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# Optical Absorption Spectroscopy of Strongly Disordered J-Aggregates: Control of Off-Diagonal Disorder

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It was shown that the low-frequency edge of the exciton absorption band of J-aggregates of 1-methyl-1′-octadecyl-2,2′-cyanine iodide (analogue of PIC) experiences a change from Gaussian to Lorentzian in frozen, binary DMF-$H_2O$ solution, upon decrease of water concentration. In a Langmuir-Blodgett film, the shape of the low-frequency edge of exciton absorption band was neither Gaussian nor Lorentzian, in contrast. A model of diagonal and off-diagonal disorder in the molecular chains is proposed to explain the observed band shapes, based on selective solvation of amphiphilic molecules by water and DMF solvent molecules.

*Keywords:* exciton dynamics; diagonal and off-diagonal disorder; J-aggregate; absorption spectroscopy

## INTRODUCTION

J-aggregates of polymethine dyes, in the form of 1D molecular chains, are very interesting objects for research of exciton dynamics features in low-dimensional systems[1–9]. J-aggregates display unique optical features such as anomalously high extinction[10] and optical nonlinearity[11], properties that are important in various applications[10,12,13]. Physical ideas and models, advanced by research in optical properties of J-aggregates, can be extremely useful in the study of the vital phenomenon of photosynthesis[14].

Work devoted to width and form of the exciton absorption band of 1D systems[3,4,15–19], as well as to superradiant relaxation of excitons[20–24], created the basis of modern ideas about the exciton's microscopic nature in J-aggregates.

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The concept of exciton delocalization length, expressed by the number of coherently coupled molecules in an excited J-aggregate, plays the key role in any explanation of basic spectral and luminescent properties of J-aggregates[3,4,13,17–19,20–24]. Not the physical length of J-aggregate, but rather the length of exciton delocalization, is the basic spatial quantization scale, defining radiant decay time of the exciton[20–24], as well as its absorption band width[3,4,17–19]. In real J-aggregates, exciton delocalization is considered to be defined by the resonant dipole-dipole interaction (RDDI) and diagonal disorder[4,17–19]. The latter is caused by the variation of optical transition frequencies of individual molecules, comprising a J-aggregate. It was shown [15–19] that, for 1D systems with diagonal disorder, the low-frequency edge of the exciton absorption band is of Gaussian contour form, while the highfrequency edge is Lorentzian. Such exciton absorption band was observed in J-aggregates of pseudoisocyanine (PIC)[18,25], 5, 5′, 6, 6′- tetrachloro-1,1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine TDBC)[3] and 5,5′,6,6′ – tetrachloro – 1,1′ -diethyl-3,3′-di(4-carboxypropyl)-benzimidazolocarbocyanine (TOCBC)[26]. In the above context, it is interesting to note that the shape of holes burned into the J-band of TOCBC was described by a Lorentz function and that the mechanism of hole formation was explained by a structural change of the J-aggregate[26]. A more detailed characterization of the diagonal disorder in 1D systems, i.e., the degree of its correlation, can be obtained by means of two-frequency pump-probe spectroscopy[3,4,27].

The influence of off-diagonal disorder on exciton dynamics and exciton spectra of 1D systems is much less investigated, especially in experiment. Off-diagonal disorder, caused by random RDDI modulation in a 1D system, results in a change of the contour of the low-frequency exciton absorption band edge from Gaussian to Lorentzian[18]. At present, this observation seems to be the only one that is accessible to experiment, offering means to judge the off-diagonal disorder in 1D systems, since both types of disorder equally affect the frequency shift of the spectrum maximum, as well as the broadening of the exciton absorption band[18]. A second principal feature of the off-diagonal disorder, displayed in 1D systems that are associated with an appearance of the density-of-state peak at the center of the exciton band[18], cannot be subjected to experimental verification by linear spectroscopy methods. It is not clear, therefore, (i) how to separate the contributions by the influence of diagonal and off-diagonal disorder to exciton spectra and dynamics of 1D systems and (ii) how strongly both types of disorder are coupled in real physical objects.

