

## TEMPERATURE DEPENDENCE OF J-BAND AGGREGATE OF THE DYE 1,1'-DIETHYL-2,2'-CYANINE BROMIDE STUDIED BY STEADY-STATE AND TIME-RESOLVED PICOSECOND FLUORESCENCE SPECTROSCOPY

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Steady-state and time-resolved picosecond fluorescence spectra of the J-band aggregate state of the dye 1,1'-diethyl-2,2'-cyanine bromide were measured at different temperatures. When the temperature was lowered below 210 K, two narrow bands centered at 572 and 577 nm appeared in the absorption and fluorescence spectra arising from the formation of the J aggregate. The time-resolved fluorescence study showed that the relaxation decay time of the J-band was  $\approx 20$  ps while that of the monomer band was  $\approx 300$  ps.

### 1. Introduction

Cyanine dyes play important roles in the biological, laser and photographic fields. The absorption spectrum of 1,1'-diethyl-cyanine dye dissolved in a strongly polar solvent was first measured by Jelley [1] as early as 1936. He observed a sharp absorption band centered at 576 nm. Later, Cooper [2] found two peaks in the absorption and resonant fluorescence spectra of 1,1'-diethyl-2,2'-cyanine bromide (DCB) which occurred at 573 and 578 nm at 77 K. These observations were attributed to the formation of strongly coupled aggregate states of molecules at low temperature. The sharp absorption bands at 573 and 578 nm were called J-bands after the discoverer, Jelley. Many researchers [3–12] studied the dye aggregation and optical properties of cyanine dyes in solution. Recently, DCB [7] has been used as the sensitizer for photographic emulsions to extend the spectral excitation range [13,14]. DCB is a popular dye in photographic science due to the large amount of information available in the literature [3–14].

Picosecond research [9–12] has been carried out on the J-band of pseudoisocyanine (PIC), 1,1'-diethyl-2,2'-cyanine chloride, a related compound to

DCB. The fluorescence decay time of the J aggregate of PIC was measured at room temperature to be  $\approx 30$  ps using an optical Kerr gate [9]. Ultrafast transient absorption spectroscopy of different aggregate states of PIC has been investigated in detail showing isomer formation [10] and bleaching [11,12]. Our work on DCB qualitatively agrees with previous picosecond work on PIC even though the two systems are not identical with regard to counterions, dipole moments, solvents and concentrations. Furthermore, different heavy ions have known effects on the relaxation rate causing for example, singlet-triplet conversion. It may be possible to use the J-band to mode-lock dye lasers to produce ultrashort laser pulses. No picosecond research has been done on DCB.

Dye aggregation produces various kinds of transition-dipole arrays of molecules resulting in different energy-level structures. The energy levels of the aggregates are different from those of the monomer resulting in different absorption and fluorescence spectra. Thus far, most investigators emphasized the steady-state absorption and fluorescence spectra of DCB. There remains a lack of information on the kinetics associated with the J-band excitation. Time-resolved picosecond fluorescence and absorption spectroscopy can provide

information about the kinetics. In addition a temperature dependence of the dynamics of the formation of the J-band is required to understand the J aggregate state. In this paper, we present steady-state absorption and fluorescence spectra and the time-resolved picosecond fluorescence spectra of DCB in the solvent ethylene glycol and water in a 1:1 volume ratio from room temperature to low temperature. In particular, the time-resolved fluorescence spectra were measured for different spectral regions for  $\lambda \leq 560$  nm,  $\lambda = 570$  nm ( $\pm 5$  nm);  $\lambda = 580$  nm ( $\pm 5$  nm) and  $\lambda \geq 590$  nm at 80 K to obtain information on the dynamics of the J aggregate. Different kinetics were observed for the monomer and J aggregate states.

## 2. Experimental

The experimental arrangement used to measure the spectra and picosecond time-resolved fluorescence has been described previously [15]. The arrangement is composed of a Nd:glass phosphate oscillator and amplifier laser system, a streak camera detection system and a computer for data storage and manipulation, an OMA system coupled to a spectrograph, and an optical dewar the temperature of which was controlled by flowing cooled nitrogen gas.

