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# Absorption line shape of Frenkel excitons in one-dimensional random chains with pairwise correlated Gaussian disorder

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## Abstract

We investigate inhomogeneous broadening of absorption line shapes of an ensemble of linear Frenkel chains with a Gaussian distribution of molecular transition energies. Two models of Gaussian disorder are considered. In one case, the molecular energies are uncorrelated variables whereas in the second model the molecular energies are pairwise correlated. A perturbative treatment in the disorder is used to determine that the broadening is larger in the presence of correlations. In the case of nonperturbative magnitudes of disorder, we find a good agreement of the theoretical treatment with numerical simulations, when the number of molecules in the system is replaced by the number of coherently bound molecules. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Despite the amount of work done during the last decades, the current understanding of quasiparticle dynamics in disordered systems is far from being complete. During the last decade, it is being realized by many researchers in the field that *correlated disorder* has profound effects in quasiparticle dynamics and produces a variety of complex and new phenomena. It is by now well known that a band of delocalized states arises in one-dimensional tight-binding Hamiltonians with short-range correlated diag-

onal and/or off-diagonal elements [1–6]. In addition, it has been recently claimed that a one-dimensional Anderson model with long-range correlated disorder exhibits delocalization [7].

In the last few years, a great deal of work was devoted to coherent and incoherent exciton dynamics in one-dimensional (1D) systems with correlated disorder, showing that correlations manifest themselves in the optical properties [8–14]. The occurrence of intersite energy correlations in molecular aggregates and some polymers like polyaniline was previously pointed out by Knapp [8] and by Dunlap et al. [2] respectively and then was demonstrated by Durrant et al. [10] in molecular aggregates of pseudo-isocyanine by means of two-color pump-probe techniques. So we believe that the interest of those theoretical works is beyond the formal study of

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exciton dynamics. We have already considered optical absorption of Frenkel excitons in unpaired as well as in paired disordered models, focusing our attention on inhomogeneous broadening due to a Gaussian distribution of on-site energies in a one-dimensional lattice [14]. By solving the microscopic equation of motion proposed by Huber and Ching [15], it was found that inhomogeneous broadening is enhanced when structural correlations arise.

In this paper, a comparative study of two types of disorder – on the one hand, uncorrelated on-site energies and, on the other hand, pairwise correlated on-site energies – is performed in order to study the influence of the short-range intersite energy correlations on the linear absorption spectra of Frenkel excitons in finite linear chains. A detailed analytical treatment, based on the perturbation theory, is used to show that broadening is larger in the presence of correlations. The same conclusion is deduced from the numerical simulation in the nonperturbative limit. In addition, it will be clearly demonstrated that the introduction of the concept of coherently bound molecules works fairly well in explaining quantitatively the numerical results for both types of disorder. The number of coherently bound molecules in the presence of correlations appears to be smaller than in their absence, meaning that correlations give rise to larger exciton scattering due to disorder. The problem whether the presence of intersite energy correlations can be deduced from the study of the linear optical response of excitons is also discussed.

## 2. Model

We consider  $N \gg 1$  (even) optically active molecules forming a regular one-dimensional lattice with spacing unity. For our present purposes, we neglect all thermal degrees of freedom (electron-phonon coupling and local lattice distortions). Therefore, the effective Hamiltonian for the Frenkel-exciton problem can be written in the tight-binding form with nearest-neighbor interactions as follows

$$\mathcal{H} = \sum_{n=1}^N \epsilon_n |n\rangle \langle n| - J \sum_{n=1}^{N-1} (|n\rangle \langle n+1| + |n+1\rangle \langle n|), \quad (1)$$

where  $|n\rangle$  is the state vector of the  $n$ th molecule with transition energy  $\epsilon_n$ . Here  $J > 0$  is the nearest-neighbor coupling, which is assumed to be constant in the whole lattice. On-site energies are subject to diagonal disorder representing inhomogeneous broadening, for which a Gaussian distribution is the proper theoretical approximation.

