Exciton dynamics and trapping in J-aggregates of carbocyanine dyes

To cite this article: M A Drobizhev et al 1996 Pure Appl. Opt. 5 569

View the article online for updates and enhancements.

You may also like

- <u>Tailoring the excited-state energy</u> <u>landscape in supramolecular</u> <u>nanostructures</u> Klaus Kreger, Hans-Werner Schmidt and Richard Hildner
- <u>Optical properties of three-layer metalorganic nanoparticles with a molecular Jaggregate shell</u> V.S. Lebedev and A.S. Medvedev
- <u>Fluorescent J-aggregates of cyanine dyes:</u> <u>basic research and applications review</u> Julia L Bricks, Yuri L Slominskii, Ihor D Panas et al.

Exciton dynamics and trapping in J-aggregates of carbocyanine dyes

M A Drobizhev†, M N Sapozhnikov†, I G Scheblykin†, O P Varnavsky†, M Van der Auweraer‡ and A G Vitukhnovsky†

† Lebedev Physics Institute, Russian Academy of Sciences, Leninsky pr. 53, 117924 Moscow, Russia

‡ Laboratory for Molecular Dynamics and Spectroscopy, K U Leuven, Celestijnenlaan 200 F, 3001 Leuven, Belgium

Abstract. Exciton relaxation processes in J-aggregates of two thiacarbocyanine dyes (TDC and THIATS) in water/ethylene glycol low temperature glass have been studied by means of steady-state, site-selective and time-resolved spectroscopy. The results of different experiments can be rationalized within the framework of exciton self-trapping (ST) in a 1D molecular chain. The measured Stokes shift is found to be proportional to the exciton-phonon coupling strength squared that is in accordance with the model of large radius ST excitons. A negative fluorescence anisotropy was observed for J-aggregates of both investigated dyes upon excitation outside the J-band. The observed monotonic dependence of the fluorescence anisotropy on the excitation wavelength is interpreted quantitatively within the framework of intraband absorption and Davydov splitting.

1. Introduction

It was discovered sixty years ago that cyanine dyes can form specific J-aggregates with a very narrow absorption band shifted to the red relative to that of a monomer [1, 2]. The transition dipole of the Frenkel exciton in these systems is predicted to be coherence-length-dependent [3]. The exciton motion in J-aggregates in isotropic solutions is considered to be restricted by one dimension and by a finite chain length. These long-chain molecular J-aggregates attract considerable attention as model systems for studies of the exciton motion in one-dimensional systems.

J-aggregates are usually embedded in amorphous media that possess a greater structural disorder as compared to molecular crystals. This disorder can be described by an inhomogeneous distribution of site energies (diagonal disorder) and a distribution of resonance coupling constants between sites (non-diagonal disorder) ([4, 5] and references therein). In addition, in reality some defects can break the chain into relatively decoupled segments. The disorder results in inhomogeneous line broadening, although the stationary states are still delocalized over particular segment lengths. Furthermore, a real chain is deformable and molecular displacements can affect the exciton dynamics via the exciton–phonon coupling.

In spite of considerable attention to these low-dimensional aggregated systems for many years, some features of their optical properties remain unclear—among them, so important a problem as the origin of fluorescent states. Are they either the final states of energy transfer process between rigid subunits (segments) of the long physical chain or localized (trapped, self-trapped) excitations of the deformed chain? In the first case the longest segments with

0963-9659/96/050569+13\$19.50 © 1996 IOP Publishing Ltd

the most delocalized states emit while in the second case the emitting states are localized ones (relative to free exciton states) being connected with local lattice distortions.

Generally speaking, little attention has been paid to the possibility of photoinduced chain deformation as a mechanism of exciton relaxation in these systems. In particular, exciton self-trapping by chain distortion can be considered as a channel of exciton relaxation in a deformable lattice. This process crucially depends on the system dimensionality and size restrictions [6–9]. It was found theoretically for 3D systems that if the parameter of exciton–phonon coupling exceeds some critical value, the stable self-trapped state (ST) appears below the bottom of the band of free exciton states (F) [10, 11]. In this case, two energy minima are separated by a potential barrier. In contrast to 3D systems, as has been shown by Rashba [10], in infinite, strictly 1D chains, self-trapping occurs for any nonvanishing exciton–phonon coupling and the barrier between ST and F states is absent.

