

Absorption lineshape of J-aggregates of thiocarbocyanine dyes: experiment and numerical study

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Received 23 January 1997; in final form 21 February 1997

Abstract

The experimental absorption spectra of J-aggregates of the carbocyanine dyes THIATS and TDC were fitted to a segment and a continuous energy disorder (CED) model. From 6 K to room temperature the best fits were obtained using an exponential distribution of segment lengths. Both models gave equally good fits when the average length in the segment model corresponded to the average localization length in the CED model. At room temperature homogeneous broadening or/and an enhanced contribution of the off-diagonal disorder must be taken into account.

1. Introduction

Even though systems with restricted geometry, particularly low-dimensional systems have been studied for a long period of time, there continues to be strong interest in the optical properties of these systems. Especially interesting are the spectral properties of one-dimensional systems, such as J-aggregates and polymers. The most characteristic feature of J-aggregates is the fact that they exhibit in their absorption spectra a narrow peak (J-band) that is typically considerably narrower than the absorption bands observed in the monomer spectra [1–3]. The interactions between the molecules in J-aggregates give rise to delocalised electronic states (Frenkel

excitons), which are associated with collective effects in optical response. The most prominent manifestations of such a collective optical response are collective spontaneous emission ('exciton superradiance') [4–7] and a large optical nonlinearity [8]. In spite of the long-standing interest in these low-dimensional aggregated systems some features of their optical properties remain unclear. Even the mechanisms of line broadening at different temperatures, which are closely connected to the dimensionality of J-aggregates, are not completely established. In this Letter we report numerical simulations of the absorption spectra of linear aggregates with different types of static and dynamic disorder. By fitting the computed spectra to experiment we have obtained the

parameters of the exponential distribution of segment lengths and of the diagonal disorder for two thiacyanocyanine J-aggregates at different temperatures.

2. Model

2.1. Model Hamiltonian

We shall consider an aggregate consisting of a set of identical molecules, assuming each molecule to have two states: a ground state $|g\rangle$ and an excited state $|e\rangle$. A good description for the aggregate excitations can be given by the linear chain Hamiltonian. In the site representation it can be written as [9–11]:

$$H_0 = \sum_n |n\rangle E_n \langle n| + \sum_n \sum_{m \neq n} |n\rangle V_{nm} \langle m|. \quad (1)$$

Here $|n\rangle$ denotes the state in which molecule n ($n = 1, 2, \dots, N$) is excited and all the others are in the ground state, E_n represents the molecular excitation energy and V_{nm} is the intermolecular interaction between molecules n and m , which is assumed to be of dipolar origin. In the general case E_n and V_{nm} vary from site to site due to diagonal and off-diagonal disorder, expressing a variation in the intermolecular interactions. Because Eq. (1) in general form is intractable, simplifying assumptions are usually made. In the basic work of Schreiber and Toyozawa [12,13] the transfer energy V_{nm} is taken to be constant, V , being nonzero only between adjacent molecules. In the most simple case when the system is not subject to any kind of disorder the Hamiltonian can be easily diagonalized, leading to the eigenfunctions:

$$|\psi_k\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin\left(\frac{\pi kn}{N+1}\right) |n\rangle \quad (2)$$

with energies

$$E_k^0 = E^0 - 2V \cos\left(\frac{\pi k}{N+1}\right) \quad (3)$$

($k = 1, 2, \dots, N$). From Eq. (2) the matrix element for the dipole transition can be calculated as

$$\begin{aligned} (\mu_k)^2 &= \left(\frac{2\mu_{\text{mon}}^2}{N+1}\right) \cot^2\left(\frac{\pi k}{2(N+1)}\right), \quad k = \text{odd} \\ (\mu_k)^2 &= 0, \quad k = \text{even} \end{aligned} \quad (4)$$

For real systems a particular disorder should be taken into account.

2.2. Disorder

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 (off-diagonal disorder) (see Refs. [11,14], 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 delocalised over particular segment lengths. Furthermore, a real chain is deformable and molecular displacements can affect the exciton dynamics via exciton–phonon coupling.