In what follows we consider two different models, namely uncorrelated and correlated disordered systems. This allows us to separate the effects merely due to optical absorption in one-dimension from those which manifest the peculiarities of the correlation between random parameters. The first model supposes  $N$  Gaussian, statistically independent, on-site energies  $\epsilon_n$  with  $\langle \epsilon_n \rangle = 0$  and  $\langle \epsilon_n^2 \rangle = \sigma^2$  for all  $n$ . Therefore, the joint probability distribution is [8,9]

$$P^{(N)}(\epsilon_1, \dots, \epsilon_N) = \prod_{n=1}^N P^{(1)}(\epsilon_n), \quad (2a)$$

where

$$P^{(1)}(\epsilon_n) = \left( \frac{1}{2\pi\sigma^2} \right)^{1/2} \exp\left( -\frac{\epsilon_n^2}{2\sigma^2} \right). \quad (2b)$$

The covariance matrix is diagonal

$$A_{mn}^u = \langle \epsilon_m \epsilon_n \rangle = \sigma^2 \delta_{mn}, \quad (2c)$$

where the superscript  $u$  refers to uncorrelated Gaussian disorder.

On the other side, to build up our correlated disordered model, we chose  $N/2$  independent variables  $\epsilon_{2n-1}$  ( $n = 1, \dots, N/2$ ) according to the same Gaussian distributions as before and then take  $\epsilon_{2n} = \epsilon_{2n-1}$ . This step is repeated at every odd site of the lattice, hence leading to a set of paired correlated on-site energies (dimers) with the following joint probability distribution

$$P^{(N)}(\epsilon_1, \dots, \epsilon_N) = \prod_{n=1}^{N/2} P^{(1)}(\epsilon_{2n-1}) \delta(\epsilon_{2n} - \epsilon_{2n-1}). \quad (3a)$$

In this case the covariance matrix is symmetric and its elements  $A_{mn}^c$  with  $n \geq m$  are given by

$$\begin{aligned} A_{mm}^c &= \sigma^2, \quad m = 1, 2, \dots, N, \\ A_{m, m+1}^c &= \sigma^2, \quad m = 1, 3, \dots, N-1, \\ A_{mn}^c &= 0, \text{ otherwise,} \end{aligned} \quad (3b)$$

where the superscript *c* refers to correlated Gaussian disorder. Thus, the energy correlation length in our case is  $N_c = 2$ .

### 3. Perturbative treatment

Having presented our model, we now describe the method we have used to calculate the linear absorption spectra in the frame of the perturbative limit for small values of the degree of disorder  $\sigma/J$  [9]. To this end, we rewrite the Hamiltonian (1) as  $\mathcal{H} = \mathcal{H}_d + \mathcal{H}_{od}$ , where  $\mathcal{H}_d$  ( $\mathcal{H}_{od}$ ) stands for the diagonal (off-diagonal) part in the site representation of the Hamiltonian (1), respectively. The diagonal contribution  $\mathcal{H}_d$  is considered as a perturbation term. The eigenstates and eigenenergies of  $\mathcal{H}_{od}$  are given by

$$|k^0\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin(Kn) |n\rangle, \quad (4a)$$

$$E_k^0 = -2J \cos K, \quad (4b)$$

where  $K \equiv \pi k/(N+1)$  and  $k = 1, \dots, N$ . In this excitonic representation, the matrix  $(\mathcal{H}_d)_{kk'}$  is off-diagonal and has the form

$$(\mathcal{H}_d)_{kk'} = \left(\frac{2}{N+1}\right) \sum_{n=1}^N \epsilon_n \sin(Kn) \sin(K'n). \quad (5)$$