The most extensive experimental material has been accumulated for J-aggregates of PIC. The exact description of molecular packing in 1-methyl1′-octadecyl-2,2′-cyanine iodide (S120) J-aggregates was very important, observed in

unimolecular layers[28] (obtained on the Langmuir-Blodgett technology). In unimolecular layers S120 molecules are packed in a "brick laying" fashion, as predicted by Kuhn[29]. Let's emphasize once again, that S120 molecules are an amphiphilic analogue of PIC molecules (see the inset on Fig. 1).

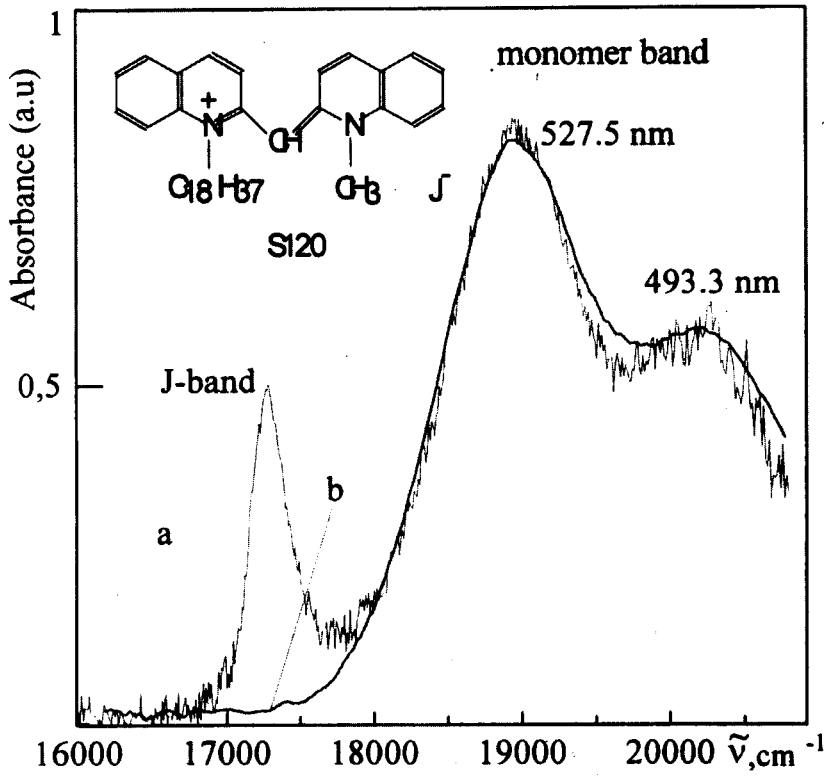


FIGURE 1 Normalized absorption spectra for: a) J-aggregates and S120 monomers in binary DMF-W solution with 50% water (T=1,5 K); b) S120 monomers in binary DMF-W solution with 15 % water (T=1,5 K). The S120 molecule is shown in the inset

In the present paper, the low-temperature absorption spectra of S120 J-aggregates have been investigated, in Langmuir-Blodgett film as well as in dimethylformamide-water (DMF-W) binary solutions of various composition. It was experimentally shown that the contour of the low-frequency edge of the S120 J-aggregate absorption band changed from Gaussian to Lorentzian, depending on the conditions of J-aggregate formation. Change of the J-band form is associated with changing the disorder type in a J-aggregate molecular chain. Large diagonal

disorder in a J-aggregate of S120 is caused by the inhomogenity of its solvate shell as a result of selective solvation of J-aggregates by water and DMF molecules. In turn, off-diagonal disorder of S120 J-aggregates is caused by a certain degree of order within the domain of the $C_{18}H_{37}$ tails.

## EXPERIMENTAL TECHNIQUES

J-aggregates of S120 were obtained in both unimolecular layers and binary solutions of DMF-W. The unimolecular layers of S120 molecules were deposited on a glass substrate, using standard Langmuir-Blodgett (LB) technology. Films investigated in the experiment contained up to twenty unimolecular layers.

