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Absorption spectra of mixed two-dimensional cyanine aggregates on silver halide substrates

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Using the coherent potential approximation (CPA), we study the absorption spectra of two-dimensional molecular aggregates formed from binary random molecular mixtures. In addition to the substitutional randomness, we include Gaussian randomness in the transition frequencies within each of the two classes of molecules. The latter is motivated by the considerable disorder that is typical for two-dimensional aggregates. By comparing to exact diagonalization results for small clusters, we show that the CPA gives an excellent description of the spectra for this kind of disorder, both in the cases of amalgamation and persistence type mixing. Taking into account long-range excitation transfer interactions mediated by the extended molecular transition dipoles, we analyze experimental spectra of amalgamation-type mixed cyanine aggregates adsorbed on AgBr {100} surfaces that are also reported here. We find good agreement between theory and experiment for the position, the width, and the general shape of the absorption line as a function of the mixing ratio. The analysis also allows us to estimate the slip angle characterizing the structure of these aggregates. © 2002 American Institute of Physics. [DOI: 10.1063/1.1499958]

I. INTRODUCTION

The collective excited state dynamics and (nonlinear) optical properties of molecular aggregates have been intensively studied for many years. The field originated from the interest in polymethine cyanine dyes as photographic sensitizers adsorbed on silver halide crystallites.^{1–3} Due to their high polarizabilities, these dye molecules have a strong tendency to cluster and form J aggregates, with a characteristic narrow absorption band,^{4,5} or H aggregates, with generally much broader bands.² With the advent of more advanced (nonlinear, ultrafast) optical techniques, the study of the Frenkel exciton dynamics in these materials has intensified over the past 15 years.⁶ Moreover, during the past decade it has been realized that very similar collective excited state dynamics takes place in chlorophyll aggregates that occur as light harvesting complexes in photosynthetic systems.⁷

In this work, we will study the optical absorption spectrum due to Frenkel excitons in mixed aggregates. These aggregates are formed in a solution of two types of dye molecules, which differ in the electronic transition frequency and are in all other aspects, in particular in their aggregation properties, very similar. Thus, upon self-assembly, these molecules form a randomly mixed aggregate, similar to binary random alloys⁸ and substitutionally disordered molecu-

lar crystals.^{9,10} The interest in mixed aggregates arises from the possibility to finetune the absorption wavelength of cyanine aggregates for photographic applications.^{1,2} At a more fundamental level, the generic properties of such binary mixtures, in particular the distinction between amalgamation-type and persistence-type of system,¹¹ are of interest. The former case refers to the situation where the mixture is characterized by one continuous exciton band and one absorption peak, while the latter type shows two separated bands. The distinction is determined by the frequency detuning between both types of molecules, the mixing ratio, the exciton band width, and the dimension of the system.^{9,11} In this paper, we will be interested in two-dimensional aggregates, such as those that are formed on AgBr surfaces for photography.

The literature of binary alloys and mixed crystals is large. Most of it is focused on bulk crystals, or quasi-one- or two-dimensional subsystems therein,^{9,10} and dates back several decades. More recently, interest in low-dimensional self-assembled molecular aggregates has grown. Muentert *et al.*^{12,13} have studied the optical properties of mixed aggregates formed from the dye pseudo-isocyanine (PIC; 1,1'-diethyl-2,2'-cyanine) and its aza-analog, which have a large frequency detuning ($\sim 4500\text{ cm}^{-1}$) and belong to the persistence-type. These aggregates were adsorbed on AgBr {111} surfaces, under which condition they are generally accepted to be two-dimensional (monolayers). The same molecules were used to study the effects of mixing in aggregates

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formed in a glassy solution,¹⁴ where the aggregation process is commonly believed to lead to one-dimensional aggregates. In one-dimensional chains, the large energy difference between both types of molecules effectively causes one type to break the exciton delocalization of the other type. Comparing the measured absorption spectrum as a function of mixing ratio to numerical simulations, confirmed the one-dimensional nature of PIC aggregates in solution.¹⁴

The Langmuir–Blodgett (LB) technique offers an alternative method to prepare two-dimensional aggregates. Also in these systems random mixing of two types of dyes has been studied. For instance, Vitukhnovsky and co-workers have studied mixed LB films of carbocyanine dyes of the amalgamation as well as the persistence type as a function of mixing ratio.^{15,16} A closely related study was carried out in mixed layer-by-layer alternate assemblies.¹⁷

In the present work, the main focus is on modeling the optical absorption of two-dimensional mixed aggregates. In addition, we will report on new experimental results on amalgamation-type mixed aggregates of two closely related thiacyanocyanine dyes adsorbed on {100} AgBr surfaces, as a function of mixing ratio, and analyze these experiments in terms of the general model presented.