The degree of topological anisotropy and therefore applicability of the one-dimensional chain model for J-aggregates have not been established experimentally so far. There is even indirect evidence in the literature for the existence of the fractal dimensionality [12]. The investigation of self-trapping or related phenomena in J-aggregates can shed light on their mesoscopic dimensionality.

Self-trapping in J-aggregates has not been established directly, but some indirect indications to this process are present in the literature [13, 14]. In [13], the authors observed a very extended and intense red tail in the fluorescence spectrum at liquid helium temperature. This tail transformed to a separate wide red-shifted peak at 77 K [13b]. The authors attributed these spectral features to self-trapping of excitons assisted by excimer formation. Mathematical analysis of the fluorescence decay kinetics in the region of the red peak provides evidence against the trapping by low-energy monomer traps [13b]. In [14a], the appearance of the red tail in the fluorescence spectrum and broadening of the spectrum during hundreds of picoseconds were attributed to the self-trapping mechanism as one of the possibilities.

Our contribution is devoted to the experimental investigation of exciton relaxation in molecular J-aggregates of two thiacarbocyanine dyes. Different mechanisms of relaxation are discussed. Special attention is paid to the effect of electron–phonon coupling on the optical spectra of J-aggregates. The fluorescent states in the systems under study can be well described by the self-trapped excitons of large radius.

From fluorescence polarization data the structure of aggregates with two molecules per unit cell is proposed. These measurements also showed that exciton diffusion between randomly oriented segments of aggregates plays a minor role in exciton relaxation.

2. Experimental

The 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine iodide (TDC), see figure 1(b), was synthesized at Niikhimfotoproekt PLC, Moscow, and used without further purification.

The triethyl ammonium salt of 3,3'-disulphopropyl-9-ethyl-5,5'-dichlorothiacarbocyanine (THIATS), see figure 1(*b*), was obtained by courtesy of Agfa NV.

For preparation of J-aggregates, THIATS and TDC were dissolved in a 3:2 volume water/ethylene glycol (WEG) mixture upon heating up to 70 °C. The solutions with a dye concentration of $\sim 5 \times 10^{-4}$ M for THIATS and 3×10^{-3} M for TDC were cooled to room temperature, put into a dismountable glass cell of 200 or 400 μ m in thickness, then cooled in a CF-204 Oxford Instruments helium cryostat to 250 K and kept at this temperature for 10–30 min. At this stage, a narrow J-band appeared in the absorption spectrum of the dye. Then the samples were placed into liquid nitrogen where they were frozen for about 30 s,



Figure 1. (a) The chemical structure of TDC. (b) The chemical structure of THIATS.

again placed into a cryostat at 80 K and finally cooled down to the desired temperature.

Polarization experiments were performed at 77 K in a liquid nitrogen cryostat. Fluorescence was excited by the polarized light of a second harmonic of a Nd:YAG laser (Antares 76s, Coherent) or of a tunable Rhodamine 6G-dye-laser pumped by the Nd:YAG laser. The samples were excited at right angles to their surface, fluorescence light being collected in the opposite direction normal to the surface through a polarizer.

Fluorescence excitation and hole burning were performed with an argon-laser-pumped CR-699-21 Coherent CW ring dye laser operated with Rhodamine 6G in a multimode regime with a linewidth of about 0.1 cm^{-1} . The transmission spectra were recorded using a stabilized filament lamp and a double spectrometer or polychromator coupled with an optical multichannel analyser. The hole spectra were detected with a resolution of $0.6-1 \text{ cm}^{-1}$. The procedure of estimation of the true hole width was described elsewhere [15].

A gated frequency mixing (up-conversion) technique was used for fast fluorescence decay measurements. The picosecond laser setup based on a Coherent Antares system consists of a synchronously pumped cavity dumped dye laser (model 702) driven by a Nd:YAG laser (Antares 76s). Upon passing through a variable optical delay line picosecond light pulses from the dye laser were mixed with the fluorescence signal from the sample in a nonlinear LiIO₃ crystal. The sum frequency light generated in the nonlinear crystal was spatially (nonlinear geometry) and spectrally (filters and an MDR-2 monochromator) separated from the laser light and the fluorescence was detected by a cooled photomultiplier. This system provided measuring picosecond fluorescence kinetics with a time resolution of about 3 ps with the excitation wavelength tuned within the 565–620 nm range.