For reasonable modeling of the excitonic line-shape it is sufficient to consider in most cases only the diagonal disorder [10,12,13]. Nevertheless, taking into account the non-diagonal disorder can lead to some important peculiarities in the spectra as was demonstrated in Ref. [11].

As to the spatial aspects of the energy disorder of real molecular chains two extreme models of the disorder have been proposed [15]:

1. the independent segments ('broken rod' or segment) model,
2. the continuous energy disorder (CED) Model.

The 'broken rod' (segment) model assumes that a few defects are distributed at random along the chain. These barriers serve to localize excitations on mutually decoupled segments. The segments are taken as defect-free linear chains of finite length. Each segment is an ideal straight linear part of the chain.

The CED model assumes a Gaussian distribution of site energies and/or an excitation exchange inter-

action. Any site to site correlation is neglected. This model assumes a continuously deformed aggregate.

A generalized approach to the problem of intersite correlation which includes both above limiting cases can be given by introducing a spatial correlation function [10,16]. In this treatment the segment model corresponds to completely correlated disorder and the CED model means a totally uncorrelated one. Although it was shown [17,18] that the CED model is a good tool for modeling the absorption spectra of J-aggregates, there is strong evidence from nonlinear two-color pump–probe spectroscopy experiments that the intersite correlation of the disorder is high for J-aggregates. This was shown both for the extensively studied PIC J-aggregates [19] and for a new carbocyanine dye TDBC [20]. The dependence of the delocalisation length on the degree of intersite correlation is discussed in Ref. [21]. Taking these observations into account the segment model of the energy disorder looks more relevant for J-aggregates.

In this Letter we consider an aggregate to be a set of segments of different lengths undergoing inhomogeneous broadening. Special attention is paid to the segment length dispersion. It was shown that chain length dispersion can play an important role in the optical spectra of 1D polymers [22]. For these polymer systems the chain length distribution was found to be close to exponential [22]. The effect of the particular type of segment lengths distribution on the optical spectra of J-aggregates has not been evaluated so far.

The experimental absorption spectra of the J-aggregates were fitted to the numerically simulated ones within the ‘broken rod’ (segment) model in accordance with recent data on highly correlated disorder in these species [19,20]. An absorption spectrum simulation within the CED model was also performed for comparison.

3. Experimental and simulation procedures

The models discussed above were used to simulate absorption spectra of J-aggregates. The results of calculations were compared with the experimental spectra of real J-aggregates.

3,3',9-Triethyl-5,5'-dichlorothiacyanine iodide (TDC) (Fig. 1a) was synthesized at Niikhimfo-

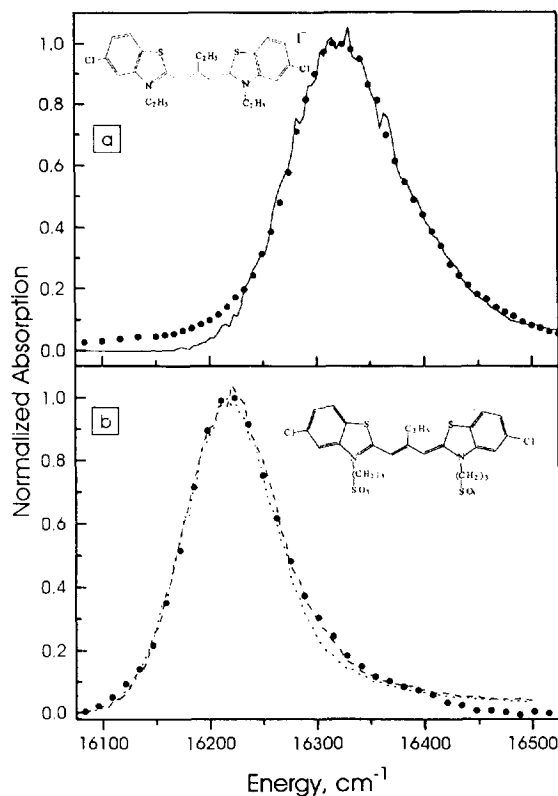


Fig. 1. (a) Simulations of the TDC absorption spectrum at 40 K: ●: experimental data; —: computer simulation. (b) Simulation of the THIATS-I absorption spectrum at 40 K: ●: experimental data; —: fit assuming an exponential segment length distribution; ···: fit assuming a Gaussian segment length distribution with average length of 12 and standard deviation of 24. The diagonal disorder is 39 cm^{-1} in both cases.

