, on the other hand, has no excimer fluorescence, reflecting that it has an anthracene-like crystal structure without dimeric units.[21] Hence, a card-packed structure is indispensable for excimer formation. In the case of acridine, although it has several kinds of crystalline forms, all of them have a structure comprising card-packed dimer units, similar to that of pyrene and α-perylene crystals.[22] Then, it would be straightforward to consider that similar excimer formation also occurs in the acridine microcrystal, resulting in the broad fluorescence spectrum. In Fig. 3, we also show the absorption spectrum of the ground state. The absorption spectrum, estimated by the Kubelka–Munk function, would be much broader than that of the 'true' absorption spectrum of the acridine crystal; however one can find a vibrational structure spaced by an energy difference of about 1500 cm^{-1}, which is also found in the absorption spectrum in the solution. This means that electronic interactions, in the Franck–Condon excited state, between an excited acridine molecule and the neighboring ground state one is much weaker than those in the relaxed excited state (fluorescence state). Namely, some relaxation process involving the intremolecular distance and orientation changes may take place in the excited state to form an excimer in an acridine microcrystal, although the process was not directly observed in the present time range.

The S_n–S_1 absorption spectrum of molecular crystals has been reported for some aromatic compounds. Kotani and Katoh reported on the spectrum of an anthracene single crystal, which has almost the same peak of the S_n–S_1 absorption band of the molecule in solution ($\lambda_{\mathrm{max}} = 600$ nm).[23] It is well known that an excimer is not formed in the crystal, and that fluorescence with a vibrational structure similar to the monomer one in solution is emitted. The other example is the β-DCA crystal, in which an excimer state is formed. We recently measured the absorption spectrum of the excimer state formed in the β-form crystal and confirmed that the shape differs from that of the monomer in solution.[24] The absorption spectrum of the excimer in the crystal is broad, and its peak ($\lambda_{\mathrm{max}} = 500$ nm) is blue-shifted compared to that of the monomer excited state ($\lambda_{\mathrm{max}} = 600$ nm). These experimental observations indicate that when an excimer is not formed in a crystal, the S_n–S_1 absorption spectrum is similar to that of the monomer in solution. We can distinguish the monomer excited state form an excimer one by comparing the shape of transient absorption spectra. In the case of acridine, no appreciable temporal change of the transient absorption spectral shape was obtained at early delay times, and the rise of the excimer absorption band corresponded to the response of our spectroscopic system. It is therefore concluded that excimer formation is completed within a few ps after excitation.

At 77 K, similar transient absorption spectra were observed immediately after excitation, which decayed slowly without any appreciable spectral change from 0 ps to 6 ns, as shown in Fig. 4. Excimer formation of the microcrystal also came to completion within a few ps after excitation, and the decay time of the excimer was estimated to be longer than 10 ns. It is notable that triplet formation is quiet slow at 77 K.

Rise and Decay Kinetics. Exciting a molecular crystal with an intense laser pulse usually brings about efficient interactions between the excited states, which leads to a bimolecular annihilation of the excited state. It sometimes plays a major role in the deactivation processes of an excited molecular crystal. We thus examined the dependences of the excited dynamics on the excitation intensity in detail. Figure 5 illustrates the time profiles of the transient absorption of the acridine microcrystal at 450 and 500 nm under two different excitation conditions. We observed a decay component at 500 nm due to annihilation of the excimer and a rise compornent at 450 nm corresponding to the formation of the T_1 state when the excitation intensity was weak. The decay at 500 nm became fast and the rise component at 450 nm almost disappeared along with increasing the excitation intensity. It is suggested that bimolecular annihilation (S–S annihilation) between the excimer states takes place, and triplet formation through S–S annihilation is not very efficient.