Solutions of J-aggregates were obtained by addition of bi-distilled water to a stock solution of S120 in DMF ($5 \cdot 10^{-5}$ $M^{-1}$). In the present experiment, samples with 50% to 70% water were investigated. The full S120 concentration (monomer molecules and J-aggregates) after dilution water was $2{,}5 \cdot 10^{-5}$ $M^{-1}$ (50 % water) and $1{,}5 \cdot 10^{-5}$ $M^{-1}$ (70 % water), respectively. In pure DMF solution, S120 aggregates are absent and addition of water leads to the appearance of the specific narrow long-wavelength absorption band, typical of J-aggregates. In a binary solution, containing J-aggregates, the concentration of S120 monomer molecules is considerably reduced, compared to the initial concentration of S120 in DMF ($5 \cdot 10^{-5}$ $M^{-1}$) as a result of both dilution with water and J-aggregate formation. Therefore, energy transfer between S120 J-aggregates and monomeric S120 molecules are excluded.

LB-films and liquid solutions, contained in an optical cuvette, were cooled at constant speed, using an optical helium cryostat.

## EXPERIMENTAL RESULTS

The typical absorption spectrum of a frozen solution represents the sum of the narrow long-wave J-band and the monomer band (Fig. 1a).

The most interesting and important case is realized in a binary solution of small water concentration, where the intensity of the J-band is less intense than that of the monomer (Fig. 1a). For the analysis of the sum-spectra and J-band separation, we used the experimental absorption spectrum of the monomer, obtained in frozen binary solution of maximal water concentration at which J-bands were still absent (Fig. 1b). The monomeric absorption spectrum consists of maximum (~528 nm) and shoulder (~493 nm) (Fig. 1b), whose relative inten-

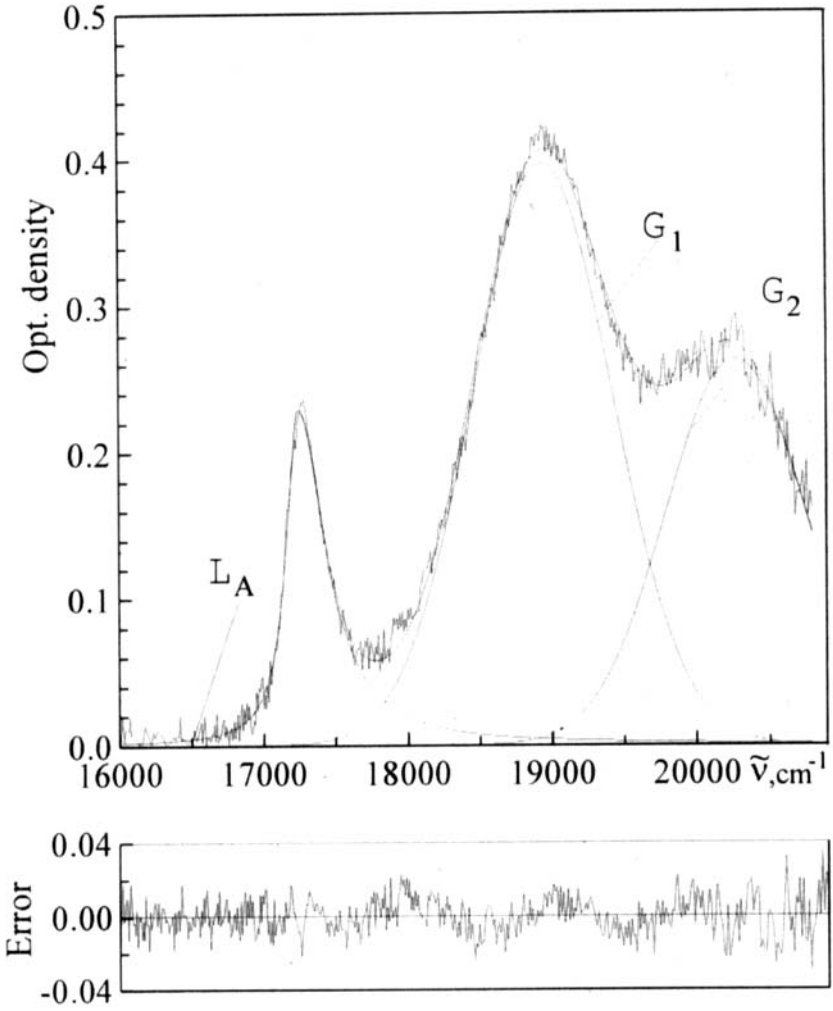


FIGURE 2 The result of approximation of absorption spectra of the J-aggregates and monomer molecules in the DMF-W binary solution with 50% water (T=1,5 K) (explanation see text)