The matrix elements  $(\mathcal{H}_d)_{kk'}$  are expressed through linear combinations of Gaussian variables  $\epsilon_n$  with zero mean and, consequently, also have a joint Gaussian distribution. Since  $\langle(H_d)_{kk'}\rangle = 0$  for all  $k$  and  $k'$ , the joint Gaussian distribution is characterized by its covariance super-matrix  $\mathcal{B}_{k_1 k'_1, k_2 k'_2} \equiv \langle(\mathcal{H}_d)_{k_1 k'_1} (\mathcal{H}_d)_{k_2 k'_2}\rangle$ , where the angular brackets indicate an average over the joint probability distribution given in (2a) or (3a). Since in what follows we will deal only with one exciton transitions, the matrix elements  $B_{kk'} \equiv \mathcal{B}_{kk',kk'} = \langle(\mathcal{H}_d)_{kk'}^2\rangle$  will consequently be the subject of our analysis. These elements are given by

$$B_{kk'} = \left(\frac{2}{N+1}\right)^2 \sum_{m,n=1}^N A_{mn} \sin(Km) \sin(K'm) \times \sin(Kn) \sin(K'n) \quad (6)$$

The diagonal elements of  $B_{kk'}$  represent the variances of the distributions of the perturbed exciton

energies  $E_k = E_k^0 + (\mathcal{H}_d)_{kk}$  while the off-diagonal elements are those for the intermode coupling matrix  $(\mathcal{H}_d)_{kk'}$ . Note that in the perturbative limit, inhomogeneous broadening of exciton levels described by  $B_{kk}$  appears to be the major effect in the linear response from the exciton system. The transition oscillator strengths are not subjected to noticeable changes.

Taking now into account (2) and (3) we obtain

$$B_{kk'}^u = \frac{\sigma^2}{(N+1)^2} S_1(k, k') \quad (7a)$$

for uncorrelated disorder whereas for correlated disorder the result is

$$B_{kk'}^c = \frac{\sigma^2}{(N+1)^2} [S_1(k, k') + S_2(k, k')]. \quad (7b)$$

For brevity we have defined

$$S_1(k, k') = 4 \sum_{m=1}^N \sin^2(Km) \sin^2(K'm) = (N+1) \left[1 + \frac{1}{2}(\delta_{kk'} + \delta_{k+k', N+1})\right], \quad (7c)$$

where the summation can be found in Ref. [9], and

$$S_2(k, k') = 8 \sum_{m=1}^{N/2} \sin(2Km - K) \sin(2Km) \times \sin(2K'm - K') \sin(2K'm) = \frac{N}{2} [\cos(K+K') + \cos(K-K')] + 2 \frac{1 + \cos(K+K') \cos(K-K')}{\cos(K+K') + \cos(K-K')} - (1 - \delta_{kk'} - \delta_{k+k', N+1}) \times \frac{\cos(K+K') + \cos(K-K')}{2 \cos(K+K') \cos(K-K')} + (\delta_{kk'} - \delta_{k+k', N+1}) \left(\frac{N}{2} - \frac{1}{2 \cos K}\right). \quad (7d)$$

The latter summation is performed in Appendix A. Therefore, the covariance matrix elements defined by (6) can be readily determined.

According to Ref. [9], in the perturbative limit the optical absorption spectrum is given by a series of  $N$  Gaussian peaks centered around the unperturbed eigenenergies. Since the state  $k=1$  carries almost the entire oscillator strength of the system, the optical absorption spectrum is dominated by a Gaussian peak centered at  $E_1^0$  with standard deviation  $\sigma_1 \equiv \sqrt{B_{11}}$ . Therefore, in the case of uncorrelated disorder we obtain (see also Ref. [16])