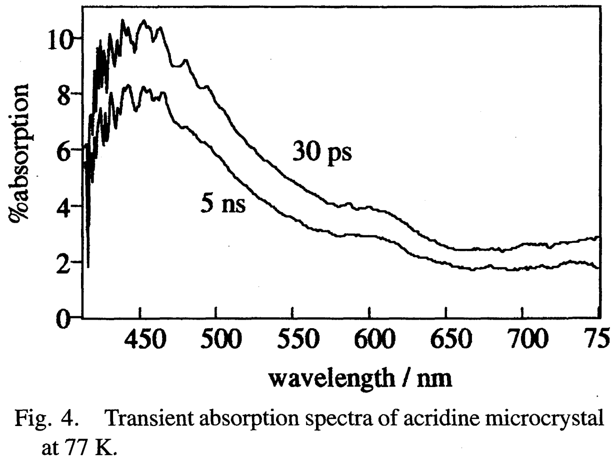


Fig. 4. Transient absorption spectra of acridine microcrystal at 77 K.

In order to analyze the time profile depending on the excitation intensity, we consider the following kinetics:

$$\begin{array}{ll} S_0 \xrightarrow{h\nu} \text{free exciton} & \\ \text{free exciton} \longrightarrow \text{excimer } (\mathrm{S}_1) \text{ within a few ps} & \\ \mathrm{S}_1 \longrightarrow \mathrm{T}_1 & k_{\mathrm{T}} \\ \mathrm{S}_1 \longrightarrow \mathrm{S}_0 & k_{\mathrm{ic}} + k_{\mathrm{f}} \\ \mathrm{S}_1 + \mathrm{S}_1 \longrightarrow \mathrm{S}_1 + \mathrm{S}_0 & k_s^2 \\ \mathrm{S}_1 + \mathrm{S}_1 \longrightarrow \mathrm{T}_1 + \mathrm{T}_1 & k_T^2 \end{array}$$

If the S–S annihilation rate constant is independent on time, and if triplet formation by the bimolecular annihilation is neglected ($k_{\mathrm{T}}^2 = 0$), the concentration of the S_1 and T_1 states is represented as a function of time by the following equations:

$$[\mathrm{S}_1] = [\mathrm{S}]_0 \frac{\exp(-t/\tau)}{1 + \tau\gamma(1 - \exp(-t/\tau))}, \tag{1}$$

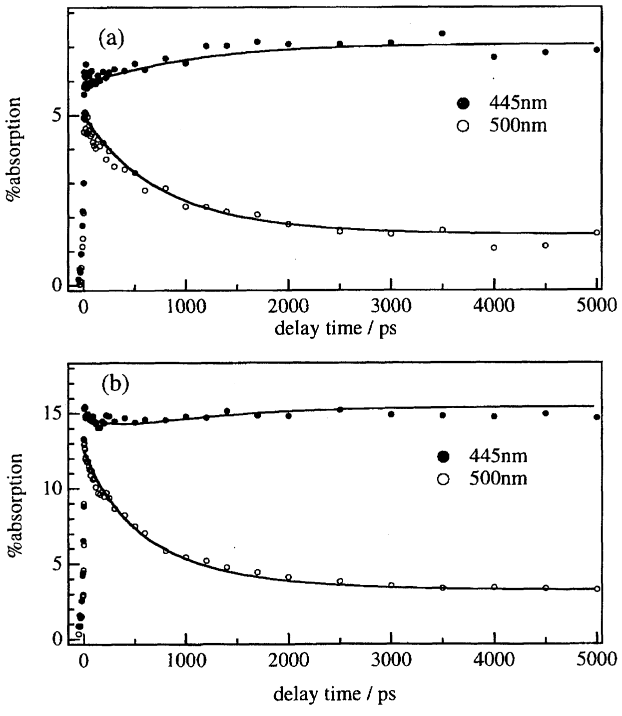


Fig. 5. Time profiles of transient absorption spectra of acridine microcrystal at two different excitation intensity; (a) 0.2 mJ cm^{-2} and (b) 0.55 mJ cm^{-2}. Curves are simulated by Eqs. 4, 5, and 6, using α=0.84, β=0.21, τ=900 ps and the fitting parameters; $(b(450\ \mathrm{nm})/a(450\ \mathrm{nm}))k_{\mathrm{T}}$=(900 ps)$^{-1}$ and γ=(450 ps)$^{-1}$ for (a) and (164 ps)$^{-1}$ for (b).

$$[\mathrm{T_1}] = [\mathrm{S}]_0 \frac{k_\mathrm{T}}{\gamma} \ln\{1 + \tau\gamma(1 - \exp(-t/\tau))\}, \qquad (2)$$

where $\tau = k_\mathrm{T} + k_\mathrm{ic} + k_\mathrm{f}$, $\gamma = k_\mathrm{s}^2[\mathrm{S}]_0$, and $[\mathrm{S}]_0$ is the initial concentration of the $\mathrm{S_1}$ state.

