Viscosity-Dependent Decay Dynamics of the S_2 State of Cyanine Dyes with 3, 5, and 7 Methine Units by Picosecond Fluorescence Lifetime Measurements

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The lifetimes of the short-wavelength (SW) fluorescence of some cyanine dyes with 3, 5, and 7 methine units were measured using a synchronously pumped picosecond dye laser in conjunction with the time-correlated single-photon counting method. The lifetimes were longest for dyes with 5 methine units, and decreased in the order of 5, 7, and 3 methine units. The lifetimes were highly dependent on the solvent viscosity. The dependences were compared with those of the fluorescence quantum yields previously reported by the authors in order to determine the relative importance of direct internal conversion (viscosity-independent) relaxation channel and that of the crossing-over to the photoisomer potential energy curve (viscosity-dependent channel). It was determined that origin of the SW fluorescence was the second excited singlet state by semiempirical molecular orbital calculations. The absolute SW fluorescence quantum yield of one of the cyanine dyes, DODC, was found to be less than 0.002 in ethanol. The relaxation rates of these cyanine dyes in the first and second excited singlet states were compared.

Fluorescence from high-lying excited states of organic molecules has scarcely been observed in the condensed phase because of a rapid non-radiative relaxation of these states to lower ones.[1] The fluorescence quantum yields of excited states higher than the S_1 state are very small for most organic molecules.

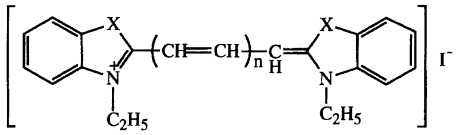
However, several papers have been published on the fluorescence from high-lying excited states of cyanine dyes.[2—10] Sequential two-photon excitation via the S_1 state with an intense pulsed laser were employed in these studies. This method is very useful to obtain impurity-free fluorescence spectra of high-lying excited states, because laser light excites only the dye molecules. We studied by this method the dependence on the solvent viscosity of the short-wavelength (SW) fluorescence intensity of some cyanine dyes, and found that a conformational change (*trans–cis* isomerization process) plays a very important role in the relaxation of the high-lying excited states of the cyanine dyes.[11]

In this paper we report on the results of direct measurements of the fluorescence lifetimes of the high-lying excited states of some cyanine dyes and their dependence on the solvent viscosity. These dependences are compared with those of fluorescence intensities reported previously. We also calculated the excitation energies and oscillator strengths of the dyes by a semiempirical molecular orbital method in order to identify the origin of the SW fluorescence. The viscosity-dependent and independent relaxation rates of the high-lying excited states are discussed.

Experimental

The structural formulae of the cyanine dyes used are shown in Fig. 1. Six cyanine dyes (3,3′-diethyloxacarbocyanine iodide (DOC), 3, 3′-diethyloxadicarbocyanine iodide (DODC), 3,3′-diethyloxatricarbocyanine iodide (DOTC), 3,3′-diethylthiacarbocyanine iodide (DTC), 3,3′- diethylthiadicarbocyanine iodide (DTDC), and 3,3′-diethylthiatricarbocyanine iodide (DTTC)) were purchased from Nippon Kankoh Shikiso Kenkyusho, Co., and were used without further purification. The purity of these dyes was checked by paper chromatography (solvents: ethanol, aqueous ethanol (50%)). Six primary alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol, and 1-octanol) were used as solvents. Each solvent was distilled four times before use in order to remove any fluorescent impurities. Glycerol (Aldrich, spectrophotometric grade) was used without further purification.

Fluorescence lifetime measurements were carried out at the Instrument Center, the Institute for Molecular Science. We used an



n	X=O	X=S
1	DOC	DTC
2	DODC	DTDC
3	DOTC	DTTC

Fig. 1. Structural formulae of cyanine dyes used.