A single 527 nm pulse of 5 ps duration was collimated to a spot size of  $4 \times 10^{-2}$  cm<sup>2</sup> at the sample position. The average energy of a pulse was  $\approx 50$   $\mu$ J. Corning 3-67 filters were used to remove scattered 527 nm light from the collected sample fluorescence. Dielectric narrow-band filters at 570 and 580 nm were used to select only the J-band peaks of the aggregate state. A dielectric long-pass filter at 590 nm and a short-pass filter at 560 nm were used to separate the fluorescence component beyond 590 nm and below 560 nm, respectively. The overall temporal response of the system is  $\approx 15$  ps which is the convolution of the laser pulse signal and the streak camera system's resolution time on the 500 ps total display time scale.

A tungsten lamp and an argon-ion laser (at 488 nm) were used to obtain the steady-state (time-integrated, wavelength-resolved) absorption and flu-

orescence spectra using a silicon intensified target camera of a PAR OMA II.

The dye DCB (from the Exciton Chemical Company) was dissolved in ethylene glycol and water of a 1:1 volume ratio. The concentration of the solution was  $2 \times 10^{-3}$  M. The solution was contained in a 0.2 mm (for absorption spectra measurements) and a 1 mm (for fluorescence measurements) optical-path cuvette. The cuvette was placed into an optical dewar. The temperature of the sample was controlled by the flow rate of cooled nitrogen gas and read out by a Keithley 177 digital microvoltmeter connected with the copper-constantan thermocouple. The temperature was lowered from room temperature to 80 K.

## 3. Results

The steady-state absorption and fluorescence spectra of DCB at different temperatures are displayed in figs. 1 and 2. The steady-state absorption spectra of DCB at 203 and 80 K are displayed for comparison in fig. 1. The changes in absorption due to the J aggregate at different temperatures are shown in fig. 2a. Two absorption bands at 572 and 577 nm become stronger as the temperature is reduced below 210 K. The intensities of these bands grow continuously as the temperature is lowered. In fig. 2b, the fluorescence spectrum (488 nm excited) is displayed at different temperatures. Two fluorescence peaks appear at 572 and 577 nm as the temperature decreases below 210 K, which are resonant with the absorption peaks. The intensities increased continuously as the temperature was lowered. The absorption and fluorescence spectra were measured on the same samples as a function of temperature.

The temperature dependence of time-resolved fluorescence profiles excited by a 6 ps laser pulse at 527 nm, is shown in fig. 3. The whole wavelength region from 550 to 660 nm of the fluorescence from DCB, was measured. The salient feature of the profiles shown in figs. 3a-3f is that the decay time increases from 15 ps at 293 K to 250 ps at 80 K. The decay times extracted from the fluorescence profiles at different temperatures are shown in fig. 4. Below 220 K a fast component

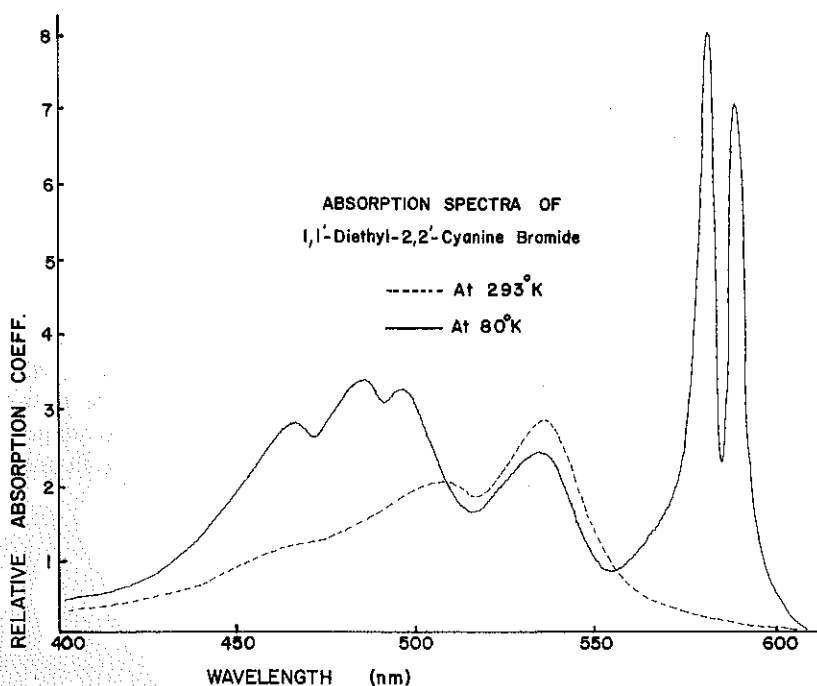


Fig. 1. Steady-state absorption spectra of DCB at room temperature and low temperature.