sities were independent of S120 concentration ($1 \cdot 10^{-3}$ $M^{-1}$ – $5 \cdot 10^{-5}$ $M^{-1}$ in DMF) and water contents of the binary solution. Based on this observation, the maximum (~528 nm) was attributed to a pure electronic transition, while the shoulder (~493 nm) was assigned to an electron-vibronic transition. Both maximum and short-wave shoulder (Fig. 1b) were well approximated by two Gaus-

sian contours: $G_1$ ($\Delta\nu_{FWHM} = 1176$ cm$^{-1}$, $\lambda_{max}$= 527,5 nm) and $G_2$ ($\Delta\nu_{FWHM} = 995$ cm$^{-1}$, $\lambda_{max}$= 493,3 nm). A fit of the monomer absorption spectra by Lorentzian contours was unsuccessful. This represents a typical feature of low-temperature inhomogeneously broadened spectra of doped molecules in dielectric matrices of different structure[30]. Hence, in the analysis of the complex spectrum (Fig. 2), the monomer band is approximated by two Gaussian contours. The J-band (Fig. 2) was initially approximated by an asymmetric complex Gauss-Lorentzian contour, in analogy to previous results[15,16,18,19]. But the best fit of the J-band was achieved by an asymmetric Lorentzian contour $L_A$ ($\Delta\nu_{FWHM}$= 380 cm$^{-1}$, $\lambda_{max}$= 580 nm) (Fig. 2). In this fit, it is very important to check the influence of the monomer absorption spectrum on the low-frequency J-band edge. As can be seen from Fig. 1, the absorption spectra of S120 monomer molecules in the binary solution with 20% and 50% water contents coincide. This is corroborated by the fact that the parameters of the Gaussian contours (G1 and G2) are practically identical at approximation of the S120 monomer absorption band with absence and presence of the J-aggregates (Fig. 1,2). Hence, the increased water concentration (50%) in the frozen matrix has not affected the spectrum of the monomer and separation of the J-band, therefore, can be achieved by subtracting from a common spectrum (Fig. 2) either (i) the experimental monomer spectrum (Fig. 1b), or (ii) two contours (G1 and G2), with parameters obtained by a fit of the spectrum shown on Fig. 2. Note also that the amplitude of the $G_1$ contour (or real spectrum of S120 molecules) is negligible in the long-wavelength region of the J-band (Fig. 1,2). The results of spectrum subtraction in both cases are identical and shown in Fig. 3.

The Lorentzian form of the low-frequency J-band edge is defined by the properties of J-aggregates and does not depend on the S120 monomer band. J-band fits of LB film and binary solution, comparing Lorentz-Lorentz and Gausss-Lorentz models, are shown in Fig. 3, 4, and 5. together with deviations and $\chi^2$ values. The $\chi^2$ is calculated from $\chi^2 = \sum_i \frac{(I_i - Y_i)^2}{I_i}$, where $I_1$ is the experimental value and $Y_1$ the fit function value. The number of the experimental points ($i$) in the Fig. 3, 4, and 5 are identical, allowing direct comparison of the $\chi^2$values.

In frozen matrix of 70 % water concentration, as well as in LB film, the peak intensity of the J-band considerably surpassed that of the monomer and spectral separation was not necessary, as described above. Both in frozen matrix and in LB film, the J-band is asymmetric, but its form is different (Fig. 4 and 5). In frozen matrix of 70 % water concentration, the best approximation of the J-band is