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apparatus similar to that of Yamazaki et al.[12] The only difference was a synchronous pumping laser; we used a Nd^{3+}: YAG laser (Coherent Antares 76-S) instead of an Ar^+ laser. The sample solution (1.0×10^{-4} mol dm^{-3} for DOC, 4.0×10^{-5} mol dm^{-3} for other dyes) in a quartz cell (1 cm) was irradiated by the second harmonic (350 nm for DTTC, 300 nm for other dyes) from a synchronously pumped, cavity-dumped dye laser (Spectra Physics DL-375). The repetition rate was 4 MHz. A small portion of the fundamental light of the dye laser was split and used for stop pulses of TAC (Ortec EG&G 457). The fluorescence of the sample was collected by a quartz lens and detected by a microchannel-plate photomultiplier tube (Hamamatsu R2809) through a suitable filter and a monochromator (Nikon P-250, 25 cm). The SW fluorescence was observed at the wavelength of maximum intensity (see Table 1 of Ref. 11); the observing wavelengths were 355 nm for DOC, 390 nm for DODC, 450 nm for DOTC, 385 nm for DTC, 427 nm for DTDC, and 496 nm for DTTC. The output pulses of the photomultiplier tube was amplified and used as start pulses of TAC. The analyzed data of TAC from a pulse-height analyzer (Seiko EG&G MCA7800) were transferred to a microcomputer. Time profiles of the laser pulse were also recorded by observing the laser light scattered from sample solution. The time axis of the TAC was calibrated by a time calibrator (Ortec EG&G 462); it was determined that the time per channel was 1.30 ps. Each decay curve was measured within ten minutes in order to avoid any jitter of the time-axis. The typical peak count was 2000. All of the measurements were made at room temperature (20—22 °C) for aerated solutions.

Results and Discussion

Lifetimes of SW Fluorescence. The observed fluorescence decay curve ($I(t)$) can be expressed by the following convolution integral:

$$I(t) = \int_0^t L(t')R(t-t')\mathrm{d}t', \quad (1)$$

where $L(t)$ is the time profile of the laser and $R(t)$ is the decay function of an excited state of a dye excited by an ideally delta function-shaped laser pulse. $R(t)$ was assumed to be a double-exponential function,

$$R(t) = a_1\exp(-t/t_1) + a_2\exp(-t/t_2), \quad (2)$$

because the observed fluorescence decay comprised two components, a rapid one and a very slow one. The latter is very weak and can be attributed to impurities. The values of the parameters (t_1, t_2, a_1, a_2) and delay time of fluorescence (Δt) were determined using a nonlinear least-squares iterative convolution method based on the Marquardt algolism.[13,14] Δt results from the wavelength-dependent time response of the photomultiplier tube.

A typical example of observed SW fluorescence decay is shown in Fig. 2. The SW fluorescence lifetimes were either comparable to, or shorter than, the pulse width of the exciting laser (FWHM ca. 50 ps).

Table 1 summarizes the observed SW fluorescence lifetimes in various solvents. The values in this table are the averaged ones of more than ten measurements. The lifetime tends to be longer with an increase in the solvent viscosity for all of the cyanine dyes studied.

Since the SW fluorescence is very weak, we did not use a polarizer/depolarizer combination in the measurements. However, we can safely say that the observed lifetimes are essentially free from distortion due to the rotational relaxation of dye molecules in the emitting states based on the following. The polarized S_1 fluorescence decay curve of DODC gave a rotational time constant of 89±6 ps for a methanol solution, and 154±10 ps for an ethanol solution. The latter is in very good agreement with the value of 160±30 ps obtained by Fleming et al. in ethanol at 20 °C.[15] Since these rotational relaxation times are much longer than the SW fluorescence lifetime (24 ps for DODC in methanol, 31 ps for DODC in ethanol), and since the main part of observed decay curves can be fitted by convolution with a single exponential