starts to appear in the decay profile of the fluorescence. The profile shape becomes a non-exponential decay. A small sharp peak grows around the maximum intensity of the time-resolved fluorescence when the temperature was lowered below 220 K. This sharp peak may be attributed to the contribution of J-bands at 572 and 577 nm which appears in this temperature region. The decay time associated with this sharp peak is fast ( $\approx 20$  ps). Narrow-band filters at 570 and 580 nm were used to separate the spectral components of the time-resolved fluorescence associated with the J-band at 572 and 577 nm at 80 K. The other spectral components at  $\lambda < 560$  nm and  $\lambda > 590$  nm were also separated using a Ditic 560 nm cut-off filter and a Ditic 590 nm cut-on filter, respectively. The results are shown in fig. 5a through fig. 5d corresponding to the four different wavelength regions of the fluorescence spectra as shown in fig. 5. The salient feature displayed in fig. 5 is shown in figs. 5b and 5c, where the time-resolved fluorescence profile is composed of fast and slow decay compo-

nents. The sharp peak with the fast decay ( $\approx 20$  ps) is comparable to the peak which appears in fig. 3f with the exception that the contrast ratio of the sharp peak with the fast decay to the slow component decay is better resolved in fig. 5. This is due to the spectral isolation by the narrow-band filters at 570 and 580 nm (10 nm pass bandwidth) of the 572 and 577 nm components associated with the J-band. Furthermore, the sharp peak is not present in figs. 5a and 5d, where the signals come from the spectral regions of  $\lambda < 560$  nm and  $\lambda > 590$  nm, respectively. These measurements indicate that the fast component of the profile is due to the emission from the J-band. The decay times of fluorescence in the spectral region  $\lambda > 590$  nm and  $\lambda < 560$  nm are  $350 \pm 30$  and  $300 \pm 50$  ps, respectively, in agreement with the slow-component decay observed in J-band spectral region. The slow component is attributed to the monomer. This provides evidence for the existence of the J-band at 572 and 577 nm with a fast decay time of  $\approx 20$  ps.

#### 4. Discussion

As shown above, there are two molecular states in DCB at low temperature in ethylene glycol and water (1:1): monomer and aggregate states. We have separated spectral and temporal contributions of monomer and aggregate states and will discuss the results of these measurements.

##### 4.1. Monomer state

When the temperature was lowered, the integral absorption of the monomer changed very little as shown by the steady-state absorption spectra (fig. 1) from 450 to 550 nm. The level of photoexcita-

tion is constant at 527 nm at different temperatures. Therefore, the relative radiative transition rate [16]  $K_r^m (\propto \int_M \epsilon(\bar{\nu}) d\bar{\nu})$  for monomer did not change much. The non-radiative relaxation rate  $K_{nr}$  decreases as temperature is lowered due to the reduction of the non-radiative, rotational, vibrational and collisional processes. In this case, the fluorescence quantum efficiency [15] from monomer  $Q_m = (1 + K_{nr}/K_r)^{-1}$  increases. The ratio of the fluorescence yields measured at 80 to 293 K is 20. This is confirmed by the time-resolved fluorescence kinetics of the monomer component of DCB at different temperatures displayed in the whole wavelength region (figs. 3a-3f). When the temperature was lowered from 293 to 80 K, the fluores-