The time profile of transient absorption at a wavelength (λ) should be represented by the composition of the two absorption bands of the $\mathrm{S_1}$ (excimer) and $\mathrm{T_1}$ states, since these two absorption bands were only observed in the present result. Namely,

$$\%\mathrm{absorption}\ (\lambda, t) = a(\lambda)[\mathrm{S_1}] + b(\lambda)[\mathrm{T_1}], \qquad (3)$$

where, $a(\lambda)$ and $b(\lambda)$ are not a function of time and proportional to the molar extinction coefficient of the S_n–$\mathrm{S_1}$ and T_n–$\mathrm{T_1}$ transitions at λ, respectively. By substituting Eqs. 1 and 2 into this Eq. 3, temporal profiles of %absorption at 450 and 500 nm are given as

$$\%\mathrm{absorption}\ (450\ \mathrm{nm}, t) = a(450\ \mathrm{nm})[\mathrm{S}]_0 \left[\frac{\exp(-t/\tau)}{1 + \tau\gamma(1 - \exp(-t/\tau))} + \left(\frac{b(450\ \mathrm{nm})}{a(450\ \mathrm{nm})}\right)\frac{k_\mathrm{T}}{\gamma} \ln\{1 + \tau\gamma(1 - \exp(-t/\tau))\}\right], \qquad (4)$$

$$\%\mathrm{absorption}\ (500\ \mathrm{nm}, t) = \alpha a(450\ \mathrm{nm})[\mathrm{S}]_0 \left[\frac{\exp(-t/\tau)}{1 + \tau\gamma(1 - \exp(-t/\tau))} + \beta\left(\frac{b(450\ \mathrm{nm})}{a(450\ \mathrm{nm})}\right)\frac{k_\mathrm{T}}{\gamma} \ln\{1 + \tau\gamma(1 - \exp(-t/\tau))\}\right], \qquad (5)$$

$$\alpha = \frac{a(500\ \mathrm{nm})}{a(450\ \mathrm{nm})}, \qquad \beta = \frac{b(500\ \mathrm{nm})}{b(450\ \mathrm{nm})}. \qquad (6)$$

The solid lines in Figs. 5(a) and 5(b) are simulation curves by using these equations so as to simultaneously reproduce the experimental profiles at the two wavelengths under the two different excitation conditions. The value of τ was set to be 900 ps, which was obtained from the fluorescence lifetime measurement with a streak-camera under a weak excitation condition, where efficient interactions between the excimer states can be negligible. The values of α and β were determined from the shape of each transient absorption spectrum; α=0.84 and β=0.21. Therefore, γ, $(b(450\ \mathrm{nm})/a(450\ \mathrm{nm}))k_\mathrm{T}$ and $a(450\ \mathrm{nm})[\mathrm{S}]_0$ are variable parameters. Among them, γ and $a(450\ \mathrm{nm})[\mathrm{S}]_0$ are proportional to the excitation intensity. The experimental results were reproduced approximately by the simulated curves, using the values of γ and $(b(450\ \mathrm{nm})/a(450\ \mathrm{nm}))k_\mathrm{T}$ in the figure caption.

In order to clarify the excitation intensity dependence on the triplet formation, the ratio of %absorption at 5 ns to that at 4 ps was plotted against %absorption at 4 ps. Figure 6 clearly shows that the efficiency of triplet formation from the excimer decreases with its initial concentration. The solid line in this figure is a calculated result based on the above reaction scheme, using the same values of γ and $(b(450\ \mathrm{nm})/a(450\ \mathrm{nm}))k_\mathrm{T}$ in Figs. 5(a) and 5(b). It well reproduces the experimental result.

According to the above results and discussion, we can conclude that intersystem crossing from the $\mathrm{S_1}$ state (excimer) in crystalline acridine occurred with a time constant of about 900 ps, which is about 15 times slower than that in a benzene solution (60 ps). Also, S–S annihilation between the excimer states takes place under an intense excitation condition, and the triplet formation yield through the S–S annihilation is not appreciable.