3. Results and discussion

3.1. Types of J-aggregate

Three types of J-aggregate can be observed in concentrated solutions of TDC and THIATS at different preparation conditions. Each type of J-aggregate can be identified by: (i) the J-band position in the absorption spectrum, (ii) the width of the absorption and fluorescence bands, (iii) the value of the Stokes shift, (iv) a general view of the entire absorption spectrum.



Figure 2. (*a*) Absorption and fluorescence spectra of J-aggregates of TDC. (*b*) Absorption and fluorescence spectra of J-aggregates of THIATS.

We use the designations J_1 , J_2 and J_3 according to [16], where these three types of aggregate were observed in solutions of TDC with another counterion. TDC and THIATS dyes have similar chemical structure (figure 1(*a*), (*b*)) and the positions of the J_1 , J_2 and J_3 bands differ only slightly for both dyes.

The J_1 type of aggregate has the lowest transition energy of the J-band (for TDC at approximately 640 nm). It is relatively unstable and is not observed in low-temperature glass.

The J_2 -band is also not observed in the absorption spectrum of fresh samples at low temperatures. However, such samples of TDC show the J_2 -band in fluorescence spectrum in the restricted temperature range.

In the next section we restrict ourselves to the study of the J_3 -aggregates only, which prevail in the absorption spectrum at low temperatures. J_3 -aggregates possess the most narrow absorption and fluorescence bands and the smallest Stokes shift among other types of J-aggregate (figure 2). The latter value at 5 K constitutes 100 cm⁻¹ for TDC and 25 cm⁻¹ for THIATS.

3.2. On the nature of the Stokes shift

Note that in J-aggregates of pseudoisocyanine (PIC) the Stokes shift was not observed in frozen solutions at low temperatures [3, 17]. However, in a number of other J-aggregated systems the Stokes shift was observed to be comparable to the absorption bandwidth [12, 14a, 17–19].

In the present contribution we focus our attention on the possible origin of the Stokes shift and, therefore, the nature of fluorescent states in J-aggregates.

Generally speaking, the Stokes shift can be caused by different exciton relaxation processes, such as (a) energy transfer between segments of the chain (or of different chains), (b) energy relaxation within the exciton band of a particular undeformable segment, which implies the optical population of not only the bottom state of the band. This is facilitated



Figure 3. Temperature dependence of fluorescence line half-width (HWHM) for TDC and THI-ATS J-aggregates. Fitting curves are explained in the text.

by sufficiently strong disorder (static or dynamic), and (c) self-trapping of the exciton via exciton–phonon interaction to the states under the bottom of the band.

In the following we will treat our experimental results within the framework of the selftrapping model (c) and show that it is possible to describe all these results self-consistently. This mechanism is inherent in 1D systems, where the F state is unstable, whereas the ST one provides the energy minimum at any exciton–phonon coupling strength. Furthermore, there is no potential barrier between the two states [6, 10]. We should emphasize that the intrinsic feature of this mechanism is the direct connection of the Stokes shift to the exciton–phonon coupling strength that is not so evident for the other two possible relaxation mechanisms (a) and (b). Within the framework of the self-trapping mechanism, the Stokes shift gradually increases from zero with increasing exciton–phonon coupling in 1D systems [20].

In this case the optical excitation creates a nearly free exciton at the bottom of the exciton band; furthermore, this exciton disturbs a lattice around it making the self-consistent ST state with lower energy. Therefore the fluorescent states are qualitatively different from the absorbing ones (this difference to be reflected in the different behaviour of the temperature broadening of fluorescence and absorption lines).