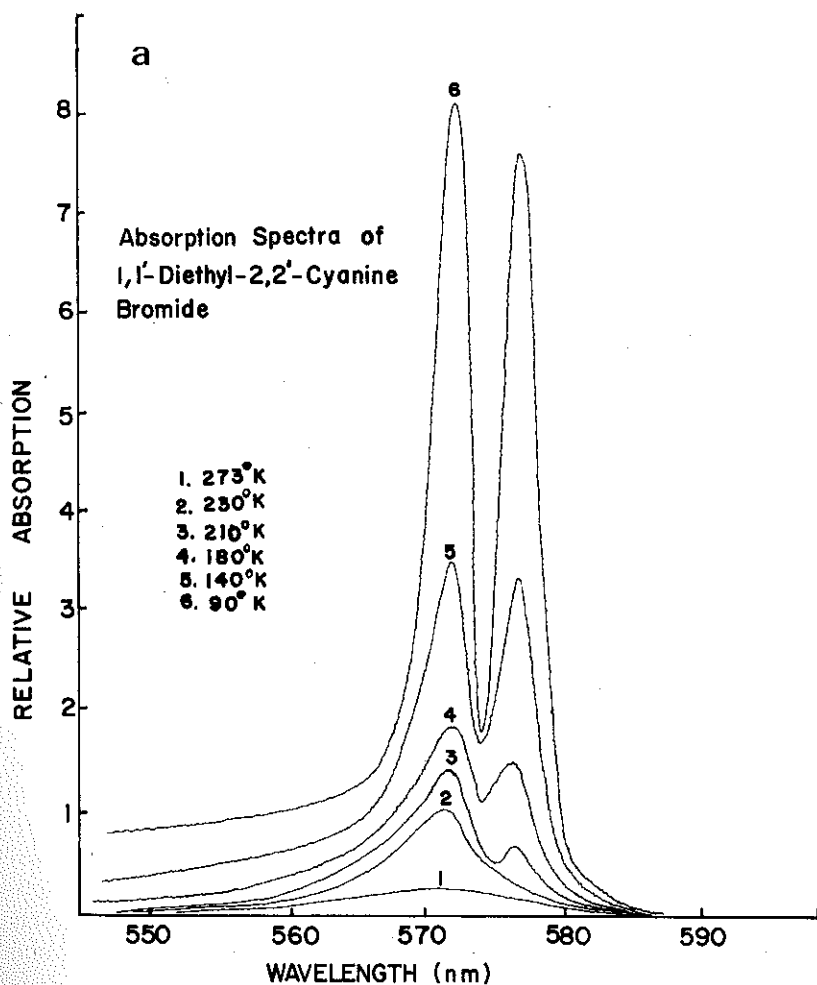


Fig. 2. For caption see next page.

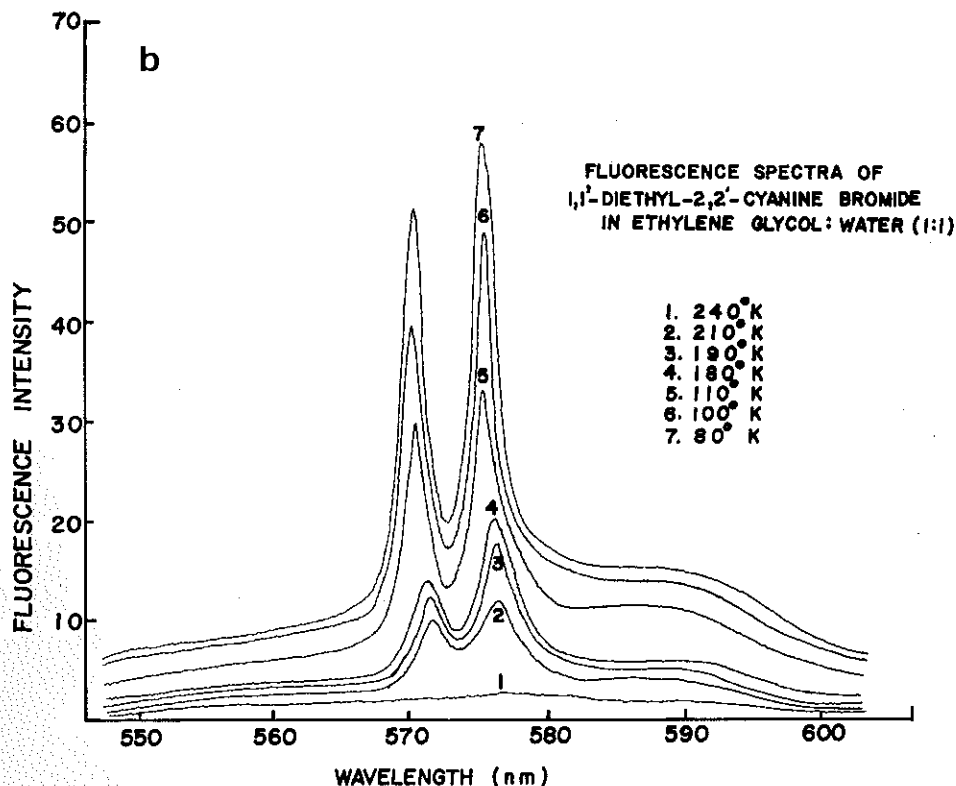


Fig. 2. (a) Steady-state J aggregate absorption spectra of a single sample of DCB at different temperatures. (b) Steady-state J aggregate fluorescence spectra of a single sample of DCB in ethylene glycol: water (1:1) at different temperatures. Excitation wavelength is 488 nm.