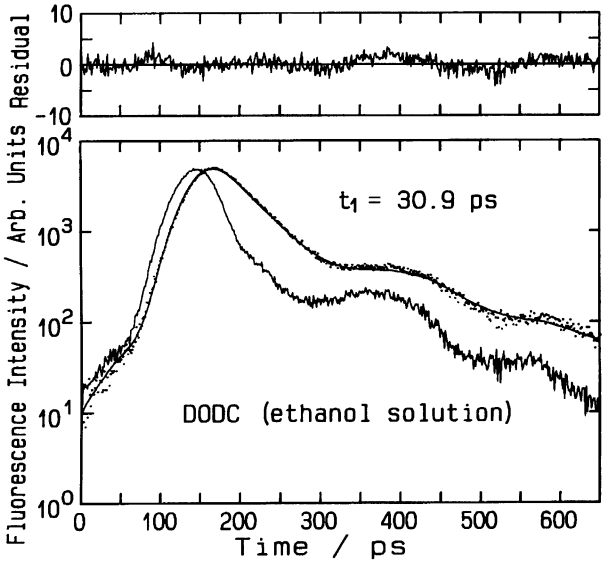

Fig. 2. Typical example of fluorescence decay curve of DODC, its simulated curve, a laser pulse profile, and residuals.

Table 1. SW Fluorescence Lifetimes of Cyanine Dyes in Various Normal Alcohols

Solvent	Viscosity	Fluorescence lifetime/ps					
	mPa s	DOC	DODC	DOTC	DTC	DTDC	DTTC
Methanol	0.6	<2.0	23.9±1.6	14.0±0.7	4.2±1.5	14.6±2.2	11.9±1.1
Ethanol	1.2	<2.0	30.9±1.8	16.2±0.5	6.2±2.3	18.9±1.1	12.3±1.4
1-Propanol	2.0	6.5±2.5	39.4±1.3	18.5±1.0	8.9±3.1	21.6±0.9	13.9±0.9
1-Butanol	2.6	8.0±2.5	41.1±1.4	19.4±0.8	8.8±2.3	23.2±0.9	13.9±0.8
1-Hexanol	5.4	10.7±3.6	45.7±2.0	21.6±1.1	9.3±2.0	25.7±3.1	17.6±0.4
1-Octanol	8.8	13.3±2.0	47.6±2.6	23.5±1.3	11.3±1.8	28.2±2.3	19.6±1.4

response function, we believe that obtained values of the SW fluorescence lifetime are free from any rotational effect, and are thus reliable.

In 1976, Tashiro and Yajima[8] measured the lifetime of the S_2 state of DTTC in methanol using a picosecond laser, and obtained a value of 35±15 ps. In the following year, Kobayashi and Nagakura [16] measured the lifetime of the S_2 state of DTTC in ethanol or in 1-butanol by observing the rise time of the $S_1 \rightarrow S_n$ absorption after direct excitation to the S_2 state. They obtained a value of less than 20 ps for an ethanol solution, and 30±5 ps for a 1-butanol solution. Though the latter value is slightly longer than ours, we believe that the method which we employed is much more reliable that those used in the 1970's.

Origin of SW Fluorescence. We have previously reported on the band positions of the SW fluorescence spectra of the cyanine dyes used in this study.[11] The observed SW fluorescence spectrum of DODC is shown in Fig. 3(a), together with the absorption spectrum. If the origin of the SW fluorescence is the S_2 state, the SW fluorescence has a very large Stokes shift. We now discuss the origin of the SW fluorescence.

Four candidates of the origin of the SW fluorescence are conceivable: (1) the S_2 state, (2) an excited singlet state higher than the S_2 state, (3) photofragments, and (4) a state whose structure is very different from that of the ground state (e.g. a twisted structure).