One aspect that makes self-assembled mixed aggregates different from mixed molecular crystals,^{9,10} is that in aggregates, in addition to the substitutional disorder, one has to account for an appreciable amount of Gaussian disorder (inhomogeneity) in the frequencies of both types of molecules, arising from random environment induced shifts. Such disorder has been the topic of many studies, as it strongly limits the collective nature of the optical properties of the aggregates.^{18–21} It is an empirical fact that two-dimensional aggregates, like those formed on AgBr surfaces or in LB films, suffer from particularly strong disorder, leading to linewidths of hundreds of wave numbers. Thus, while in the classical treatment of mixed crystals one assumes a dichotomic distribution of transition frequencies (each molecule has either frequency ω_A or ω_B), in aggregates we have to allow for a bi-Gaussian distribution, in which the frequency of each molecule is randomly taken from a distribution with two gaussian peaks, one centered at ω_A and the other at ω_B .

The analysis of the optical properties of a bi-Gaussian disorder model, as sketched above, can be done using standard numerical simulations.^{19,22} For one-dimensional aggregates, this has become common practice. In the two-dimensional case, however, this is less straightforward, mainly because the number of molecules involved grows quadratically in the system's linear size. This limits exact diagonalization to rather small clusters. For instance, in Refs. 15 and 16 clusters of 10×10 molecules were used to analyze the experiments. Even if the disorder is rather large, this size may be too small in view of the fact that in two dimensions the exciton delocalization is less affected by disorder than in one dimension. In addition, in such small clusters, it is difficult to correctly deal with the long-range (dipole–dipole) nature of the excitation transfer interactions.

This has motivated us to use an alternative method, namely the coherent potential approximation (CPA),^{23,24} which is a mean-field approximation that is not limited to

FIG. 1. Lattice of the two-dimensional aggregates considered in this paper. Each lattice point is occupied by a molecule that is elongated in the $\mathbf{a}_1$ direction. The angle α between both lattice vectors is referred to as the slip angle. Also indicated are the auxiliary quantities $d = a_2 \sin \alpha$, the distance between two adjacent rows of molecules, and $s = a_2 \cos \alpha$, the relative shift of two adjacent rows of molecules. The optical transition of each molecule is characterized by an extended dipole, modeled as two charges, $-q$ and $+q$, separated by $L = \lambda \mathbf{a}_1$.

small clusters. The method, which has been derived in various different ways,⁸ becomes exact in the small-disorder limit. It has, *inter alia*, been used with varying success to predict and analyze optical properties of isotopically mixed aromatic crystals (dichotomic disorder), both in the amalgamation and the persistence case.^{9,10} The CPA has also been used to calculate the absorption spectra of one-component systems with Gaussian diagonal disorder (mono-Gaussian disorder). By comparing to numerical simulations on small clusters, Huber and co-workers have shown that in this case the method works well in one, two, and three dimensions, provided the Gaussian disorder distribution is narrower than the exciton band width.^{25,26} From their work it has also become clear that the CPA for such continuous disorder models should be implemented with care. Taking a less-fortunate route for solving the self-consistency equation for the complex self-energy, can give rise to large errors.^{26–28}

As far as we know, the CPA has not been used or tested against numerical simulations for the case of bi-Gaussian disorder. We therefore devote part of this paper to report on the implementation and validity of the CPA for our type of disorder (Sec. III), after having described the aggregate model in detail in Sec. II. In Sec. IV, we present experimental absorption spectra obtained for mixed two-dimensional aggregates of two closely related cyanine dyes on a AgBr {100} substrate and we give a detailed analysis of these spectra using our model calculations. Finally, in Sec. V we conclude.

II. MODEL

We consider a two-dimensional aggregate occupying a lattice with lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ (see Fig. 1). Each unit cell is occupied by one polarizable two-level molecule, which is centered at the lattice point. The molecular transition dipole is oriented along its long axis, which lies in the $\mathbf{a}_1$ direction. This situation is applicable to aggregates of cyanine dyes on silver halide substrates; we will come back to the more detailed description of such aggregates and their relevant parameters in Sec. IV. An important parameter in the literature of cyanine aggregates, is the slip angle α between $\mathbf{a}_1$ and $\mathbf{a}_2$, or in other words, the angle between a column of molecules and the molecular dipole. This angle determines to an important extent whether an aggregate appears as a J or an H aggregate, i.e., whether it has an absorption peak that is

red or blue shifted relative to the single molecule absorption band.²⁹ Each molecule is uniquely referred to by its position $\mathbf{n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$, with $n_j = 0, \dots, N_j - 1$. Periodic boundary conditions in both lattice directions are assumed throughout this paper.