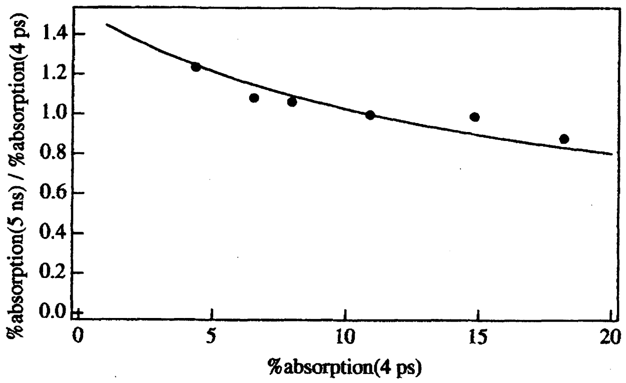


Fig. 6. A plot of relative triplet formation yield against the initial concentration of the excimer state. The solid curve is simulated on the basis of Eqs. 4, 5, and 6.

Temperature Dependence of Fluorescence Lifetime. The temperature dependence of the intersystem crossing yield and its rate constant should give us useful information concerning the mechanism of the intersystem crossing. However, the above results indicate that the decay dynamics of the excimer and the triplet formation yield are sensitive to excitation intensity; also, under the excitation condition of transient absorption spectroscopy, we must more or less take the bimolecular annihilation into account. Thus, we examined the temperature dependence of the fluorescence lifetime using a streak camera under a very weak excitation condition, where the excitation intensity was less than 0.1 $\mu\mathrm{J\,cm^{-2}}$, 1000 times smaller than that in the transient absorption experiment.

We measured the time-resolved fluorescence spectra at several temperatures from 213 to 331 K and at 77 K. The observed spectra are similar to that with stationary irradiation in Fig. 3, independent on the time and temperature. The fluorescence decay obeyed a first-order kinetics, and the lifetime was obtained to be 85 ns at 77 K. On the other hand, decay curves above 213 K were not represented by a single exponential function, but were analyzed approximately by a double-exponential one: ca. 90% of a fast decay component and ca. 10% of a slow one. Although the reason for the non-exponential fluorescence decay is not yet clear, there are several possible interpretations: a disorder of molecular alignment (defect or kink) in the crystal, delayed fluorescence due to T–T annihilation, and so on. In any case, at the present stage of the investigation we simply consider that the fast decay one would refer to a main relaxation of the excited singlet state in the crystal, and we discuss its temperature dependence.

The fluorescence lifetime of the acridine microcrystal decreased by a factor of about 100 for a temperature range from 77 to 331 K, as shown in Fig. 7. The temperature effect is drastic compared with the excimer fluorescence of α-perylene and β-DCA crystals in which the lifetime moderately decreases with increasing temperature. Upon a temperature change from 77 to 300 K, the lifetime reduced only by half for the β-DCA crystal,[5] and it is almost constant for the α-perylene crystal.[4] For the latter two crystals, the intersystem crossing is expected not to be a main deactivation process of the excimer state.[4,5] Moreover, the excimer fluorescence lifetime of the acridine microcrystal at 77 K (85 ns) is comparable to that of α-perylene and β-DCA crystal at room temperature. These results clearly indicate that the intersystem crossing is a dominant nonradiative deactivation process of the excimer in the acridine microcrystal at a high temperature region, and that the process requires thermal activation energy. An Arrhenius plot for $1/\tau - 1/\tau_0$, where τ_0 is the lifetime at 77 K, is shown in Fig. 7. A linear relation was proved, from whose slope we obtained an activation energy of $\Delta E = 1040\ \mathrm{cm}^{-1}$.