cence decay time of the envelope increased from 15 to 250 ps giving a ratio of 17. The fluorescence decay profile can be fitted very well to a single exponential function at each temperature (dashed lines are theoretical curves in fig. 3). The monomer decay times are plotted in fig. 4. Since the radiative transition rate  $K_r$  of the monomer does not change much at various temperatures via the absorption data, the non-radiative relaxation processes must decrease drastically to account for the increase in the decay time at low temperature, i.e. the monomer non-radiative transition rate  $K_{nr}$  decreases at low temperature. That is, the fluorescence decay time of the monomer  $\tau_m = (K_r + K_{nr})^{-1}$  increases. As the temperature is lowered the motions of the molecule are inhibited by the higher viscosities of the solvent. One attributes this to a non-radiative decay to ground-state manifold

with an activation energy of  $\approx 0.65$  kcal/mol.

When the temperature is lower than 210 K (see figs. 3d–3f), a sharp peak in time appears with a fast risetime and decay time. Since the J-band appears below 210 K, the sharp peak is attributed to the contribution of the J-band at 572 and 577 nm. This is confirmed by isolating this spectral region for temporal analysis. This is discussed in the next section.

#### 4.2. J aggregate state

When the temperature was lowered below 210 K, the J aggregate in DCB begins to appear as shown in the absorption and fluorescence spectra (see figs. 2a and 2b). The absorption and fluorescence at 572 and 577 nm of the J-band become gradually stronger as the temperature is lowered.