The Frenkel exciton Hamiltonian for this monolayer reads ($\hbar = 1$):^{30,31}

$$\hat{H} = \sum_{\mathbf{n}} \omega_{\mathbf{n}} \hat{b}_{\mathbf{n}}^{\dagger} \hat{b}_{\mathbf{n}} + \sum_{\mathbf{n}, \mathbf{m}} J_{\mathbf{nm}} \hat{b}_{\mathbf{n}}^{\dagger} \hat{b}_{\mathbf{m}}, \quad (1)$$

where $\mathbf{n}$ and $\mathbf{m}$ run over all lattice vectors. Here, the Pauli operators $\hat{b}_{\mathbf{n}}^{\dagger}$ and $\hat{b}_{\mathbf{n}}$ create and annihilate an excitation on molecule $\mathbf{n}$, respectively, $\omega_{\mathbf{n}}$ is the transition frequency of molecule $\mathbf{n}$, and $J_{\mathbf{nm}}$ is the excitation transfer interaction between molecules $\mathbf{n}$ and $\mathbf{m}$ ($\mathbf{n} \neq \mathbf{m}$).

As discussed in the Introduction, we will consider binary mixtures, in which each aggregate lattice site is occupied at random by one of two types of molecules. These two types, referred to as A and B, differ in the average value of their transition frequencies: ω_A and ω_B , respectively. Moreover, to account for the appreciable disorder in the transition frequencies in self-assembled aggregates (see Introduction), we allow each molecule to have a random frequency offset relative to the average frequency of its class. These offsets are taken from a Gaussian distribution. The binary and gaussian randomness can be lumped into one bi-Gaussian disorder distribution from which all frequencies are taken at random and without correlations, $\mathcal{P}(\{\omega_{\mathbf{n}}\}) = \prod_{\mathbf{n}} \mathcal{P}(\omega_{\mathbf{n}})$, with

$$\mathcal{P}(\omega_{\mathbf{n}}) = \frac{1}{\sqrt{2\pi}\sigma} \left[c_A \exp\left(-\frac{(\omega_{\mathbf{n}} - \omega_A)^2}{2\sigma^2}\right) + c_B \exp\left(-\frac{(\omega_{\mathbf{n}} - \omega_B)^2}{2\sigma^2}\right) \right]. \quad (2)$$

Here, c_A and $c_B (= 1 - c_A)$ denote the concentrations of each of the types of molecules (measured per lattice site) and we have assumed that both types are characterized by the same strength σ of the Gaussian disorder. Also in all other respects the two types of molecules will be regarded identical. This holds in particular for their transition dipoles and the interactions determined by those, which thus obey the translational symmetry $J_{\mathbf{nm}} = J(\mathbf{n} - \mathbf{m})$. It is well-known that for cyanine dyes in a two-dimensional arrangement, point-dipole interactions are not realistic. We therefore work with the more appropriate extended-dipole model,^{32–34} in which the transfer interactions derive from two charges $-q$ and q that are separated by a finite vector $\mathbf{L} = \lambda \mathbf{a}_1$ (see Fig. 1). For the moment, we will leave λ a free parameter in the interval $[0, 1]$; we will come back to its value for cyanine molecules in Sec. IV. The dipole moment associated with these charges is given by $\mu = q|\mathbf{L}|$; it should be realized that while $\mathbf{L}$ and q are free, their product should be such as to recover the known dipole strength of the molecules (see end of Sec. IV).