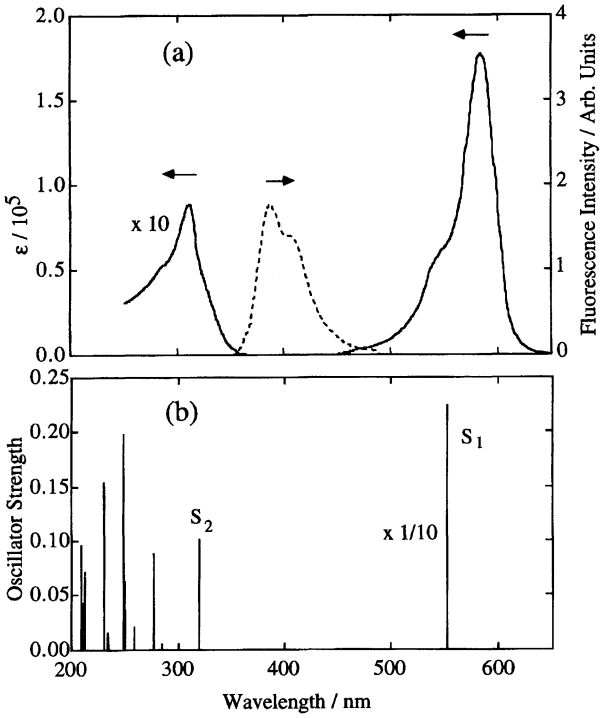

Fig. 3. (a) Absorption spectrum (solid line) and SW fluorescence spectrum (broken line) of DODC. SW fluorescence spectrum was measured by means of sequential two-photon excitation method via the S_1 state with N_2 laser pumped dye laser. (b) Absorption spectrum of DODC calculated by PPP-CI method.

In order to identify the origin of the SW fluorescence, the transition energies and oscillator strengths were calculated for DODC by the PPP-CI method.[17] The MNDO-PM3[18] optimized geometry of the ground state was employed in the calculations. The all-trans isomer was found to be most stable in the ground state. Figure 3(b) shows a simulated absorption spectrum of DODC. Although the transitions in the UV region are highly congested, the value of the oscillator strength of the S_2 state is not too small compared with those of the upper states. Singlet states higher than the S_2 state are not expected to emit fluorescence because the internal conversion from these states must be very rapid. Only the S_2 state has a sufficient energy gap to the lower singlet state, and is expected to emit. If the SW fluorescence is due to photofragments, its intensity should increase with time, which was not observed. If the origin of the SW fluorescence has a structure which is very different from that of the ground state, a large Stokes shift may be understood. It this case, however, the intensity of the SW fluorescence should be small in a viscous solvent; the observation of strong SW fluorescence in a viscous solvent, or even in a rigid grass at 77 K, cannot be explained. We therefore conclude that it is most reasonable to assign the S_2 state as the origin of the SW fluorescence.

Absolute SW Fluorescence Quantum Yield. Though it was difficult to observe SW fluorescence by direct cw excitation, the SW fluorescence spectra of DODC were obtained using a conventional spectrometer (JASCO FP-777). An interference filter was necessary to eliminate stray light of the Xe lamp from the excitation beam. The absolute quantum yield of the SW fluorescence was determined using quinine sulfate as a standard. The value was ca. 0.0018 for an ethanol solution at 300 nm excitation at 25 °C. The absolute value of the SW fluorescence quantum yield of DODC in ethanol was also estimated on the basis of the ps fluorescence lifetimes and PPP-CI calculations.[19] Table 2 summarizes the results. The obtained value (0.0015) is in very good agreement with the above-stated value (0.0018). The quantum yields of the S_2 fluorescence of the other dyes must be smaller than that of DODC because they have shorter fluorescence lifetimes.