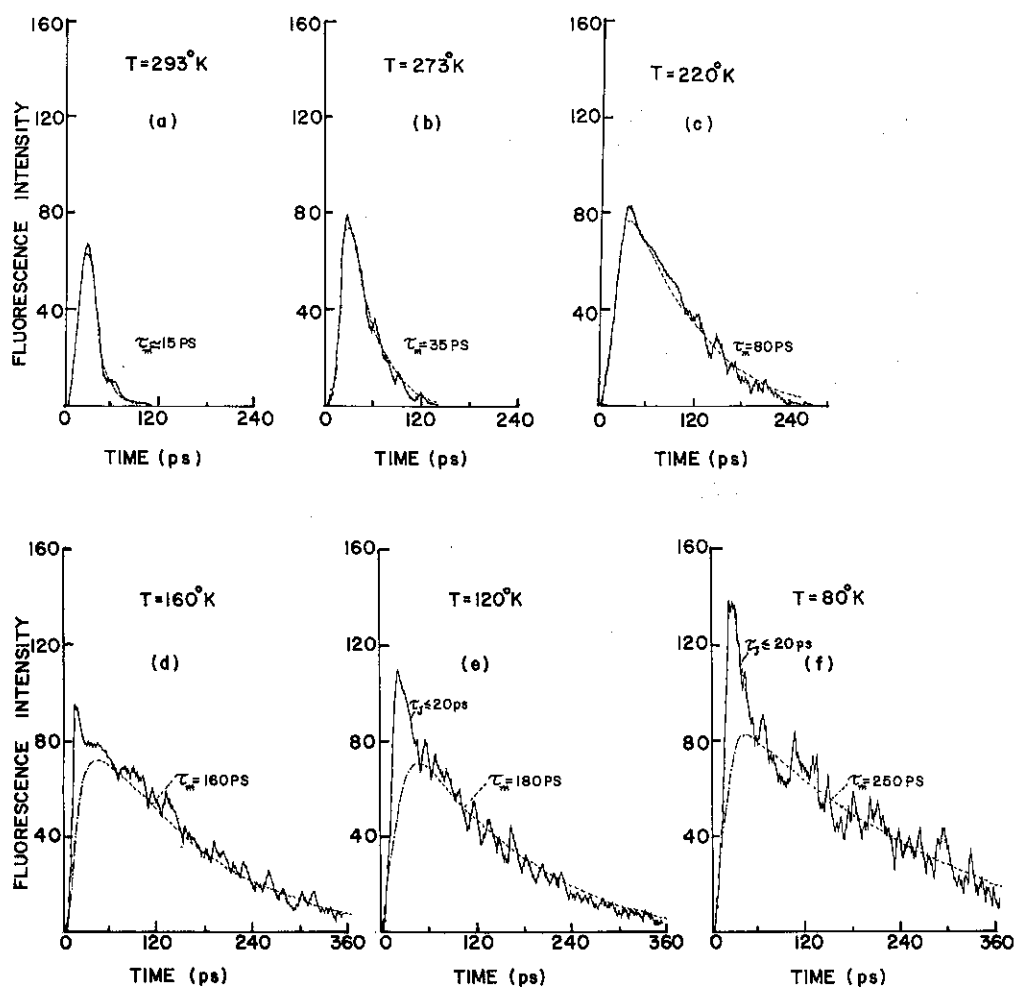


Fig. 3. Temperature dependence of time-resolved fluorescence spectra of a single sample of DCB excited by a laser pulse at 527 nm. All wavelengths beyond 550 nm were measured. The sweep length of the streak camera was 500 ps with a resolution of 15 ps. Setting of the zero time is arbitrary. The fluorescence decay time of slow components are: (a)  $\tau_m = 15$  ps; (b)  $\tau_m = 35$  ps; (c)  $\tau_m = 80$  ps; (d)  $\tau_m = 160$  ps; (e)  $\tau_m = 180$  ps; (f)  $\tau_m = 250$  ps, and the decay time of fast components are: (e)  $\tau_f \leq 20$  ps and (f)  $\tau_f \leq 20$  ps.

Both the relative fluorescence intensity and absorption band of the J-band at 90 K increase  $\approx 5$  times more than that at 210 K (the temperature of the onset of the J-band, see figs. 5 and 6). The long component in fig. 5 is attributed mainly to the monomer emission. The decay time of the J-band, on the other hand, does not increase like the monomer when the temperature is lowered. As the temperature is lowered, more molecules aggregate yielding a stronger J-band absorption at lower temperature which in turn, produces a correspond-

ing larger emission at the J-band. This could arise from the larger size. The increase of the effective absorption of the J-band causes the radiative transition rate  $K_r$  ( $\propto \int_j \epsilon(\bar{\nu}) d\bar{\nu}$ ) to increase. Usually non-radiative processes tend to decrease as the temperature is lowered which causes the non-radiative transition rate  $K_{nr}$  to decrease. In the case of the J-band the value of  $K_{nr}/K_r$  should decrease as the temperature is lowered. Therefore, the fluorescence quantum efficiency of the J-band,  $Q_J = K_r / (K_r + K_{nr}) = (1 + K_{nr}/K_r)^{-1}$ , should in-

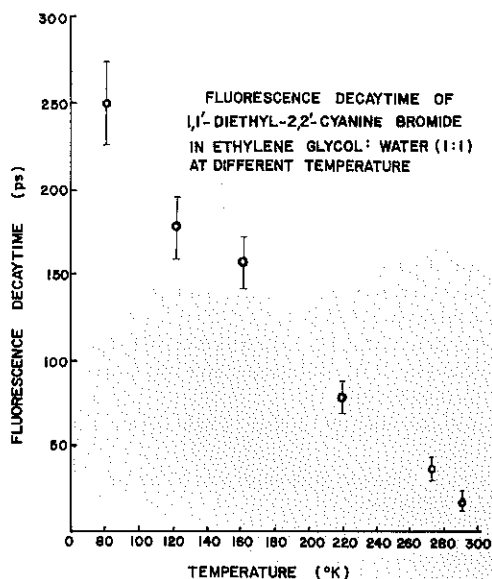


Fig. 4. The monomer fluorescence decay time as a function of temperature.