toproekt PLC (Moscow) and used without further purification. The triethyl ammonium salt of 3,3'-disulfopropyl-5,5'-dichloro-9-ethyl thiacyanine (THIATS) (Fig. 1b) was obtained by courtesy of Agfa N.V.

For the preparation of the J-aggregates the TDC (or THIATS) was dissolved in a 3:2 v/v water/ethylene glycol (WEG) mixture upon heating up to 60°C . The solutions with a dye concentration of $\sim 10^{-4}$ – 10^{-3} M were cooled to room temperature, put into a dismantable glass cell of $300 \mu\text{m}$ in thickness, then cooled and kept at 250 K for about 10 min. At this stage a narrow red-shifted J-band appears in the absorption spectrum. The samples were then quickly frozen in liquid nitrogen, and placed into a nitrogen or helium cryostat.

To measure the absorption spectra a Jobin–Yvon polychromator coupled with a PARC OMA-2 optical multichannel analyzer was used. Some spectra were recorded with a DFS-52 (LOMO) double spectrometer with 0.1 nm spectral resolution.

Some experimental data on the spectral hole burning in J-aggregates were used for evaluation of the homogeneous broadening [23]

We started the simulations of the absorption spectra with the following simple model of the energy disorder: the energies of the sites E_0 within one particular segment of the chain are equal, but they are different for different segments due to environmental influences. We assume a 1D nature of the aggregate (linear segment), where the width of the excitonic band equals $4V$. The latter is considered to be equal for all segments. Two types of disorder were taken into consideration.

1. Disorder in the lengths of segments N due to the stochastic nature of the aggregation process. We examined segment lengths to have either Gaussian

$$P_g(N_j) = \frac{1}{\sqrt{2\pi}} \frac{1}{N_0} \exp\left(-\frac{(N_j - N_0)^2}{\Delta N_0^2}\right)$$

or exponential

$$P_e(N_j) = \frac{1}{N_0} \exp(-N_j/N_0)$$

distribution, where $P(N_j)$ is the probability of encountering a chain of length N_j , N_0 is the average length, j is the number of a segment and ΔN_0 is the standard deviation of the aggregate length (in the case of the Gaussian distribution).

2. Disorder in the band center positions E_j^0 of each segment due to the inhomogeneities of the neighborhood ('diagonal disorder' for segments) is supposed to be independent of the length of the segment. We consider this distribution to be Gaussian with standard deviation D_s . The energy levels and their oscillator strengths for all segments were calculated as for an ideal chain using Eq. (3) and Eq. (4).

Each spectrum was combined as an average over 500000 segments generated by the Monte Carlo method. For every segment the energies and oscillator strengths for all states were calculated and added to the sum array, then the spectrum obtained was

normalized to unity. The 'noisy' look of the simulated spectra is related to the limited number of segments used for the calculations.

In some cases the convolution of the above generated spectrum with a Lorentzian of variable width (HWHM) A_0 was used to fit experimental data. The Lorentzian red tail in the spectrum of the linear chain could be the consequence of either homogeneous broadening or the influence of off-diagonal disorder [17].

Thus, the average length of a segment N_0 (entirely integer), the standard deviation of the segment length ΔN , the standard deviation of the band center position D_s , the excitonic bandwidth $4V$ and the Lorentzian contribution A_0 could be taken as variable fit parameters.

The simulations showed a strong dependence upon some fitting parameters while others almost did not influence the result. Although all the parameters influence the position and width of the spectrum, the excitonic bandwidth mainly determines the position of the maximum of the spectrum, while D_s and N_0 (Fig. 2) determine the slope and the form of the red and blue wings respectively along with the overall width of the simulated spectrum.