Figure 3 shows the temperature dependence of the fluorescence linewidths (HWHM) for TDC and THIATS. Note the negative second derivative of the experimental curve even at low temperatures, which is rather unusual for excitonic states in molecular crystals. One can also see that the line of TDC broadens faster than that of THIATS which correlates with the difference in the Stokes shift. To describe quantitatively the dependences of the linewidths D (in cm⁻¹) we used the well known relation for localized excitations in the classic approximation [21, 22]

$$D = (a + bT)^{1/2}$$
(1)

where the parameter *a* describes the static disorder (inhomogeneous) contribution and $b = 4 \ln 2k_{\rm B}E_{\rm LR}/h$. The $E_{\rm LR}$ is the lattice relaxation energy released after phototransition. The broadening of the line of TDC is well described by (1) only in the limited low-temperature range. It was found that $E_{\rm LR} = 53 \pm 4 \text{ cm}^{-1}$ in the range from 6 to 54 K. Extending the fitting range to higher temperatures gives higher mean square deviations. It is evident from figure 3 that at T > 60 K the linewidth increases slower than the model function (1) with $E_{\rm LR} = 53 \text{ cm}^{-1}$. In the case of THIATS, the fitting of experimental points by (1) gives $E_{\rm LR} = 13 \pm 1 \text{ cm}^{-1}$ in the same temperature range. We should emphasize here that a good quantitative relation between the Stokes shift and the parameter of temperature line broadening ($E_{\rm LR}$) is observed for the two systems studied. Indeed, a decrease of the Stokes shift is four times for THIATS as compared to TDC results in the proportional



Figure 4. Adiabatic potentials (appropriate to TDC aggregates) calculated according to [20b], with $B = 1400 \text{ cm}^{-1}$ and g = 0.35; E_{LR} is the energy of lattice relaxation. The bold arrows represent the optical transitions. The broken curve is the parabolic approximation of the low-energy region of potential.

decrease in E_{LR} . This unambiguously suggests the essential role of the electron–phonon coupling in the creation of the Stokes shift. Another interesting feature is a quite small value of E_{LR} as compared to that usually observed for isolated molecules (100–1000 cm⁻¹).

Apart from the relative agreement of the Stokes shift and the parameter of temperature line broadening we attempted to relate the absolute values of these observables in the case of TDC aggregates.

Let us consider the specific form of the adiabatic potential of the ST exciton in the 1D lattice. This potential is given by the sum [20]

$$P(Q) = E(Q) + Q^2/2$$

where Q is the average lattice distortion in the area of an ST exciton and E(Q) is the binding energy of an exciton in the lattice deformed by the exciton itself. By definition [20], a positive direction of Q is decided so that E(Q) < 0 for Q > 0 and E(Q) = 0 for Q < 0. The function E(Q) can be calculated only if the parameter g of exciton-phonon coupling is known [20b]. The constant g is a ratio of the lattice relaxation energy gained by the complete localization of an exciton on a single site S and the half-width of the exciton band B:g = S/B. Higai and Sumi [20b] calculated the dependence of the Stokes shift (SS) on g in the 1D discrete lattice. Using their calculations we obtained g = 0.35 for TDC. (The value B was estimated as a difference between the absorption peaks of J-aggregates and monomers at low temperature to be 1400 cm⁻¹.) As a result we can calculate the adiabatic potential P(Q) for our system (figure 4). It is evident that this potential is asymmetric. In the energy range from -34 to 0 cm^{-1} (0-49 K), it can be described well by a parabola with a minimum at $Q_{\min} = 10.7$. Therefore, we can obtain, in this temperature range, $E_{\text{LR}} = Q_{\min}^2/2 = 57 \text{ cm}^{-1}$. This value is in good agreement with that obtained from the fluorescence temperature broadening that proves the ST model considered.

The high-temperature behaviour of the linewidth can be explained in this framework by



Figure 5. Temperature dependence of the width of spectral holes burnt near the maximum of the absorption bands of TDC and THIATS J-aggregates. Full curves are the approximations by direct processes (see [15]).

the following considerations. The optical transitions that occur during the time when Q < 0 do not contribute to the linewidth because in this area the potential curves of the ground and excited states are not shifted (see figure 4). Therefore, the temperature broadening slows down.