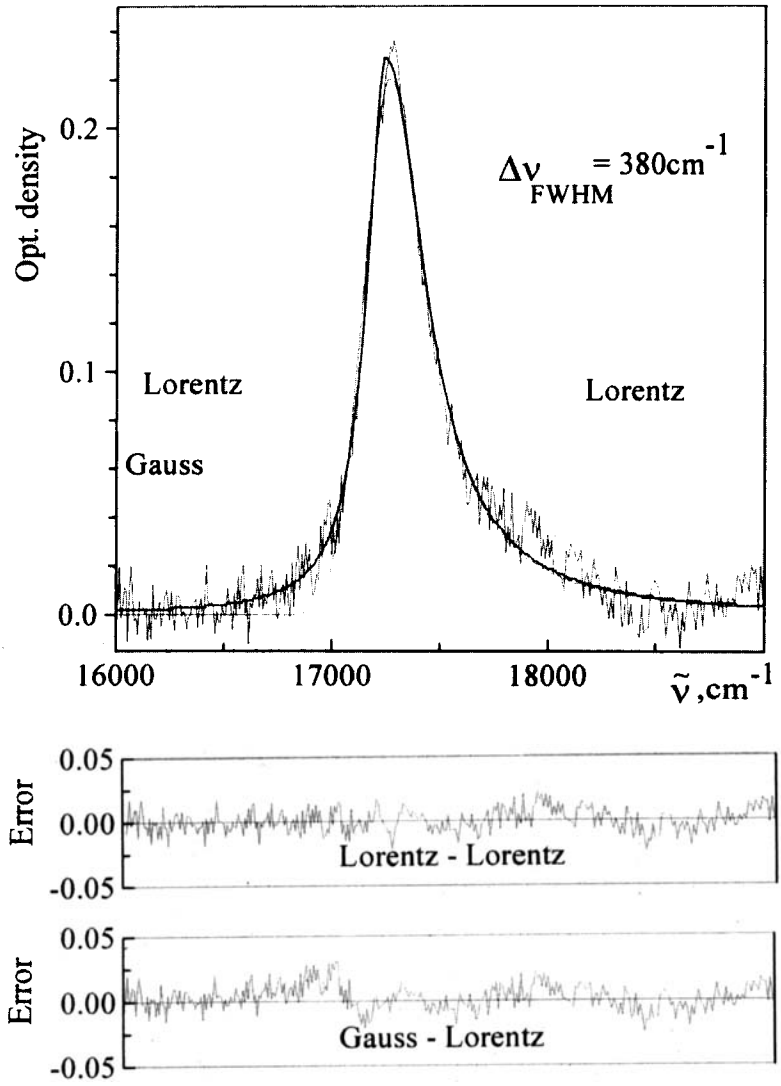


FIGURE 3 J-aggregates absorption band in the binary solution with 50% water (T=1,5 K). $\chi^2$ = 0.47 for Lorentz-Lorentz and 0.83 for Gauss-Lorentz fit

achieved by a complex Gauss- contour (Fig. 4). In LB film, in contrast, a satisfactory fit can neither be achieved by asymmetric Lorentzian nor complex Gauss-Lorentzian contour (Fig. 5).

## ANALYSIS OF EXPERIMENTAL RESULTS

The analysis of the absorption band of J-aggregates in both LB film and frozen matrices (50% and 70% water) showed that only in a matrix with 70% water (Fig. 4), the J-band was of the form observed earlier for J-aggregates of PIC[18,25], TDBC[3] and (TOCBC)[26]. Such form of J-band is caused by diagonal disorder in the molecular chain. The absorption band of S120 J-aggregates ($\Delta\nu_{FWHM}$= 380 $cm^{-1}$) is much wider than that composed of PIC ($\Delta\nu_{FWHM}$= 34 $cm^{-1}$)[20], TOCBC ($\Delta\nu_{FWHM}$ 65 $cm^{-1}$)[26] and TDBC ($\Delta\nu_{FWHM}$ = 160 $cm^{-1}$)[3], testifying to the larger diagonal disorder in S120 J-aggregates. The diagonal disorder in J-aggregates is associated with fluctuations of local molecular fields, defined by properties of the glass dielectric matrix, and ultimately by the structure of the J-aggregate solvation shell. The different environments and counter-ions of S120, PIC[20] and TDBC[3] J-aggregates cannot be responsible for the large value of $\Delta\nu_{FWHM}$, observed in case of S120. The main contribution is caused by features of the solvate shell structure, influenced by the amphiphilic properties of S120 molecules that are not found in PIC and TDBC. Upon addition of water to DMF, the solvate shell of the S120 molecule becomes inhomogeneous, due to selective solvation of both polar chromophore and its $C_{18}H_{37}$-chain. Water molecules accumulate in the region of the chromophoric part of the S120 molecule, while DMF molecules prefer the $C_{18}H_{37}$ section. Apparently, selective solvation is more pronounced in J-aggregates of S120. The density of water molecules is considerably increased near the J-aggregate chromophore, but extremely low in the region of the $C_{18}H_{37}$section. The inhomogeneous solvation shell gives rise to strong fluctuations of the local intermolecular fields along a J-aggregate axis, creating a significant diagonal disorder, which defines the large value of $\Delta\nu_{FWHM}$, in case of S120 J-aggregates.