Solvent Viscosity Dependence of the SW Fluorescence Lifetimes and Quantum Yields. In Fig. 4, the solvent viscosity dependence of the SW fluorescence lifetimes of DODC obtained in the present study is compared with that of the SW fluorescence quantum yields previously reported.[11] Although the lifetime increases with increasing solvent viscosity, the tendency is less pronounced that for the quantum yield. In other words, the quantum yields depend more strongly on the solvent viscosity than the lifetimes. This can be rationalized by one or both of the following reasons: (1) The rotational relaxation affects the two-photon transition probability.[20] The rotation in the S_1 state could lower the transition probability to high-lying excited states. Thus, in the consecutive two-photon absorption in a low-viscous solvent, such as methanol, the absorption probability of the second photon could be very low because of rotational relaxation in the S_1 state. (2) When a variety of higher excited

Table 2. Fluorescence Maxima, Oscillator Strengths, Fluorescence Lifetimes, Natural Lifetimes, and Fluorescence Quantum Yields of DODC in Ethanol at 20 °C

State	Fluorescence wavelength /nm	Oscillator strength	Fluorescence lifetime/ns	Natural lifetime/ns	Quantum yield
S_1	607	2.25[a)]	1.09[b)]	2.22	0.49[c)]
S_2	390	0.101[a)]	0.031	20.5	0.0015

a) PPP-CI calculations. b) Ref. 21. c) Ref. 23.

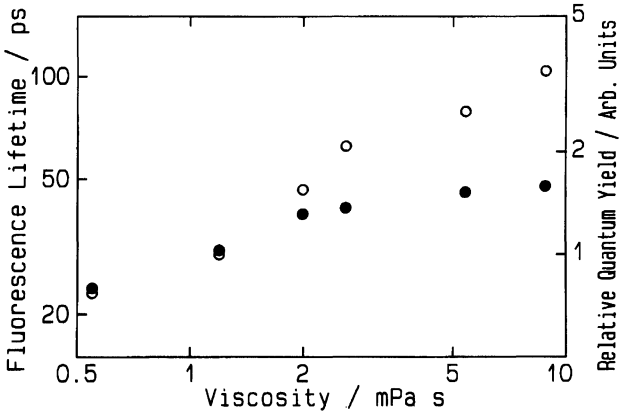

Fig. 4. Fluorescence lifetime (●) and fluorescence quantum yield (○) of DODC S_2 state vs. solvent viscosity.

states S_n ($n>2$) are generated upon excitation in addition to the S_2 state, and rates of the non-ratiative decay process (crossing-over to the photoisomer potential energy curve) in the S_n ($n>2$) states depend on the solvent viscosity, the SW fluorescence intensity depends on the solvent viscosity more than the SW fluorescence lifetimes, as detailed in the following. According to our results of PPP-CI calculations, the state density of the UV region above the S_2 state is very high. Since the oscillator strength of the $S_0 \rightarrow S_2$ transition is by far not the largest one among them, many high-lying excited states must be generated besides the S_2 state by visible two-photon excitation, and probably by UV one-photon excitation. It is unlikely that the quantum yield of internal conversion from the initially excited states (S_n states, $n>2$) to the S_2 state is unity. On the contrary, crossing-over to the photoisomer potential energy curve can be the dominant process in relaxation from the S_n ($n>2$) states. As a result, the apparent SW fluorescence quantum yield could be small in a low-viscous solvent. In a viscous solvent, crossing-over to the photoisomer potential energy curve from the S_n states is depressed, and the quantum yield of direct internal conversion from the S_n states to the S_2 state increases, which in turn increases the quantum yield of the SW fluorescence. Therefore, the SW fluorescence intensity depends on the solvent viscosity more than the SW fluorescence lifetime. In the previous paper,[11] we overestimated the dependence of the SW fluorescence quantum yield on the solvent viscosity because we did not take proper account of the crossing-over to the photoisomer potential energy curve in the S_n states ($n>2$).

Relaxation Rates of DODC in the S_1 and S_2 States. Velsko and Fleming proposed a kinetic model for the deactivation of the S_1 state of DODC.[21] They stated that the nonradiative decay process includes both the direct internal conversion and the crossing-over to the photoisomer potential energy curve; while the former is independent of the solvent viscosity, the latter is dependent on the solvent viscosity. In the previous paper we pointed out that same discussion could be made for high-lying excited states of cyanine dyes.