The low values of the Stokes shifts and lattice relaxation energies of the system studied can be explained if one takes into consideration the dimensionality of the system. Indeed, the large Stokes shifts are inherent only in 3D systems where localized excitation tends to occupy only a single site [23, 24]. In this case the lattice relaxation energy $E_{LR} = S$ must be greater than *B* for self-trapping to occur. It is easy to show that for a 3D lattice SS = 2S - B > B and, therefore, the Stokes shift must at least be greater than the bandwidth *B*. On the other hand, the stable ST state in the 1D lattice occupies a great number of sites if a parameter g = S/B does not exceed some critical value (~0.75) [20]. In the 1D case, the Stokes shift for large-radius ST states can be expressed as $SS = 1.5E_{LR}$ [25] (see figure 4) and hence can have any value, which vanishes when the coupling constant *g* tends to zero [20, 25]. The value of an average number N_b of unit cells covered by the lattice distortion in the ST exciton at g = 0.35 can be estimated from the same model [20b] to be about 7 for the TDC aggregate.

We also performed the hole-burning experiments in absorption bands of J-aggregates of the two dyes. Temperature dependences of the hole width are shown in figure 5. It is evident that at T < 10 K the hole width depends only slightly on temperature. In addition, the hole width of TDC rises faster than that of THIATS and the low-temperature limit of the width is greater for TDC. This can imply that the exciton–phonon coupling as measured in absorption is also greater for TDC.

Taking into account that the homogeneous absorption line broadening reflects the behaviour of the non-relaxed nearly free exciton, we used the simplest model of exciton-

phonon interaction [22, 26]. This model assumes a single mode of electronic excitation per site, the Franck–Condon approximation for absorption transition, a single and harmonic mode w of lattice vibration per site (Einstein model), linear and site-diagonal electron– phonon interaction of contact (short-range) type. Within this framework in the case of weak exciton–phonon scattering ($D_T \ll B$), where D_T is the disorder parameter of on-site transition energies due to thermal vibrations, the linewidth is determined by the golden rule [22]

$$g^* = \pi D_{\mathrm{T}}^2 r(E). \tag{2}$$

Here r(E) is the density of excitonic states (DOS) at transition energy. It is assumed that r(E) is constant in the range from E - hw to E + hw. At very low temperatures $D_T^2 = Shw$ [22] and, therefore,

$$g^* = \pi h w Sr(E). \tag{3}$$

Thus, all other factors being equal, we can try to obtain the parameter S (and consequently g) from the low-temperature limit of the homogeneous linewidth. Besides our hole-burning results we analysed a number of data [12, 17, 18, 27–29] obtained by the photon echo and hole-burning techniques in order to obtain a relation between the parameter g and the Stokes shift in a number of different systems. As a rough approximation we take a phonon frequency w equal for all systems. To obtain g^* we subtracted the fluorescence lifetime contribution from the low-temperature homogeneous linewidth measured by hole burning or photon echo (see e.g. [12])

$$g^* = (\pi c T_{nth})^{-1} = (\pi c T_2)^{-1} - (2\pi c T_1)^{-1}.$$
(4)

As concerns the density of states, it depends on the static disorder parameter D_0 and varies considerably from one system to another, which is reflected in inhomogeneous absorption line widths W varying from 30 to 250 cm⁻¹ at low temperatures (see table 1). It was shown [5] that in the case of the diagonal static disorder W scales as $D_0^{4/3}$. Furthermore, an amplitude of the normalized DOS for the 1D disordered lattice in the low-energy side $r(E) \sim D_0^{-1}$ [30]. Therefore, in a first approximation $r \sim W^{-3/4}$ and to obtain a value proportional to S one must multiply the observed g^* by $W^{3/4}$. Taking into account also the different values of the bandwidths B for different systems we compose the combination $g^*W^{3/4}/B$ which is proportional to g. All the parameters used for this combination are collected in table 1.

The Stokes shifts obtained for these systems are also given in this table. Figure 6 shows the dependence of the Stokes shift in units of *B* on the parameter $g^*W^{3/4}/B \sim g$. It is evident that the dependence is close to a quadratic one that is an intrinsic feature of self-trapping in 1D systems only [20]. The quadratic part of this dependence is predicted in the range of small values of *g*, where the ST excitons are of large radius [20]. The radii N_b of these states are calculated using the dependence $N_b(g)$ predicted in [20b] and presented in the table.