The initial value of the excitonic bandwidth as a fit parameter was obtained as the measured offset between the maxima of the absorption spectrum of the aggregate and monomer (the infinite segment length approximation).

In this way the transfer energy V was estimated to be 700 and 775 cm^{-1} for the J-aggregates of TDC (Fig. 1(a)) and THIATS (Fig. 1(b)) respectively. These estimations were adjusted slightly to make the maxima of the simulated spectrum and the experimental one coincide. Then N_0 and D_s were varied to obtain a quantitative agreement of the red and blue wings of the spectra. This sequence of adjustments is allowed by the fact that the width of the simulated spectrum depends only slightly on the interaction V . Thus we obtained a unique set of adjustment parameters which fit the experiment.

4. Results

Following the above segment model we have succeeded in fitting absorption spectra of THIATS and TDC at different temperatures.

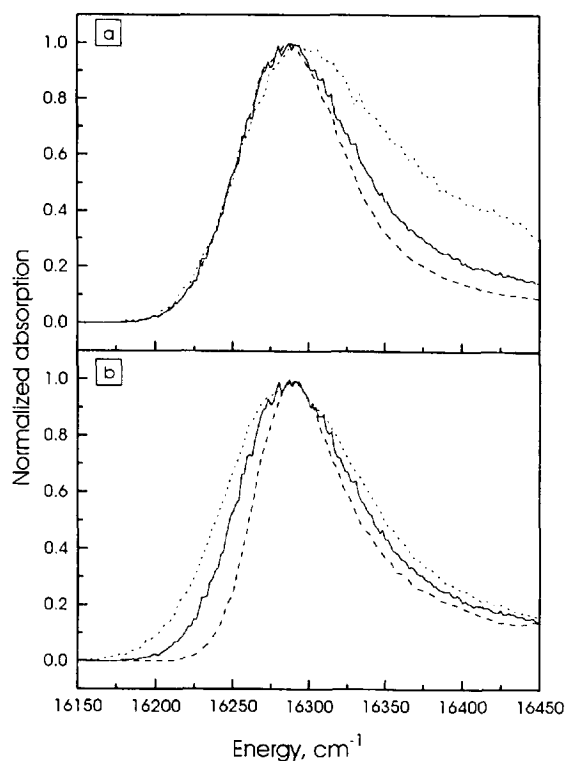


Fig. 2. Demonstration of the dependence of the simulated spectrum upon the fitting parameters. (a) Upon average segment length: —: $N_0 = 7$, ---: $N_0 = 4$, ···: $N_0 = 10$; the disorder is taken to be 28 cm^{-1} for all cases. (b) Upon diagonal disorder: —: $D_S = 28 \text{ cm}^{-1}$, ---: $D_S = 20 \text{ cm}^{-1}$, ···: $D_S = 35 \text{ cm}^{-1}$; average segment length is taken to be 7 for all cases.

Two types of J-aggregates of THIATS were used in this work. Depending on the preparation procedure samples, having either a 25 cm^{-1} or zero Stokes shift of the fluorescence spectra, could be prepared. We refer to them as THIATS-II and THIATS-I respectively. For all the samples we tried to fit their absorption spectra, applying both types of length distribution. In all cases the results of the fitting assuming an exponential distribution appeared to be better than those based on a Gaussian distribution (see Fig. 1(b), compare solid and dotted lines). This can be accounted for by the fact that in the case of a Gaussian length distribution the overall fraction of short segments is considerably smaller than in the case of an exponential one. This is a crucial parameter for fitting the blue wing of the absorption spectrum in the segment model, because this wing is mainly due to the shorter segments. The results of the simulations of the spectra of THIATS and TDC are presented in Table 1.

For the case of THIATS-I at 77 K (Fig. 1b) and THIATS-II at 20 K we could obtain a nearly perfect fit with a unique set of parameters. This is possible because the experimental spectra possess Gaussian red and Lorentzian blue wings which minimize the correlation between the fitting parameters. It is of particular interest that THIATS-I, which does not show a Stokes shift, forms longer segments than THIATS-II even at higher temperatures.