The extended dipole–dipole transfer interactions are now given by (irrespective of the types of molecules involved)

$$J(\mathbf{n}) = \frac{\mu^2}{\epsilon |\mathbf{L}|^2} \left(\frac{2}{|\mathbf{n}|} - \frac{1}{|\mathbf{n} + \mathbf{L}|} - \frac{1}{|\mathbf{n} - \mathbf{L}|} \right) \quad (3)$$

with ϵ the dielectric constant of the environment. It is useful to define the quantity $J = -2\mu^2/(\epsilon |\mathbf{a}_1|^3)$, whose physical meaning is the interaction between two nearest-neighbor molecules along the $\mathbf{a}_1$ axis in case all dipole strength is concentrated in one point ($\lambda \rightarrow 0$). We note that $J < 0$. The advantage of introducing J , is that it does not depend on the choice of λ , so that its absolute value $|J|$ may be used as the unit of energy. In terms of $|J|$, the transfer interactions may be written,

$$J(\mathbf{n}) = \frac{|J|}{2\lambda^2} \left(\frac{2a_1}{|\mathbf{n}|} - \frac{a_1}{|\mathbf{n} + \lambda \mathbf{a}_1|} - \frac{a_1}{|\mathbf{n} - \lambda \mathbf{a}_1|} \right), \quad (4)$$

where $a_1 = |\mathbf{a}_1|$ (similarly, $a_2 = |\mathbf{a}_2|$). It is instructive to calculate the actual interaction between nearest-neighbors in the $\mathbf{a}_1$ direction: $J((n_1 = 1, n_2 = 0)) = J/(1 - \lambda^2)$, which is thus seen to always be negative and to exceed in absolute value the point-dipole interaction. Also, one easily checks that in the limit $|\mathbf{L}|/|\mathbf{n}| \rightarrow 0$, the general expression correctly reduces to the interaction between two point dipoles separated by the position vector $\mathbf{n}$. Finally, we note that the periodic boundary conditions are imposed on the interactions by taking the relative position vector between two molecules along the path with minimal distance along the virtual torus formed by the periodic system. In practice, this means that all measured lengths are limited to half of the system size.

To end this section, we consider the special case of a homogeneous monolayer, i.e., we take only one type of molecule $c_A = 1$ ($c_B = 0$) and $\sigma = 0$. Obviously, the one-exciton sector of the Hamiltonian is now diagonalized by Bloch states characterized by their wave vector $\mathbf{k} = (k_1, k_2)$,

$$|\mathbf{k}\rangle = N^{-1/2} \sum_{\mathbf{n}} e^{-i\mathbf{k} \cdot \mathbf{n}} \hat{b}_{\mathbf{n}}^{\dagger} |g\rangle, \quad (5)$$

where $|g\rangle$ is the state without molecular excitations and $N = N_1 N_2$, the total number of molecules in the system. The summation over $\mathbf{n}$ runs over all lattice vectors and the wave vector components are quantized by $k_i = 2\pi l_i / N_i$, with $l_i = 0, 1, 2, \dots, N_i - 1$ ($i = 1, 2$). The corresponding exciton energies are given by

$$\Omega_{\mathbf{k}} = \omega_A + \sum_{\mathbf{n} \neq (0,0)} J(\mathbf{n}) \cos(\mathbf{k} \cdot \mathbf{n}). \quad (6)$$

Keeping in mind our earlier remark about the boundary conditions, the summation over $\mathbf{n}$ in this expression is generated by summing over $n_i = 0, \pm 1, \pm 2, \dots, \pm (N_i/2 - 1), N_i/2$, with $i = 1, 2$ (upper boundary is changed in an obvious way if N_i is odd). Substituting Eq. (4) into Eq. (6) gives the band structure $\Omega_{\mathbf{k}}$, which, in addition to having its scale set by $|J|$, strongly depends on the slip angle α , the ratio a_2/a_1 , and the value of λ .

III. ABSORPTION SPECTRUM: CPA VERSUS SIMULATIONS

Linear response theory within the rotating wave approximation gives for the absorption spectrum of a system with

dimensions small compared to an optical wave length and with all molecular dipoles equal in size (μ) and orientation the general expression,

$$I(\omega) = -N\mu^2 \text{Im} \langle \langle \mathbf{k}=\mathbf{0} | \hat{G}(\omega) | \mathbf{k}=\mathbf{0} \rangle \rangle. \quad (7)$$

Here, $|\mathbf{k}=\mathbf{0}\rangle$ denotes the totally symmetric one-exciton Bloch state [cf. Eq. (5)], $\hat{G}(\omega)$ is the Green operator,

$$\hat{G}(\omega) = (\omega \hat{1} - \hat{H} + i\eta)^{-1} \quad (8)$$

(η a positive infinitesimal constant), Im denotes the imaginary part, and the outer brackets indicate the average over the disorder realizations. We stress that the appearance of the Bloch state with momentum zero holds for arbitrary disorder and is simply related to the fact that all molecules have the same interaction, in magnitude and phase, with the exciting light.