$$\sigma_1^u = \sqrt{\frac{3}{2} \frac{\sigma^2}{N+1}}. \quad (8a)$$

In the correlated case, assuming the limit  $N \gg 1$ , we get

$$\sigma_1^c = \sqrt{3 \frac{\sigma^2}{N+1}}. \quad (8b)$$

As it can be seen from Eqs. (8), both magnitudes scale as  $N^{-1/2}$ , showing the so-called motion narrowing effect [8]. In addition, the standard deviation is larger for correlated inhomogeneous broadening and the difference increases on increasing  $\sigma$ . Similar conclusions were drawn by Knapp [8], Knoester [9] and Fidler et al. [17] for chains with long-range correlated disorder as well as in Ref. [14] by solving the microscopic equation of motion for the present problem. The two times increase of the numerical prefactor of  $\sigma_1^2$ , from  $3/2$  to  $3$  upon introducing intersite correlations, has a rather clear explanation. Indeed, for an uncorrelated distribution of on-site energies, the summation in Eq. (5) runs over all sites of the chain while in the presence of pairwise intersite energy correlations,  $N/2$  serves in fact as an effective number of sites in the sum appearing in Eq. (5): since  $\epsilon_{2n-1} = \epsilon_{2n}$  ( $n=1, 2, \dots, N/2$ ), we can replace  $[2/(N+1)]\sum_{n=1}^N \rightarrow [2/(N/2+1/2)]\sum_{n=1}^{N/2}$  in Eq. (5). This clearly reflects the fact that for pairwise correlated disorder, a *dimer* (two sites with equal energies) should be considered as a *single unity*. In other words, the effective number of sites involved in the motion narrowing effect is now determined by the chain length  $N$  counted in units of the energy correlation length  $N_c$  (being two in our case), and thus appears two times smaller compared to the former. The generalization of this result to an arbitrary value of  $N_c$  is straightforward and simply consists of replacing the factor  $3/2$  by  $(3/2)N_c$  when passing from Eq. (8a) to Eq. (8b).

As it was noted above, for perturbative magnitudes of disorder, inhomogeneous broadening of the exciton levels is the main effect of randomness. Having calculated the covariance matrix  $B_{kk'}$ , we can now formulate a condition for treating the disorder as perturbation and thus for the validity of the results given in (8). The off-diagonal elements  $(\mathcal{K}_d)_{kk'}$  mixes the exciton states, resulting in their localization on chain segments of a typical size smaller than the chain length [8,16,17] and leading to failure of the results (8). Regarding the exciton optical response we are dealing with, mixing of the lowest state ( $k=1$ ) with the others is of major importance. Hence, one should compare the energy difference  $E_2^0 - E_1^0 \approx 3\pi^2 J/(N+1)^2$  with the typical fluctuation of  $(\mathcal{K}_d)_{21}$  represented by  $\sqrt{B_{21}}$ . The perturbative approach is valid provided  $\sqrt{B_{21}} < E_2^0 - E_1^0$  and fails otherwise. Thus, the equality

$$\sqrt{B_{21}} = \frac{3\pi^2 J}{(N+1)^2} \quad (9)$$

determines a value of  $\sigma$  (for a fixed chain length  $N$ ), which separates the ranges of perturbative and nonperturbative magnitudes of disorder. The matrix elements  $B_{21}$  are given either by Eq. (7a) or by Eq. (7b) and in the limit  $N \gg 1$  read

$$B_{21}^u = \frac{\sigma^2}{N+1}, \quad (10a)$$

$$B_{21}^c = \frac{2\sigma^2}{N+1}. \quad (10b)$$

Note that  $B_{21}^c$  is also two times larger than  $B_{21}^u$  similar to that found for the corresponding diagonal matrix elements of  $B$  (see above), i.e., the magnitude of intermode mixing in the presence of pairwise correlations is larger than in their absence. As in the previous case, the generalization of this result to an arbitrary  $N_c$  is straightforward, and consists of replacing the factor 2 by  $N_c$  in Eq. (10b).

#### 4. Coherently bound molecules

According to Knapp [8], at nonperturbative magnitudes of disorder, not all molecules of the chain contribute to the optical spectra of the whole ensemble.

ble, but only a portion of them that depends on the degree of disorder  $\sigma/J$ . As it was mentioned above, the reason is the localization of the excitonic states arising from disorder. Therefore, the so-called number of *coherently bound molecules*  $N^*$  (covered in average by optically active localized exciton states) should replace the number of molecules in the system,  $N$ . In Ref. [16], a simple rule for estimating  $N^*$  was formulated whenever the disorder is uncorrelated. It exploits the findings that i) the lowest localized exciton states can be classified in several groups of states (two or sometimes three), each one localized on a certain chain segment of a typical size  $N^*$ , ii) each segment does not overlap with the others [16] (for more details, see also Refs. [18,19]) and, what is most important, the states of each group have the energy structure similar to that for an homogeneous chain of size  $N^*$ , i.e., given by Eq. (4b) with  $N$  replaced by  $N^*$ .