Mechanism of Triplet Formation in the Crystalline Phase. We now consider the mechanism of intersystem crossing in the acridine crystal in relation to excimer formation. As described above, the acridine crystal has a structure comprising card-packed dimer units which are arranged in anti-parallel pairs concerning the nitrogen atom.[16] In this dimer unit, the $^1\pi\pi^*$ electronic structure can be stabilized by excimer formation, while the $^1n\pi^*$ structure will not, because the lone-pair electron orbital on the nitrogen atom is orthogonal to the π-orbital of the neighboring ground state molecule. A $\pi\pi^*$ electronic character of the excimer state has been confirmed from the experimental evidence that the broad fluorescence was obtained in spite of the rather short lifetime (900 ps). Although it is difficult to determine the stabilization energy of excimer formation, we here roughly estimate it to be $1500\ \mathrm{cm}^{-1}$, which is half of the energy difference between the excimer fluorescence peak and 0–0 transition of the monomer one in benzene solution. This value may be overestimated, because the monomer excited state, itself, should be somewhat stabilized in the crystal.

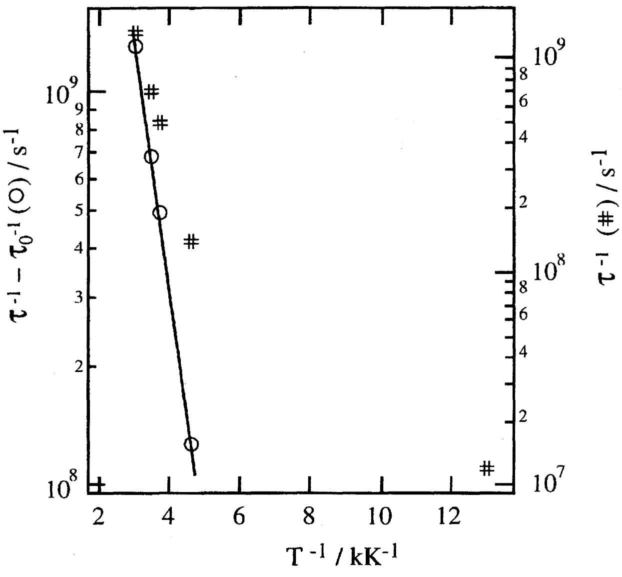
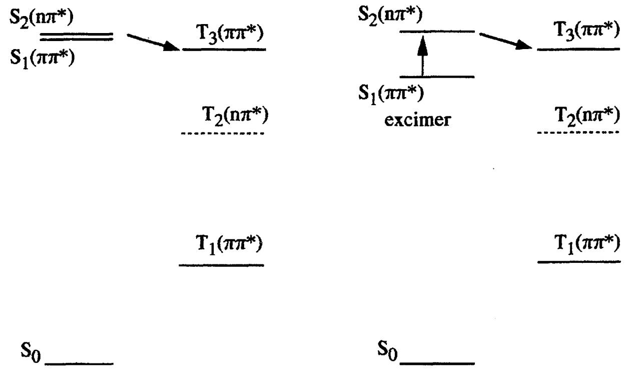


Fig. 7. Temperature dependence of the fluorescence lifetime (τ) of acridine microcrystal and the Arrhenius plot for $1/\tau - 1/\tau_0$, where τ_0 is the lifetime at 77 K.



in benzene solution (ref. 10)

in crystalline phase

Scheme 1.

Scheme 1 illustrates energy diagrams of acridine in the crystalline phase and in benzene solution[10] related to the intersystem crossing process. The energy levels of the triplet and $^1n\pi^*$ states are here assumed not to change drastically from solution to the crystalline phase, because of a very weak dipole–dipole interaction between these excited states and the ground state. Fast intersystem crossing of acidine is considered to occur only through the transition from $^1n\pi^*$ to $^3\pi\pi^*$ (T_3).[7—11] In an aprotic solvent, the energy levels of the lowest $^1n\pi^*$ and $^1\pi\pi^*$ states are very close to each other, and the time constant of triplet formation is very short (60 ps in benzene). On the other hand, in the crystalline phase, since the $^1\pi\pi^*$ state is selectively stabilized by excimer formation, as described above, the internal conversion from $^1\pi\pi^*$ to $^1n\pi^*$ reguires thermal activation energy, resulting in slower triplet formation from the S_1 state. This interpretation is well confirmed from the temperature dependence of the fluorescence lifetime. Also, the obtained activation energy is consistent with the stabilization energy of $^1\pi\pi^*$ due to excimer formation, which was estimated from the fluorescence spectrum.