It should be emphasized here that neglecting the non-diagonal terms in electron-phonon interaction used in the model [22, 26] can be justified for sufficiently strong (according to Davydov [31]) exciton-phonon interaction, which possibly takes place in crystals with molecules having permanent dipole moments, like carbocyanine dyes [10]. Considerable Stokes shifts observed in a number of J-aggregates can prove this assumption. The PIC J-aggregates in WEG look exceptional in this context because they possess no Stokes shift [17]. In this case the parameter of exciton-phonon coupling for PIC shown in the table can be regarded as an upper limit for the diagonal part g of the interaction.

Table 1. All the data are given for J-aggregates in water/ethylene glycol frozen matrices, except for the last row, where a Langmuir–Blodgett film was used. The results for THIATS and TDC are obtained in this paper, other data refer to the literature. All the data were obtained at liquid helium temperatures.

	$T_2^{\rm a}(\rm ps)$ $g_2(\rm cm^{-1})$	$T_1^{\rm a}(\rm ps)$ $g_1(\rm cm^{-1})$	g^* (cm ⁻¹)	W (cm ⁻¹)	$B^{b}(\mathrm{cm}^{-1})$	$g^*W^{3/4}/B$	SS (cm ⁻¹)	SS/B	N _b ^d
PIC	40 [27] 0.265	70 [17, 27] 0.076	0.19	30 [17,27]	[17, 27] 1300	0.0017	[3, 17] <1	<10 ⁻³	200 ^e
THIATS		18 ^c							
	1.2	0.29	0.9	120	1550	0.021	25	0.016	17
TDBC		18 [18]							
	1.5 [18]	0.29	1.2	160 [18]	2080 [18]	0.026	40 [18]	0.019	15
TC	6.4 [12]	18 [12]							
	1.66	0.29	1.37	240 [12]	2500 [12]	0.033	80	0.032	11
TDC		18 ^c							
	1.65	0.29	1.36	220	1400	0.055	100	0.071	7
PIC in	5.4 [28]	10.5 [28]							
LB-film	1.97	0.53	1.44	130 [28]	1400	0.065	130	0.093	6

^aThe data were obtained at absorption maximum (or interpolated to it).

^bThe half-width of the exciton band was obtained as the difference between the absorption maxima of the monomer and the J-peak (as measured at liquid helium temperatures).

^cAssumed to be equal to 18 ps as for TDBC and TC [18, 12] that is also confirmed by our preliminary measurements. ^dEstimated using calculations of Higai and Sumi [20b] from the measured values of SS/B.

^eThe rough lower limit estimate from the relative value of $g^*W^{3/4}/B$, which is proportional to N_b^{-1} [10, 24].





3.3. Polarized fluorescence

The special feature of the J₃-aggregates is the presence of a strong H-band in the absorption spectrum [16], which is observed in our case at 521 nm for TDC (figure 2(a)) and at 514 nm

Anisotropy

-0.



Figure 7. Absorption spectrum of Jaggregates of TDC (thick curve) and fluorescence anisotropy action spectrum of the J-band (circles). The dotted curve is the calculated fluorescence anisotropy in the case of intraband excitation within the W-like model; the thin curve-the same curve taking into account the depolarizing scattering.

for THIATS (figure 2(b)). The optical density of the H-band is several times greater than that of the J₃-band for both dyes.

The H-transition can be related to particular geometrical arrangements of the molecules within the aggregate in which the angle between the transition dipoles of molecules and the chain direction is large enough [32]. Within the framework of the so-called W-like arrangement both H- and J-bands are observable in the absorption spectrum [32] of the same aggregate. In fact, this means that the chain arrangement with two molecules per unit cell results in the splitting of the exciton band into two bands (Davydov splitting [31]).