The rule proposed in Ref. [16] for estimating  $N^*$  consists simply of applying the perturbative criterion (9) to a typical localization segment, i.e., substituting  $N$  by  $N^*$  in Eq. (9). It was found in Refs. [16,18] that this approach works surprisingly well in fitting the numerical data concerning the optical response of one dimensional Frenkel excitons. In doing so, the number of coherently bound molecules is estimated as follows [16]

$$N^* + 1 = \left( \frac{3\pi^2 J}{\sqrt{B_{21}^*}} \right)^{1/2}, \quad (11)$$

where for uncorrelated disordered systems, one should take  $B_{21}^*$  according to Eq. (10a), also replacing  $N$  by  $N^*$  since the motion narrowing effect is now related to a certain localization segment of typical length  $N^*$ . For  $N_u^*$  one then obtains

$$N_u^* + 1 = \left( \frac{3\pi^2 J}{\sigma} \right)^{2/3}. \quad (12a)$$

Admitting the correctness of formula (8a) for the standard deviation of the exciton absorption spectrum, and again replacing  $N$  by  $N^*$ , one finally arrives at

$$\sigma_1^u = \sqrt{\frac{3}{2}} \frac{\sigma^{4/3}}{(3\pi^2 J)^{1/3}}. \quad (12b)$$

It should be noticed that, regarding the exciton absorption line width, the scaling law  $\sigma^{4/3}$  was found in the corresponding numerical simulations in Refs. [17,20–22] as well as by means of the coherent potential approximation in Ref. [23].

The above approach can be generalized to the case of correlated disorder in a straightforward fashion. The number of coherently bound molecules is then estimated as

$$N_c^* + 1 = 2^{-1/3} \left( \frac{3\pi^2 J}{\sigma} \right)^{2/3}. \quad (13a)$$

We further stress that  $N_u^* > N_c^*$ , resulting from the fact that  $B_{21}^u < B_{21}^c$ . From this result we are led to the conclusion that correlated disorder affects the exciton dynamics more than the uncorrelated one, at least for the case of short-range intersite energy correlations. Numerical simulations prove this finding (see Section 5).

The standard deviation of the optical absorption spectrum in the case of correlated disorder shows a similar scaling law

$$\sigma_1^c = (54)^{1/6} \frac{\sigma^{4/3}}{(3\pi^2 J)^{1/3}}, \quad (13b)$$

but with different numerical prefactor. Here, one has  $\sigma_1^u < \sigma_1^c$ , as occurs in the perturbative limit.

## 5. Numerical results and discussions

The quantities subjected to calculations will be the absorption line shape and the factor of enhancement of the exciton radiative rate relative to the monomer spontaneous emission rate, carrying information about the number of coherently bound molecules  $N^*$ . The absorption line shape is calculated as [17]

$$I(E) = \frac{1}{NR} \left\langle \sum_{j=1}^N \theta \left( \frac{R}{2} - |E - E_j| \right) \mu_j^2 \right\rangle, \quad (14)$$

where  $R$  is the resolution and  $\theta$  is the Heaviside step function. In our calculations we take  $R = 0.001$ . The angular brackets indicate an average over an ensemble of randomly generated systems. The sum over  $j$  runs over all eigenstates and  $E_j$  denotes their

eigenenergies. The oscillator strength of the  $j$ th eigenstate with components  $a_j^{(n)}$  is given by

$$\mu_j^2 \equiv \left( \sum_{n=1}^N a_j^{(n)} \right)^2, \quad (15)$$

where the dipole moment of the isolated monomer is taken to be unity.

The factor of radiative rate enhancement is defined through the average oscillator strength per state at energy  $E$  [17]

$$\mu_{\text{av}}^2(E) = \frac{I(E)}{\rho(E)}, \quad (16)$$

where

$$\rho(E) = \frac{1}{NR} \left\langle \sum_{j=1}^N \theta \left( \frac{R}{2} - |E - E_j| \right) \right\rangle, \quad (17)$$

is the normalized density of states. We take  $\max\{\mu_{\text{av}}^2(E)\}$  as a measure for the enhancement of the exciton radiative rate [17] or, in other words, for the number of coherently bound molecules  $N^*$ .