An alternate mechanism, which may be proposed on the basis of the El-Sayed rule,[25] is a transition from $^1\pi\pi^*$ (S_1) to $^3n\pi^*$ (T_2). Although the energy level of the T_2 state was not determined experimentally, its location was theoretically estimated to be 3000—4000 cm^{-1} below $^1\pi\pi^*$ (S_1) for the monomer in solution.[26] Hence, the transition from the S_1 state to the T_2 state is exothermic in the crystalline phase, and the energy gap of the transition will still be large even when an excimer is formed. In such a case, the temperature dependent intersystem crossing from the S_1 state observed here can not be expected. Therefore, we can safely neglect the $^1\pi\pi^*$ (S_1)–$^3n\pi^*$ (T_2) transition in the intresystem crossing process of the acridine microcrystal.

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References

1) R. Katoh, M. Kotani, Y. Hirata, and T. Okada, *Chem. Phys. Lett.*, **264**, 631 (1997).

2) N. Ikeda, K. Imagi, H. Masuhara, N. Nakashima, and K. Yoshihara, *Chem. Phys. Lett.*, **140**, 281 (1987).

3) N. Ikeda, H. Koshioka, H. Masuhara, and K. Yoshihara, *Chem. Phys. Lett.*, **150**, 452 (1988).

4) K. Mizuno and A. Matsui, *J. Lumin.*, **38**, 323 (1987).

5) U. Mayer, H. Auweter, A. Braun, H. C. Wolf, and D. Schmid, *Chem. Phys.*, **59**, 449 (1981).

6) A. Inoue, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **45**, 1973 (1972).

7) Y. Hirata and I. Tanaka, *Chem. Phys.*, **25**, 381 (1976).

8) L. J. Noe, E. O. Degenkolb, and P. M. Rentzepis, *J. Chem. Phys.*, **68**, 4435 (1978).

9) V. Sundstrom, P. M. Rentzepis, and E. C. Lim, *J. Chem. Phys.*, **66**, 4287 (1977).

10) K. Kasama, K. Kikuchi, S. Yamamoto, K. Uji-ie, Y. Nishida, and H. Kokubun, *J. Phys. Chem.*, **85**, 1291 (1981).

11) K. Kasama, K. Kikuchi, K. Uji-ie, S. Yamamoto, and H. Kokubun, *J. Phys. Chem.*, **86**, 4733 (1982).

12) T. Asahi, M. Matsuo, and H. Masuhara, *Chem. Phys. Lett.*, **256**, 525 (1996); T. Asahi, M. Matsuo, H. Masuhara, and H. Koshima, *J. Phys. Chem. A*, **101**, 612 (1997).

13) T. Asahi, A. Furube, and H. Masuhara, *Rev. Sci. Instrum.*, **69**, 361, (1998).

14) R. W. Kessler and F. Wilkinson, *J. Chem. Soc., Faraday Trans.1*, **77**, 309 (1981).

15) K. Watanabe, T. Asahi, H. Fukumura, H. Masuhara, K. Hamano, and T. Kurata, *J. Phy. Chem. B*, **101**, 1510 (1997).

16) G. Körtum, "Reflectance Spectroscopy," Springer, New York (1969).

17) A. Matsui and H. Nishimura, *J. Phys. Soc. Jpn.*, **49**, 657 (1980).

18) X. S. Song and R. T. Williams, "Self-Trapped Excitions," Springer, New York (1993), Chap. 8, and references theirin.

19) K. Mizuno, M. Furukawa, A. Matsui, N. Tamai, and I. Yamazaki, "Ultrafast Phenomena VI," Springer, New York (1988), p. 492.

20) M. Furukawa, K. Mizuno, A. Matsui, N. Tamai, and I. Yamazaki, *Chem. Phys.*, **138**, 423 (1989).

21) D. C. Phillips, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr.*, **13**, 365 (1960).

22) J. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 1237 (1963).

23) M. Kotani and R. Katoh, in "Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena," ed by N. Mataga, T. Okada, and H. Masuhara, Elsevier, North-Holand (1992), p. 425.

24) N. Fukazawa, H. Fukumura, and H. Masuhara, *Chem. Phys. Lett.*, **222**, 123 (1994).

25) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

26) L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).