Table 1
Results of the simulation of the absorption spectra

Dye	Temperature (K)	Average segment length N_0	Main contribution length N_{ma} (Min – Max) ^b	Segment energy disorder D_S , (cm^{-1})
THIATS-I	77	12 ± 0.5 ^a	16 (9–30)	39 ± 1 ^a
THIATS-II	6	7.5 ± 0.5 ^a	14 (10–18)	29 ± 1 ^a
THIATS-II	20	7.5 ± 0.5 ^a	14 (10–18)	30 ± 1 ^a
THIATS-II	293	7.5 ± 0.5 ^a	14 (10–18)	$28(150)$ ^c
TDC	9	13 ± 1 ^a	19 (7–35)	45 ± 3 ^a
TDC	40	13 ± 1 ^a	19 (7–35)	45 ± 3 ^a
TDC	70	10 ± 1 ^a	15 (7–35)	55 ± 3 ^a

^a The good fit remains in the limits shown.

^b The absorption segment length is determined by the maximal contribution to the absorption maximum. These lengths give the main contribution (> 0.5) into the maximum of the absorption spectrum (see Fig. 3).

^c Satisfactory fits are possible only if a convolution of the calculated spectrum with a Lorentzian is performed. The width of the Lorentzian is necessarily much larger than the width of the static energy disorder D_S .

The average coherent length of the exciton in J-aggregates can be correctly estimated from radiative lifetime measurements taking into account the effect of super-radiant enhancement [6,7]. In the segment model with a broad distribution of segment lengths many different segments contribute to the radiative decay in the vicinity of the line maximum. This fact should lead to non-exponential radiative decay which was indeed observed in some experiments [24,25]. We have calculated the distribution function of the segment lengths contributing to the absorption J-peak in accordance with their oscillator strengths. The result is shown in Fig. 3. The contribution of different segments to the absorption depends not only on the value of the average segment length, but also on its oscillator strength. It should be stressed that the average segment length contributing most to the absorption maximum is twice as long as the parameter of the exponential distribution of segment lengths N_0 . This is connected with an enhancement of oscillator strength for long segments.

The segment model described above does not account explicitly for the disorder induced by phonons in the adiabatic approximation [12,13]. However, for the low-temperature spectra, when the phonon population is low, a good fit by the segment model was obtained, because for THIATS and TDC the homogeneous linewidth is in this case consider-

ably smaller than the aggregate absorption linewidth [23].

There is a qualitative difference between the room temperature spectra and the lower temperature spectra: the red wing of the room temperature spectrum is Lorentzian, this explains why the attempts to fit the calculated room temperature spectrum to the experiment were not successful. The experimental red wing was systematically higher than the calculated one. This suggests at room temperature the occurrence of homogeneous broadening, caused by an exciton–phonon interaction. This hypothesis is supported by the spectral hole-burning experiment at room temperature: in comparison with the cooled aggregate, where the width of the hole burned in the absorption spectrum is much narrower than the total width, at room temperature the hole width is comparable with the total width [23].

The physical reason for the exciton delocalisation length being less than the aggregate length is the disorder. In the CED model of the energy disorder we have calculated the exciton delocalisation length giving the main contribution to the absorption maximum. In the segment model we take the length distribution as given without regard to the physical reason of the length distribution origin. In order to compare the segment model and the CED model, spectra, simulated in the framework of the segment