Energy will be measured in units of  $J$ , so that we will fix the value  $J=1$  and focus our attention on the standard deviation  $\sigma$ , ranging from 0.05 up to 0.50. We have diagonalized the Hamiltonian (1) for chains of  $N=250$  with free-end boundary conditions. The number of randomly generated systems is 1000 for each value of  $\sigma$ .

As a typical example of the results of our simulations, we show in Fig. 1 the optical absorption spectra for uncorrelated and correlated (upper and lower curves of each panel, respectively) for two different values of the degree of disorder. The main absorption band shows the characteristic asymmetry discussed in detail for uncorrelated disorder in Refs. [17,20,24]. The low-energy side is Gaussian-shaped while the high-energy side is Lorentzian-shaped. From Fig. 1 several conclusions can be drawn. First, the shift to lower energies increases on increasing  $\sigma$  in both models. Second, and more important from the experimental viewpoint, there are substantial differences regarding the width of the optical spectra. In all cases we have studied we found that the standard deviation  $\sigma_1$  is larger for correlated inhomogeneous broadening, and that the difference goes up as  $\sigma$

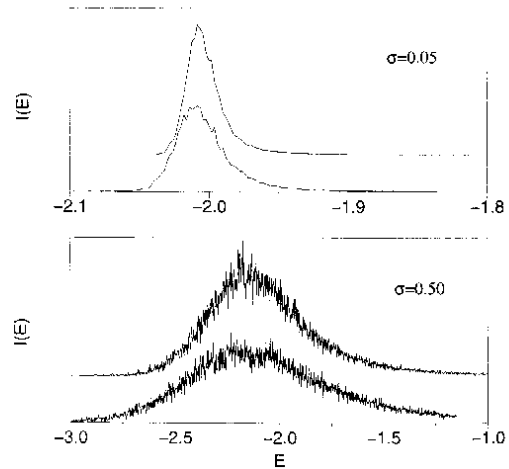


Fig. 1. Absorption spectra for one-dimensional random lattices with Gaussian distribution of uncorrelated (upper curves on each panel) and correlated (lower curves on each panel) on-site energies of with  $\sigma = 0.05$  and  $\sigma = 0.50$ .

rises. These findings are in agreement with our theoretical estimates.

To accurately determine the standard deviation  $\sigma_1$  we fitted the low-energy side of the spectra using Gaussians. We found that fits were fairly good. Fig. 2 shows that  $\sigma_1$  scales as  $\sigma^{4/3}$  for both uncorrelated and correlated disorder, as predicted by our estimates (12b) and (13b). The standard deviation of the spectra can be parameterized as  $\sigma_1 = C\sigma^{4/3}/(3\pi^2J)^{1/3}$ , where the constant is  $C_u = 1.42$  and  $C_c = 2.17$  for uncorrelated and correlated disorder, respectively. These values are slightly larger than those obtained from the estimates (12b) and (13b), namely  $C_u = 1.22$  and  $C_c = 1.94$ ; nevertheless, the coincidence should be admitted as being highly surprising. Note that the value  $C_u = 1.42$  is in agreement with that obtained by other authors [17,20–23].

Fig. 3 presents the data of numerical simulations of the factor of radiative rate enhancement  $\max\{\mu_{\text{av}}^2(E)\}$  versus the disorder degree  $\sigma$ , also for both types of disorder (upper and lower straight lines for uncorrelated and correlated disorder, respectively). We observe here the scaling  $\sigma^{-2/3}$  in both cases and also the result  $(\max\{\mu_{\text{av}}^2(E)\})_u > (\max\{\mu_{\text{av}}^2(E)\})_c$  or, in terms of the number of coherently bound molecules,  $N_u^* > N_c^*$ , thus confirming our theoretical prediction formulated in Section 4.