We observed a large negative fluorescence anisotropy (FA) in the J_3 -fluorescence band of TDC and THIATS upon non-resonant excitation ($I_{ex} = 532, 575$ nm). If exciting at 532 nm, the FA for TDC is equal to -0.16, being very close to the theoretical limit of -0.2 for perpendicularly oriented emission dipoles. First of all, this shows that there is no energy transfer between randomly oriented aggregate chains (segments of the chain) during the excitation relaxation [33]. When the excitation wavelength exceeds 590 nm, the FA becomes positive and reaches the value of +0.37 for near resonant excitation, figure 7. This value is close to the theoretical limit of +0.4 for parallel dipoles.

The observed monotonic fluorescence anisotropy dependence of excitation wavelength can be interpreted quantitatively in the framework of intraband absorption and the W-like model of the aggregate chain. The unit cell of the chain in the W-like model consists of two identical two-level molecules. The transition dipoles of all molecules lie in the same plane and make an angle δ with the chain direction.

The transition dipole to the H-state (top of the exciton band) is perpendicular to the chain direction while to the J-state (bottom of the exciton band) it is parallel to the chain direction. Hence, the value of the FA of the J-band must be -0.2 for excitation to the H-band (perpendicular dipoles) and +0.4 for excitation to the J-band (resonant excitation, parallel dipoles).

From the excitation wavelength dependence of the FA the transition dipole moment of each molecule was estimated to make an angle of $65-70^{\circ}$ with the chain direction for both dyes.

Note that molecularly thin single crystals of thiacarbocyanine dye, very similar to ours, formed at a surfactant monolayer, have at least two differently oriented dye molecules per unit cell [34, 35]. The authors proposed the herringbone structure for these two-dimensional crystals with an angle between the molecules of about 80° . This was proved by absorption polarization and electron diffraction methods [34].

Now let us consider the FA behaviour within the fluorescence J-band when the excitation



Figure 8. (*a*) Fluorescence and fluorescence anisotropy spectra of the J-band of THIATS. (*b*) Fluorescence and absorption spectra of the J-band of TDC. (*c*) Fluorescence anisotropy spectrum of the J-band of TDC.

wavelength is fixed. The FA structure was found for the first time for J-aggregates (figure 8). This structure was observed for J-aggregates for both TDC and THIATS dyes. For THIATS the FA spectrum exhibited two maxima: a first at 615 nm and a second at 622 nm (the fluorescence has a maximum at 616.5 nm, the excitation wavelength is 575 nm). For TDC this structure was not so clearly resolved and revealed itself as a shoulder (figure 8(c)).

We suppose that the second peak in the fluorescence band results from the temperatureinduced photo-rearrangement $J_3 \rightarrow J_2$ [36]. The J_3 and J_2 structures must be highly correlated in orientation in order that the FA value remained large in the second (J_2) peak.

The fluorescence spectrum of the J-aggregates of THIATS dye exhibits only one band at about 616 nm; however, the double-peak structure in the FA spectrum is also observed (figure 8(a)).

We should emphasize that the absolute value of the FA has a maximum around the maximum of the absorption spectrum rather than that of the fluorescence (figure 8(b) and (c)). In general, the absolute FA value decreases when the wavelength increases within the fluorescence band. This decrease of the FA reflects the exciton relaxation accompanied by reorientation of the emission dipole. The nature of this relaxation supposedly connects with the lattice deformation due to exciton–phonon coupling which results in the self-trapping of the exciton [20, 23].

4. Conclusions

Relevant parameters of exciton-phonon coupling have been estimated from independent measurements of the temperature dependence of spectral hole width and fluorescence line shape. The results of the experiments are interpreted in the framework of exciton self-trapping (ST) in a 1D molecular chain. The measured Stokes shift is found to be proportional to the exciton-phonon coupling strength squared, that is in accordance with the model of large radius ST excitons.

A negative fluorescence anisotropy was observed for J-aggregates of both investigated dyes upon excitation outside the J-band. The observed monotonic dependence of fluorescence anisotropy on excitation wavelength is interpreted quantitatively in a framework of intraband absorption and Davydov splitting. The physical structure of J-aggregates corresponding to this model includes two molecules per unit cell with an angle between transition dipoles and the chain axis of ~65–70°.

The fluorescence anisotropy was found to vary non-monotonically as a function of the emission wavelength within the fluorescence J-band.

Acknowledgment

The authors are grateful for INTAS grant 93-85, FKFO and DWTC through IUAP II-16.