The concept of selective solvation of S120 J-aggregates provides an explanation for the change of the J-band form, when changing the water concentration from 70 % to 50 % in frozen binary matrix. From the fact that J-bands in binary solution and LB film practically coincide, it can be deduced that binary solutions accommodate 1D structures, which are fragments of the "brick laying"[28,29] packing of the J-aggregate, i.e., the J-aggregates of S120 consist of piles, in which molecules are packed with relative displacement. The pile structure of S120 J-aggregates in solution is distorted, because of the dynamic molecular surrounding that takes the chromophoric part of the molecule out from the pile, due to collision of surrounding molecules with the $C_{18}H_{37}$ chain (Fig. 6). The $C_{18}H_{37}$ chain might act as a lever. At increased water concentration in binary solution, the polarity of the J-aggregate solvate shell increases, while DMF molecules concentrate in the region of the $C_{18}H_{37}$ chains, causing a smaller angle at

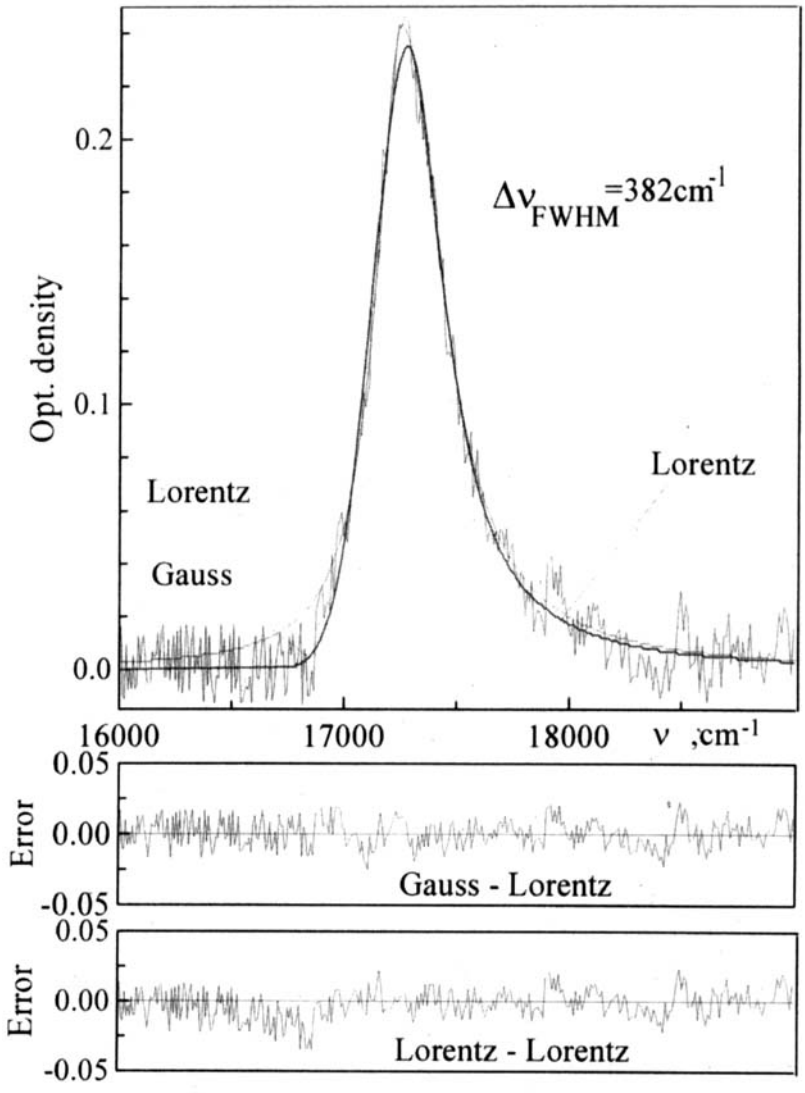