Let us now discuss the problem whether or not the information relative to intersite energy correlations can be revealed from the *linear* exciton optical response, having in mind the application to linear aggregates of dye molecules (namely, J-aggregates). As it is well known (see, for instance, Ref. [8] and references therein), optical excitations in these systems are Frenkel excitons. The width of the absorption spectrum  $\sigma_1$  will be the observable, providing the data of interest. The numerical factor  $C$  in the dependence  $\sigma_1(\sigma)$ , equal to  $C_c = 2.17$  in our particular case of pairwise intersite correlations, differs from that for the case of absence of correlations ( $C_u = 1.42$ ). Therefore, this coefficient carries the necessary information. To determine  $C$  one should measure three parameters:  $J, \sigma_1$  and  $\sigma$ . The magnitude of intersite coupling  $J$  can be measured with appropriate precision from the dimer absorption spectrum of dilute dye solutions, when the aggregation does not take place. The absorption band of J-aggregates usually appears as an isolated peak, so that its width  $\sigma_1$  is also rather easily measured. With regard to  $\sigma$ , one should assume that its magnitude can be determined from the monomer absorption spectrum. Then, we get all the parameters to be fixed in order to calculate the necessary constant  $C$ . Exceeding  $C$  over 1.42 means that correlations are present in the system.

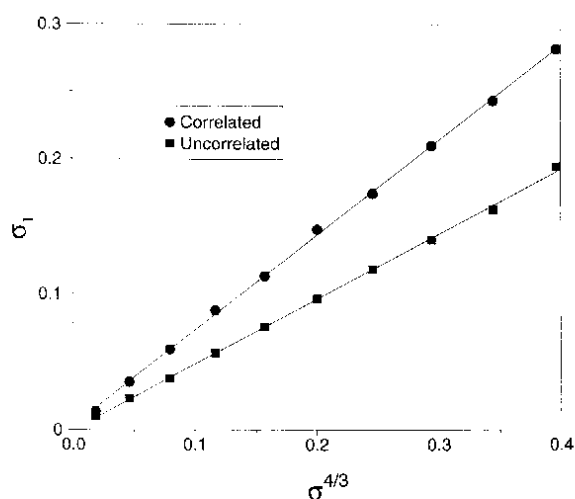


Fig. 2. Standard deviation  $\sigma_1$  as a function of  $\sigma^{4/3}$  for correlated and uncorrelated disordered systems. Solid lines represent the least square fits.

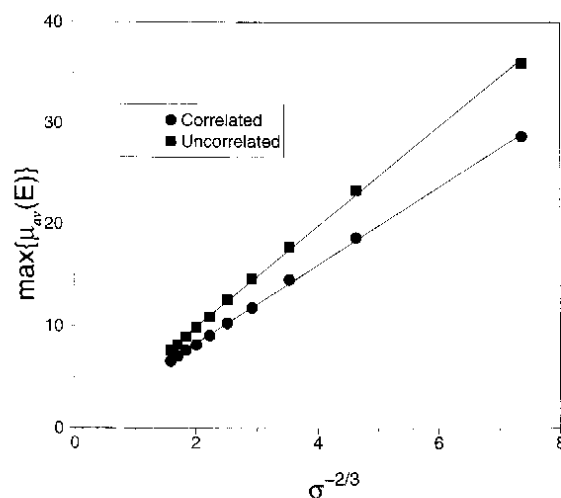


Fig. 3. Factor of the radiative rate enhancement,  $\max\{\mu_{av}^2(E)\}$ , as a function of  $\sigma^{-2/3}$  for correlated and uncorrelated disordered systems. Solid lines represent the least square fits.

Often, the spectra of monomers are structured even at low temperature. In such cases, the determination of their width  $\sigma$  seems highly questionable. In turn, the analysis of two-exciton transitions, present in the *nonlinear* optical response from the system, can serve as an appropriate method to probe the presence of intersite energy correlations [9,10].