In this section, we first estimate the direct internal conversion rate and rate of the crossing-over to the photoisomer potential energy curve in the S_2 state of DODC. A glance at the Table 1 shows that the SW fluorescence lifetime of DODC was almost constant in the high-viscosity range (1-hexanol and 1-octanol). We then measured the fluorescence lifetime in a more viscous solvent, glycerol. Despite the strong impurity fluorescence and rapid photodecomposition of the dye, we could obtain a lifetime of 46.4±1.2 ps for DODC. This value is almost the same as that in 1-hexanol or in 1-octanol. Under the plausible assumption that the rate of crossing-over to the photoisomer potential energy curve of DODC in glycerol is negligibly small, the direct internal-conversion (viscosity-independent) rate constant is estimated to be 2.2×10^{10} s^{-1}, which is much smaller than that of internal conversion of pyrene vapor in the S_2 state (5.8×10^{11} s^{-1}).[22] The viscosity-dependent relaxation rate constant (rate constant of crossing-over to the photoisomer potential energy curve) of DODC in ethanol can also be estimated to be 1.1×10^{10} s^{-1} from the observed fluorescence lifetime and the viscosity-independent decay (direct internal conversion) rate constant determined. It can be said that crossing-over to the photoisomer potential energy curve is as fast as direct internal conversion in the S_2 state of DODC in ethanol.

Secondly, we compare the relaxation rate constants in the S_2 state with those in the S_1 state. Velsko and Fleming reported that the S_1 fluorescence lifetime of DODC in 1-decanol was 1.59 ns, and estimated the radiative rate constant of 4.3×10^{8} s^{-1} in 1-decanol.[21] Assuming that no isomerization occurs in this solvent, the nonradiative relaxation rate constant of DODC in the S_1 state was estimated to be 2.0×10^{8} s^{-1} in 1-decanol. Using this value as the direct internal conversion (viscosity-independent) rate constant in other solvents, we can estimate the rate constant of crossing-over to the photoisomer potential energy curve (the viscosity-dependent relaxation rate constant) in the S_1 state to be 2.9×10^{8} s^{-1} in ethanol. A comparison of the S_2 and S_1 states tells us that the direct internal conversion in the S_2 state is about 110-times faster than that in the S_1 state, and the cross-

ing-over to the photoisomer potential energy curve in the S_2 state is about 40-times faster than that in the S_1 state. In the S_1 state, however, the quantum yield of crossing-over to the photoisomer potential energy curve has a small value of 0.32, because the fluorescence quantum yield is very large (0.49 in ethanol).[23] This value is almost the same as that in the S_2 state (0.33). As a result, the dependences of the fluorescence lifetime on the solvent viscosity in the S_1 and in the S_2 states are similar.

Dependence of the SW Fluorescence Lifetimes on the Length of the Methine Chains. The measured SW fluorescence lifetimes strongly depend on the solvent viscosity for all the dyes studied. A larger viscosity dependence is observed for shorter dyes. This means that the relative importance of the internal conversion (viscosity-independent relaxation) rate in comparison with the rate for crossing-over to the photoisomer potential energy curve (viscosity-dependent relaxation) increases with the length of the methine chain. However, the dependence of the SW fluorescence lifetimes on the length of the methine chains is not simple; pentamethine dyes have the longest SW fluorescence lifetimes. The energy-gap law predicts that the direct internal conversion rate of the S_2 state to the S_1 state decreases with the energy difference between the two states. Though a longer cyanine dye has a lower S_1 energy level, the length of the cyanine dyes affects the energy level of the S_2 state only slightly. As a result, the direct internal-conversion rate should be smaller for longer dyes. However, since the state density in the S_1 state which accepts energy increases rapidly with energy separation, the larger vibrational state density of the S_1 state of hephamethine dyes at the S_2 energy level, compared to pentamethine dyes, probably explains the short lifetimes of DOTC and DTTC than those of DODC and DTDC, respectively.