FIGURE 4 J-aggregates absorption band in the binary solution with 70% water (T=1,5 K). $\chi^2 = 0.31$ for Gauss-Lorentz and 0.69 for Lorentz-Lorentz fit

which the $C_{18}H_{37}$ chains will be able to deviate, due to its hydrophobic properties, and the molecular disorientation in a J-aggregate will be smaller $\varphi_1$ $\varphi_2$ (Fig. 6). This disordering effect is the reason of the appearance of dynamic off-diagonal disorder, because it results in random modulation of RDDI between

molecules in the J-aggregate. Upon freezing of a binary solution, the dynamic off-diagonal disorder becomes static. This static off-diagonal disorder in a 1D system results in a change of the low-frequency edge of the exciton absorption band, which assumes a Lorentzian form (Fig. 3), a feature that is observed for S120 J-aggregates in frozen matrix of low water concentration (Fig. 3).

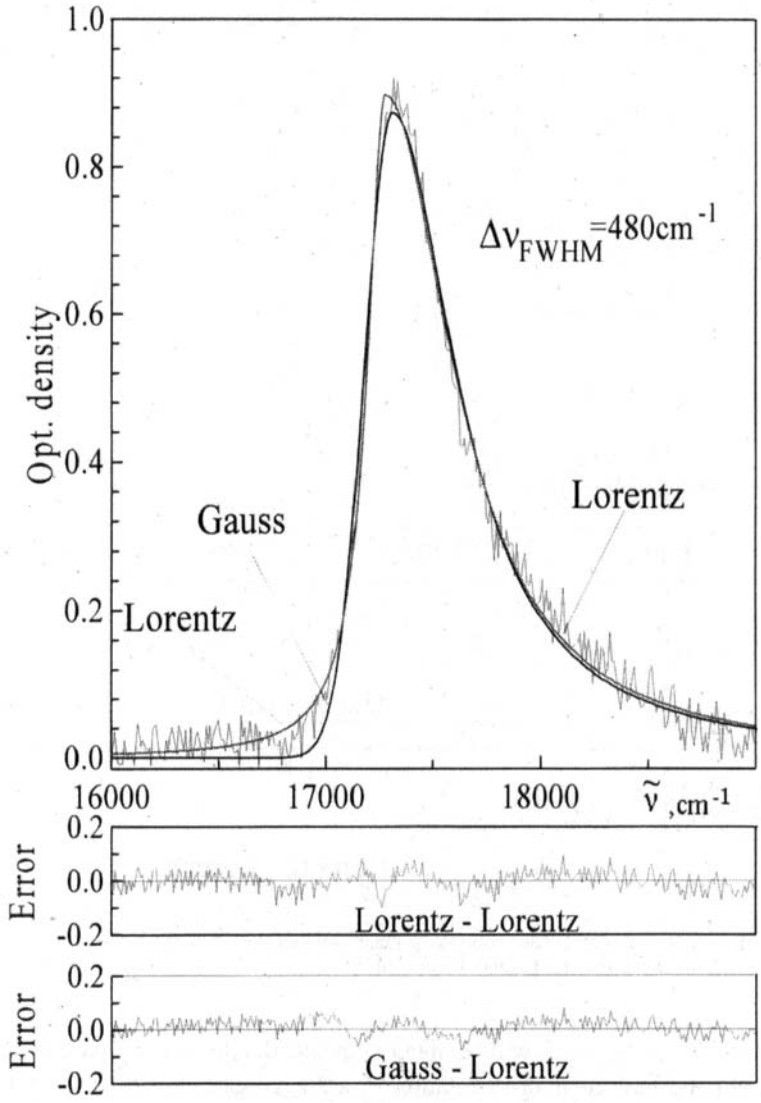


FIGURE 5 J-aggregate absorption band in a LB film (T=1,5 K). $\chi^2$= 0.81 for Lorentz-Lorentz and 0.77 for Gauss-Lorentz fit