References

- [1] Scheibe G 1936 Angew. Chem. 49 563
- [2] Jelley E E 1936 Nature 138 1009
- [3] De Boer S and Wiersma D A 1990 Chem. Phys. Lett. 165 45
- [4] Klafter J and Jortner J 1978 J. Chem. Phys. 68 1513
- [5] Fidder H, Knoester J and Wiersma D A 1991 J. Chem. Phys. 95 7880
- [6] Rashba E I 1982 Excitons ed E I Rashba and M D Sturge (Amsterdam: North-Holland) p 543
- [7] Ueta M, Kanzaki H, Kobayashi K, Toyozawa Y and Hanamura E 1986 Excitonic Processes in Solids (Berlin: Springer)
- [8] Song K S and Williams R T 1993 Self-Trapped Excitons (Berlin: Springer)
- [9] Rashba E I 1994 Synth. Met. 64 255
- [10] Rashba E I 1957 Opt. Spektrosk. 2 75, 88
- [11] Toyozawa Y 1961 Prog. Theor. Phys. 26 29
- [12] Fidder H and Wiersma D A 1993 J. Phys. Chem. 97 11603
- [13a] Maliukin Yu V and Tovmachenko O G 1993 Pis. Zh. Exp. Teor. Fiz. 58 385
- [13b] Maliukin Yu V, Seminozhenko V P and Tovmachenko O G 1995 JETP 107 812
- [14a] Kamalov V F, Struganova I A and Yoshihara K 1993 Chem. Phys. Lett. 213 599
- [14b] Kamalov V F, Struganova I A, Tani T and Yoshihara K 1994 Chem. Phys. Lett. 220 257
- [15] Drobizhev M A et al 1995 Chem. Phys. Lett. 234 425
- [16a] Hada H, Honda C and Tanemura H 1977 Photogr. Sci. Eng. 21 83
- [16b] Honda C and Hada H 1977 Photogr. Sci. Eng. 21 91
- [17] Fidder H, Terpstra J and Wiersma D A 1991 J. Chem. Phys. 94 6895
- [18] Moll J, Daehne S, Durrant J R and Wiersma D A 1995 J. Chem. Phys. 102 6362
- [19] De Boer S and Wiersma D A 1989 Chem. Phys. 131 135
- [20a] Sumi H and Sumi A 1994 J. Phys. Soc. Japan 63 637
- [20b] Higai S and Sumi H 1994 J. Phys. Soc. Japan 63 4489
- [21] Krivoglaz M A 1956 Opt. Spektrosk. 1 54
- [22] Schreiber M and Toyozawa Y 1982 J. Phys. Soc. Japan 51 1528
- [23] Sumi H and Toyozawa Y 1971 J. Phys. Soc. Japan 31 342
- [24] Toyazawa Y and Shinozuka Y 1980 J. Phys. Soc. Japan 48 472
- [25] Eremko A A, Gaididei Yu B and Vakhnenko A A 1985 Phys. Status Solidi b 127 703
- [26] Toyozawa Y 1983 Organic Molecular Aggregates ed P Reineker, H Haken and H C Wolf (Berlin: Springer) p 90

- [27] Fidder H and Wiersma D A 1995 Phys. Status Solidi b 188 285
- [28] Terpstra J, Fidder H and Wiersma D A 1991 Chem. Phys. Lett. 179 349
- [29] Hirschmann R and Friedrich J 1989 J. Chem. Phys. 91 7988
- [30] Halperin B I 1965 Phys. Rev. A 139 104
- [31] Davydov A S 1971 Theory of Molecular Excitons (New York: Plenum)
- [32] McRae E G and Kasha M 1958 J. Chem. Phys. 28 721
- [33] Galanin M D 1950 Trudy Lebedev Fiz. Inst. 5 339
- [34] Kirstein S and Mohwald H 1992 Chem. Phys. Lett. 189 408
- [35] Kirstein S and Mohwald H 1995 Adv. Mater. 7 460
- [36] Drobizhev M A et al 1995 Light on Organized Molecular Systems (Eurolights-2) (Hengelhoef, Belgium) Abstracts p 115