SW Fluorescence of Other Compounds. It was difficult to measure the fluorescence lifetimes of the high-lying excited states for other organic compounds. For example, pinacyanol, a cyanine dye, emits strong SW fluorescence upon UV excitation. However, it can be assigned to emission from photofragments because of its too-long lifetime. Fluorescence from high-lying excited states was observed for rhodamine dyes, rhodamine 6G and rhodamine B. Though the intensities of this SW fluorescence were large enough to be observed, their lifetimes were too short to be measured. Similarly, the SW fluorescence of naphthacene was too short-lived to be determined. The SW fluorescence lifetimes of the cyanine dyes presently studied were measurable because of the presence of large energy gaps between their S_1 and S_2 states. We are now planning to carry out transient-absorption measurements using a femtosecond laser to study the rapid relaxation of high-lying excited states of organic molecules.

Conclusions

The lifetimes of the SW fluorescence were longest for the cyanine dyes with 5 methine units, and decreased in the order of 5,7, and 3 methine units. The lifetimes were highly dependent on the solvent viscosity. A comparison of the dependences with those of the fluorescence quantum yields indicated the importance of crossing-over to the photoisomer potential energy curve (viscosity-dependent relaxation channels) in the initially excited states (S_n states, $n>2$). It was determined that the origin of the SW fluorescence was the S_2 state by semiempirical molecular orbital calculations. The value of the absolute SW fluorescence quantum yield of DODC in ethanol was determined (0.0018 by CW excitation experiment, 0.0015 by ps fluorescence lifetime measurements and PPP-CI calculations). The relaxation rates of the S_2 and S_1 states for DODC in ethanol were determined; it was found that direct internal conversion (viscosity-independent relaxation) in the S_2 state is about 110-times faster than that in the S_1 state, and that the crossing-over to the photoisomer potential energy curve (viscosity-dependent relaxation) in the S_2 state is about 40-times faster than that in the S_1 state.

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19) Einstein's A coefficient is expressed as follows:

$$A = \tau_0^{-1} = e^2 h \varepsilon c^{-3} m^{-1} \nu^2 f,$$

where τ_0 is natural lifetime, e is the electronic charge, h is Planck's constant, ε is the dielectric constant of the solvent, c is the speed of light, m is the mass of an electron, ν is the transition frequency, and f is the oscillartor strength. Though the natural lifetime of the S_2 state, $\tau_0(2)$, can be estimated from this equation directly, we estimated the value of $\tau_0(2)$, by comparison with that of the S_1 state, $\tau_0(1)$, on the bassis of the following equation:

$$\tau_0(1)\nu(1)^2 f(1) = \tau_0(2)\nu(2)^2 f(2),$$

where $\nu(i)$ and $f(i)$ (i=1, 2) are fluorenscence frequency, and the oscillator strength calculated by PPP-CI method, of the i_{th} excited singlet state, respectively. $\tau_0(1)$ was calculated by the equation

$$\tau_0(1) = \tau(1)/\Phi(1),$$

where $\Phi(1)$ and $\tau(1)$ are the fluorescence quantum yield and the fluorescence lifetime of the S_1 state, respectively. The experimental values of $\Phi(1)$ and $\tau(1)$ in ethanol at 20 °C have been reported to be 0.49[23] and 1.09 ns,[21] respectively. The value of $\tau_0(1)$ obtained in this way is 2.22 ns; a little smaller than the value calculated from the absorption spectrum of DODC, 2.54 ns.[23] The value of $\tau_0(2)$ was estimated to be 20.5 ns putting fluorescence wavelengths of S_1 and S_2 state are 607 nm and 390 nm, respectively. The value of the absorlute fluorescence quantum yield of the S_2 state, $\Phi(2)$, was calculated to be 0.0015 from the equation,

$$\Phi(2) = \tau(2)/\tau_0(2).$$

These results are shown in Table 2.

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