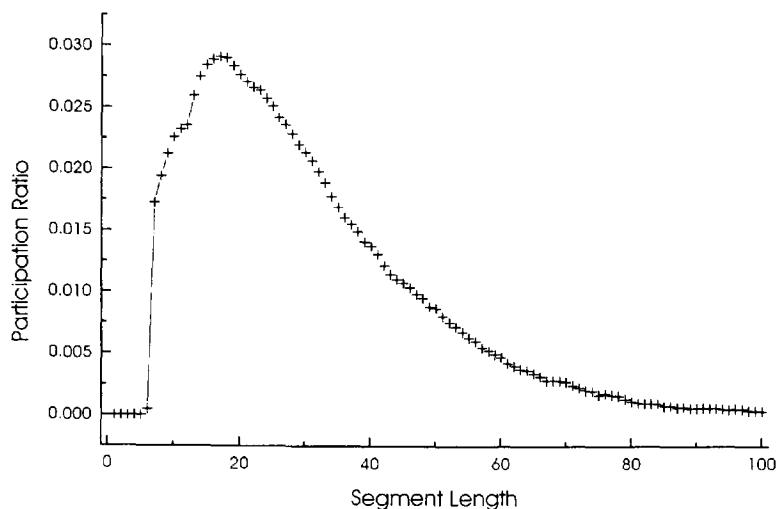


Fig. 3. Distribution of the segment lengths giving the maximal contribution to the absorption maximum.

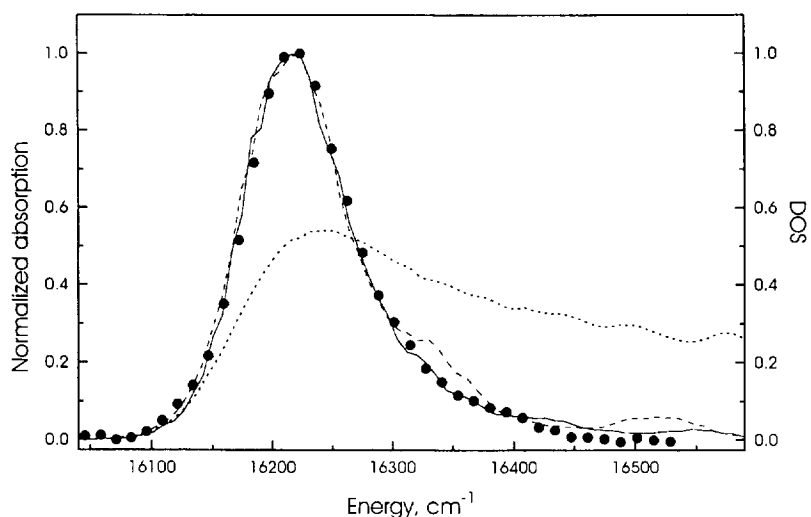


Fig. 4. Fit of the THIATS-I spectrum using the Hamiltonian diagonalization method: ●: experimental data, —: fit using 44×44 matrices diagonalization, ---: fit using 25×25 matrices diagonalization, ···: density of states (DOS) for this case.

model, were fitted in terms of the CED model. This implies the diagonalization of totally uncorrelated realizations of the Hamiltonian (1) for different aggregate sizes. The realizations of Hamiltonian matrices of sizes from 25×25 to 200×200 were made. The eigenvalues and corresponding eigenfunctions were found using the algorithm presented in Ref. [26]. By fitting the experimental spectrum (see Fig. 4) the value of the energy disorder D_E and the

inverse participation ratio [12,13] (and, consequently, the exciton delocalisation length at the maximum of the absorption spectrum) were obtained. The results of the calculations did not depend upon the overall aggregate size when the latter was greater than 40 ($N^{\text{del}} \ll 40$).

It is evident that an ensemble of aggregates with perfectly correlated disorder within a given aggregate (each molecule of segment n has the same