One way to approach the evaluation of Eq. (7), is to numerically diagonalize the one-exciton Hamiltonian in the presence of disorder. The eigenvalues give the exciton eigenfrequencies, at which the system absorbs; the absorption strength is given by the oscillator strength, which is the squared sum of the amplitudes of the exciton state on each molecule. The result is averaged over many randomly generated disorder realizations. Usually, in such a simulation the value of η is kept finite to mimic the effect of homogeneous broadening or to smoothen the statistical noise. As this method is well known (see, e.g., Refs. 19,22), we do not give more detailed expressions here.

As argued in the Introduction, brute force simulations are computationally quite demanding for two-dimensional systems. We therefore consider the coherent potential approximation (CPA) as an alternative method to evaluate Eq. (7). This method is well known as well^{35,36} and we only give a few essential expressions in order to make the implementation for our type of disorder explicit.

In the CPA, it is assumed that the disorder averaged Green function of the actual system is identical to the Green function of an effective medium with translational symmetry. The price paid for restoring the symmetry, is that one has to add to the Hamiltonian an unknown, frequency dependent and complex self-energy $\Sigma(\omega)$. Using as reference the system with $c_A=1$ ($c_B=0$) and $\sigma=0$ (i.e., the system diagonalized at the end of Sec. II), we find for the averaged Green operator,

$$\langle \hat{G}(\omega) \rangle = \sum_{\mathbf{k}} \frac{|\mathbf{k}\rangle \langle \mathbf{k}|}{\omega - \Omega_{\mathbf{k}} - \Sigma(\omega) + i\eta}, \quad (9)$$

with $\Omega_{\mathbf{k}}$ as in Eq. (6), leading to the absorption spectrum,

$$I(\omega) = -N\mu^2 \text{Im}(\omega - \Omega_{\mathbf{k}} - \Sigma(\omega) + i\eta)^{-1}. \quad (10)$$

From this it is seen that for small self-energies, $\text{Im} \Sigma(\omega)$ is related to disorder-induced broadening of the $\mathbf{k}=\mathbf{0}$ absorption line, while $\text{Re} \Sigma(\omega)$ is related to a line shift. For large self-energy (i.e., strong disorder), this simple picture breaks down. In the CPA, the self-energy is determined in a self-consistent way, by requiring that the t matrix for scattering on a single molecule within the effective medium, averaged over the disorder realizations of that molecule, yields zero.

The approximation in this method resides in neglecting correlations between scattering events on different molecules. As a result, the first neglected terms in the CPA are of fourth order in the molecular t matrices.^{11,23,24} The resulting self-consistency equation reads:^{35,36}

$$\langle t_{\mathbf{n}} \rangle = \left\langle \frac{\omega_{\mathbf{n}} - \Sigma(\omega)}{1 - (\omega_{\mathbf{n}} - \Sigma(\omega)) \langle \hat{G}(\omega) \rangle_{\mathbf{nn}}} \right\rangle = 0, \quad (11)$$

where the disorder average implies integration over $\omega_{\mathbf{n}}$, weighted by $\mathcal{P}(\omega_{\mathbf{n}})$, and the site diagonal element of the averaged Green function is given by

$$\langle \hat{G}(\omega) \rangle_{\mathbf{nn}} = \frac{1}{N} \sum_{\mathbf{k}} \frac{1}{\omega - \Omega_{\mathbf{k}} - \Sigma(\omega) + i\eta} \equiv g_0(\omega). \quad (12)$$

For one-dimensional systems with nearest-neighbor interactions and dichotomic disorder, the self-consistency equation is a third-order equation, from which it is fairly straightforward to solve the self-energy.²⁴ This can also be done for three-dimensional systems with dichotomic disorder and a hemispherical density of states.¹¹ In general, however, an exact solution is not available and one has to resort to numerical schemes. To this end, it is useful to rewrite Eq. (11) as

$$\Sigma(\omega) = \left[\int dx \frac{\mathcal{P}(x)x}{1 - (x - \Sigma(\omega))g_0(\omega)} \right] \times \left[\int dx \frac{\mathcal{P}(x)}{1 - (x - \Sigma(\omega))g_0(\omega)} \right]^{-1}, \quad (13)$$

which holds for arbitrary distribution $\mathcal{P}(x)$. Equation (13) lends itself well towards iterative solution by using the right-hand side to obtain a new value for Σ on the left-hand side. Simple manipulations show that the first right-hand side factor equals $\Sigma(\omega)$, so that, in principle, the expression may be simplified further to yield

$$\Sigma(\omega) = \Sigma(\omega) \left[\int dx \frac{\mathcal{P}(x)}{1 - (x - \Sigma(\omega))g_0(\omega)} \right]^{-1}. \quad (14)$$