As $\Delta\nu_{FWHM}$ of a J-band is associated with diagonal disorder, Figures 3, 4, and 5 show that J-aggregates in LB film are characterized by a larger disorder than in solution, the cause of which is unclear at present. The form of the J-band low-frequency edge in a LB film is not described by Gaussian nor Lorentzian contour (Fig. 5), in contrast to PIC in LB film, having a Lorentzian contour[18]. The off-diagonal disorder of S120 J-aggregates in LB film occupies, therefore, a position between frozen matrix of 50 % and 70 % water concentration (Fig. 3 and 4). On a microscopic level, the mechanism for the appearance of off-diagonal disorder for S120 J-aggregates in LB film and frozen matrix is identical, i.e., it is associated with $C_{18}H_{37}$chain ordering: at smaller ordering more chromophore molecules are taken out of the molecular pile.

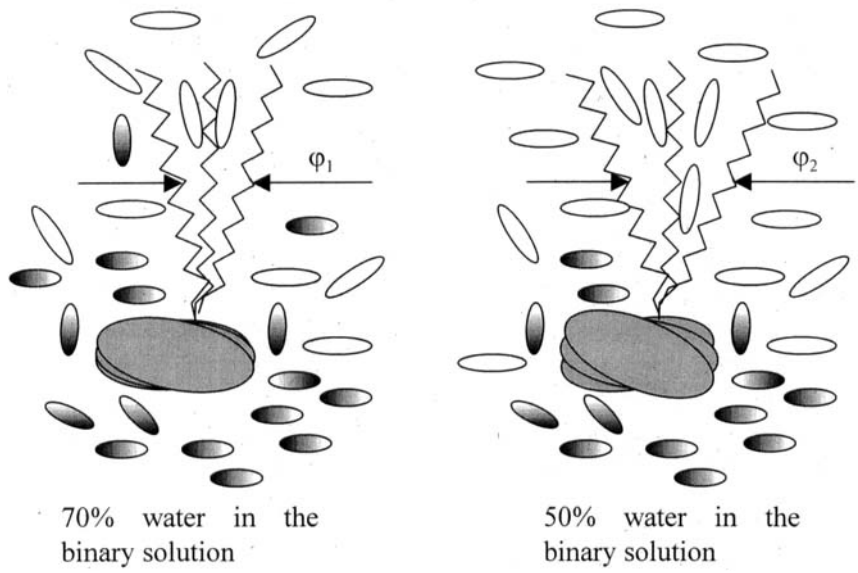


FIGURE 6 Simplified scheme of J-aggregate and solvate shell microstructure in the binary solution with water portion variation: φ – ⬭ ◖⬭ spatial angle for $C_{18}H_{37}$ tails; – DMF molecules; – water molecules.

According to previous results[18], both types of disorder in 1D systems can lead to the long-wavelength shift and broadening of the exciton absorption band, with latter displayed by a change of $\Delta\nu_{FWHM}$. While the disorder in S120 J-aggregates is clearly changed (Fig. 3, 4, and 5), however, there is no change in $\Delta\nu_{FWHM}$, and upon increase of the water concentration to 70 %, one can observe a long-wavelength shift of the J-band by 16 $cm^{-1}$. Unfortunately, there are no

theoretical considerations concerning the simultaneous influence of both diagonal and off-diagonal disorder on the exciton band spectral characteristics for 1D systems. Therefore it is not clear, as far as both influences are additive.

Up to the present, the main experimental results on exciton spectra and exciton dynamics of J-aggregates were explained by the diagonal-disorder model only. First hints to off-diagonal disorder were obtained from the shape of the PIC absorption band in LB film[18], but detailed studies of the influence of off-diagonal disorder on exciton dynamics and exciton spectra of 1D systems are still lacking. The results of the present work might serve as a base for future studies, as a method to control disorder in real 1D systems (J-aggregates) was discovered.



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