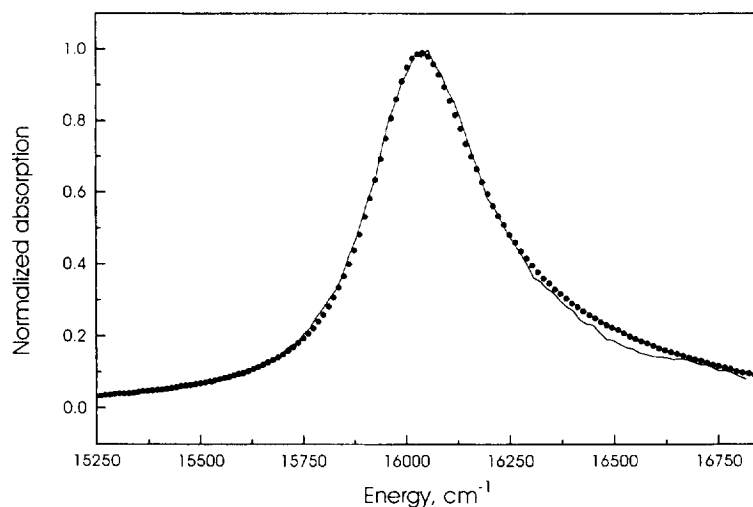


Fig. 5. Simulation of the absorption spectrum of THIATS-II at room temperature. The convolution with a Lorentzian lineshape is introduced: ●: experimental data, —: fit.

disorder realization D_E^n randomly chosen for that segment), results in an absorption spectrum that is the convolution of the homogeneous aggregate spectrum and the (Gaussian) inhomogeneous distribution of energies E_j^0 . Consequently, in the case of perfectly correlated disorder the FWHM of the absorption J-band is determined mainly by the Gaussian distribution of frequency offsets of individual aggregates (as in the case of an ensemble of non-aggregated dyes) rather than the exchange narrowing value [10]. However, the resulting lineshape can still be asymmetric (non-Gaussian) when the exponential segment length distribution is taken into account.

In all cases the value of the energy disorder for the CED model (for THIATS-I-135 cm^{-1}) divided by the square root [10] of the delocalisation length N^{del} (for THIATS-I- $N^{\text{del}} = 12$, $\sqrt{12} \approx 3.46$, $135/3.46 \approx 39$), derived in terms of the CED from the inverse participation ratio [12,13] for levels at the maximum of the absorption spectrum, coincides with the energy disorder of the segment model (for THIATS-I-39 cm^{-1}). The exciton delocalisation length at the maximum of absorption spectrum in the CED model corresponds to the parameter N_0 of the exponential segment length distribution of the segment model. This fact is in agreement with the results of [27,28] where the energy level structure of Frenkel excitons with a particular localization length for the low-lying states in the CED model is shown to be similar to that of an individual ideal segment with a length equal to the localization length in the CED model.

5. Conclusions

The absorption spectra of J-aggregates of two carbocyanine dyes have been measured in the temperature range from 6 to 293 K and fitted by the simple segment model. From 6 K to room temperature the best results were obtained using an exponential distribution of segment lengths rather than a Gaussian one. The average segment length giving the maximal contribution to the absorption intensity maximum is higher than the parameter N_0 of the exponential distribution. It should be noted that both the CED and segment models give equally good fits of the experimental spectra. The best fit parameter

obtained for the distribution of segment lengths (average lengths) in the segment model corresponds to average localization length obtained in the CED model. Hence, there is no criterion to decide which model suits the case better on the base of modeling only the absorption spectra. In the case of the CED model the site disorder correlation function is equal to zero, what means zero correlation length, and in the segment model the correlation length is nonzero and equal to the distribution parameter. The last is in agreement with two-color pump-probe experiments, estimating the correlation length to be nonzero, which points to the segment model as being more adequate for this case.

At high temperatures (room temperature, 77 K in some cases) an additional Lorentzian should be added (convoluted with) the calculated segment model spectra to fit reasonably the experimental data (Fig. 5). It possibly corresponds to a large homogeneous temperature broadening or/and enhanced contribution of the off-diagonal disorder. There is no need to introduce the above Lorentzian to fit the low temperature absorption spectra. This fact corresponds well to the relatively small homogeneous linewidth at low temperature.

Acknowledgements

The authors thank INTAS grant 93-85ext, FKFO and DWTC through IUAP II-16. This work was also supported by the Russian Foundation for Basic Research, grant 96-02-16527. MVdA is a 'Onderzoeksdirecteur' of the F.W.O. (Fonds voor Wetenschappelijk Onderzoek Vlaanderen). We also thank Dr. M.N. Ushomirsky (NiiKhimfotoproekt PLC, Moscow) for presenting the TDC for our work.

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