## 6. Conclusions

In summary, we have studied the effects of inhomogeneous broadening on the absorption spectrum corresponding to the one-dimensional Frenkel-exciton Hamiltonian for random systems. Two different models have been considered; in both cases broadening arises from a Gaussian distribution of on-site energies. In uncorrelated disordered systems, on-site energies are chosen according to a Gaussian distribution at every site, whereas in correlated disordered systems this selection is made only at odd sites and even sites take the value of the preceding one. By comparing the obtained spectra in both models, larger both the red shift of the absorption band and inhomogeneous broadening were found whenever intersite energy correlations are present in the lattice. The theoretical estimates based on the concept of motion

narrowing along with the aid of the number of coherently bound molecules work fairly well in explaining the numerical data. The number of coherently bound molecules decreases upon introduction of correlations, meaning larger exciton scattering due to disorder in the presence of short-range intersite energy correlations.

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### Appendix A. Evaluation of $S_2(k, k')$

In this Appendix we present the main steps we followed to evaluate  $S_2(k, k')$  defined in (7d). We rewrite

$$S_2(k, k') = 2 \sum_{m=1}^{N/2} [\cos(K) - \cos(4Km - K)] \times [\cos(K') - \cos(4K'm - K')] \quad (\text{A.1})$$

and decompose this sum in the following way

$$S_2(k, k') = N \cos(K) \cos(K') - 2 [\cos(K) \cos(K') [C(4K) + C(4K')] + \cos(K) \sin(K') S(4K') + \cos(K') \sin(K) S(4K)] + \cos(K + K') C[4(K + K')] + \sin(K + K') S[4(K + K')] + \cos(K - K') C[4(K - K')] + \sin(K - K') S[4(K - K')], \quad (\text{A.2})$$

where

$$C(4K) \equiv \sum_{m=1}^{N/2} \cos(4mK) = -\frac{1}{2},$$

$$S(4K) \equiv \sum_{m=1}^{N/2} \sin(4mK) = -\frac{1}{2} \tan(K), \quad (\text{A.3})$$

so that

$$\begin{aligned} & \cos(K) \cos(K') [C(4K) + C(4K')] \\ & + \cos(K) \sin(K') S(4K') \\ & + \cos(K') \sin(K) S(4K) \\ & = -\frac{1 + \cos(K + K') \cos(K - K')}{\cos(K + K') + \cos(K - K')}. \end{aligned} \quad (\text{A.4})$$

Furthermore, taking into account that

$$\begin{aligned} C[4(K + K')] & \equiv \sum_{m=1}^{N/2} \cos[4(K + K')m] \\ & = -\frac{1}{2}(1 - \delta_{k+k', N+1}) \\ & \quad + \frac{N}{2} \delta_{k+k', N+1}, \\ S[4(K + K')] & \equiv \sum_{m=1}^{N/2} \sin[4(K + K')m] \\ & = -\frac{1}{2}(1 - \delta_{k+k', N+1}) \tan(K + K'), \\ C[4(K - K')] & \equiv \sum_{m=1}^{N/2} \cos[4(K - K')m] \\ & = -\frac{1}{2}(1 - \delta_{kk'}) + \frac{N}{2} \delta_{kk'}, \\ S[4(K - K')] & \equiv \sum_{m=1}^{N/2} \sin[4(K - K')m] \\ & = -\frac{1}{2}(1 - \delta_{kk'}) \tan(K - K'), \end{aligned} \quad (\text{A.5})$$

we get

$$\begin{aligned} & \cos(K + K') C[4(K + K')] \\ & + \sin(K + K') S[4(K + K')] \\ & + \cos(K - K') C[4(K - K')] \\ & + \sin(K - K') S[4(K - K')] \\ & = -\frac{\cos(K + K') + \cos(K - K')}{2\cos(K + K') \cos(K - K')} \\ & \quad \times (1 - \delta_{kk'} - \delta_{k+k', N+1}) \\ & \quad + \left( \frac{N}{2} - \frac{1}{2\cos K} \right) (\delta_{kk'} - \delta_{k+k', N+1}). \end{aligned} \quad (\text{A.6})$$



Summing now all the terms in (A.2), we arrive at Eq. (7d) of the main text.

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