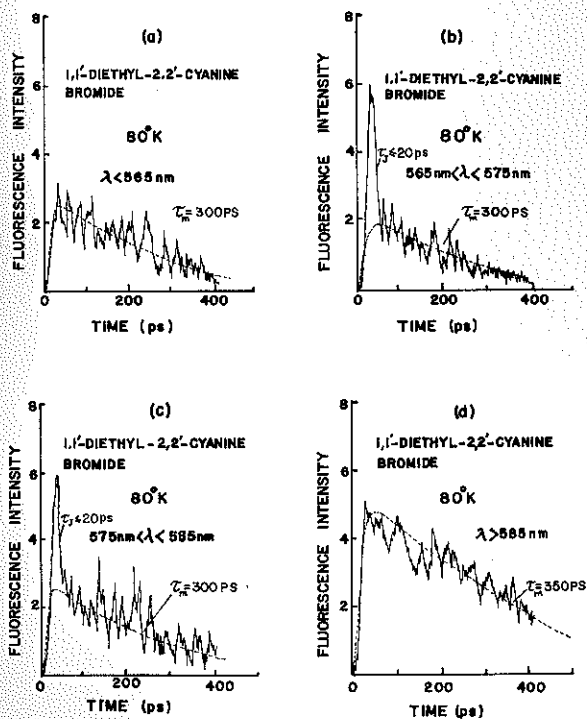


Fig. 5. Time-resolved fluorescence spectra in the four wavelength regions: (a)  $\lambda < 565$  nm; (b)  $565 \text{ nm} < \lambda < 575$  nm; (c)  $575 \text{ nm} < \lambda < 585$  nm; (d)  $\lambda > 585$  nm. The sweep scale was 500 ps with a resolution of  $\approx 15$  ps.

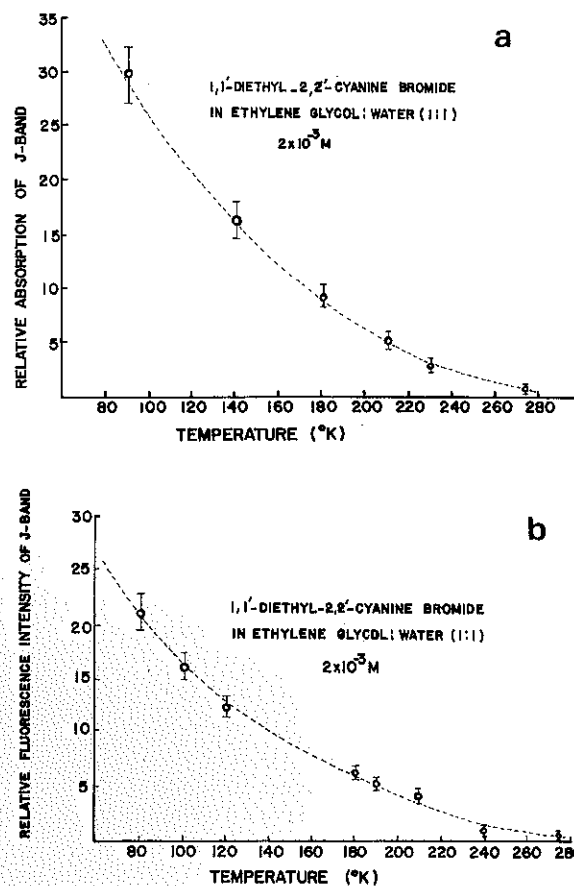


Fig. 6. (a) Temperature dependence of the relative steady-state integral absorption of J aggregate in DCB. (b) Temperature dependence of relative fluorescence efficiency of J aggregate in DCB.

crease rapidly if all the photons are absorbed on lowering the temperature. However, since the size distribution and concentration of the different aggregate species are not known, it is difficult to accurately estimate the absorption coefficient and the radiative rates associated with the J-band. The relative quantities can only be calculated from the data at this time. Since the size of the J-band absorption is not known, one can only say at this time that the quantum yield of the J-band either remains unchanged or is increased upon the J-band formation from 210 to 80 K. Due to the limited resolution of the instrument, the fluorescence lifetime of the J-band was determined to be less than

or equal to 20 ps at 80 K. The rapid decay and intense emission of the J-band is associated with the aggregate state. These observations most likely arise from a cooperation between the transition dipole moments of the individual oscillators of the aggregate. The yields from the aggregate and monomer states are comparable. Thus, a larger volume dipole emitting species having enhanced polarizability and emission rates is created. Subpicosecond spectroscopy is required to resolve the J-band kinetics at different temperatures.

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