This yields an alternative iterative scheme. We have found however, that for both mono-Gaussian and bi-Gaussian disorder, the iteration procedure using Eq. (13) is much more stable and converges considerably faster than the scheme based on Eq. (14). Apparently deviations of the first and second factors of Eq. (13) from their final values tend to balance each other during the iteration process. For noniterative solutions, Eq. (14) is generally the preferred one, as it allows one to cancel the factor of $\Sigma(\omega)$ on both sides, which leaves a rather simple looking equation, $\int dx \mathcal{P}(x)(1 - (x - \Sigma(\omega))g_0(\omega))^{-1} = 1$. This equation is convenient for the case of dichotomic disorder¹⁰ and has also been used by Huber for mono-Gaussian disorder,²⁸ which permits for several further steps that cannot be taken for bi-Gaussian noise.

We have thus solved for the self-energy by iteration of Eq. (13). As starting value for the iteration we have used the virtual crystal value, $\Sigma_0(\omega) = c_B \omega_B$, of the absorption line shift relative to the pure dye A system with zero disorder. We note that, in fact, the CPA result is invariant under changing the host lattice.³⁵ Thus, instead of choosing the pure A system as our reference, we could also have started from the

FIG. 2. Comparison of linear absorption spectra obtained using the CPA (solid) and numerical simulations (dashed) for square lattices of 20×20 molecules, with one type of molecule only ($c_A = 1$) and only nearest-neighbor point-dipole interactions included. With maxima shifting from right to left, the curves correspond to disorder values of $\sigma/|J| = 2.0, 3.0, 4.0$, and 5.0 , respectively. The simulations were averaged over 5000 disorder realizations and their statistics were improved by using the smoothening procedure of Ref. 37.

pure B system or from any linear combination of the two. Finally, as a technical remark, we note that for a reliable iteration, care should be taken to choose the domains of integration in Eq. (13) large enough.

In the remainder of this section, we present several results for absorption spectra calculated using the CPA. The aim is twofold. First, it allows us to illustrate and discuss some of the general aspects of spectra of mixed aggregates, which will be useful when discussing the experimental spectra in Sec. IV. Second, it allows us to assess the validity of (our implementation of) the CPA. This will be done by comparing for small lattice sizes and several parameter sets the CPA results to numerical simulations. The statistics of these simulations was improved by carrying out smoothening procedures such as those described in Refs. 37 and 38. We note that also in the numerical simulations, we have included periodic boundary conditions on the interactions (cf. Sec. II).

Figure 2 shows the comparison between CPA and simulations for a square lattice ($a_1 = a_2$; $\alpha = 90^\circ$) of 20×20 lattice sites and only nearest-neighbor point-dipole interactions in the two lattice directions included. This means that the interaction in the $\mathbf{a}_1$ direction is J , while the interaction in the $\mathbf{a}_2$ direction is $-J/2$. All other interactions are neglected. While not being realistic for actual systems, this is a useful test case for the CPA. Only one type of molecules was considered, $c_A = 1$, and $\sigma/|J|$ was varied from 2.0 to 5.0. As is observed, hardly any difference exists between the CPA and the numerical results. In fact, the maximum deviations between both methods were found to be 2%, occurring mainly around the peak maxima. This level of agreement proves that the CPA, based on our iterative scheme, does an excellent job in describing one-component systems with disorder of up to the bandwidth (which equals $6|J|$). We also stress that owing to the periodic boundary conditions and the use of only nearest-neighbor interactions, the results do not depend on the lattice size anymore: expanding the lattice to 30×30 sites does not visibly alter the calculated spectra.

We next turn to the case of actual bi-Gaussian disorder, i.e., mixed crystals. The solid curves in Fig. 3 show the spectra calculated using the CPA for three values of the detuning $\Delta \equiv \omega_A - \omega_B$ as a function of mixing ratio and at a fixed

FIG. 3. Absorption spectrum according to the CPA (solid) and numerical simulations (dashed) for mixed two-dimensional aggregates of lattice geometry as discussed in the text. A lattice of 10×10 sites was used and extended dipole-dipole interactions between all molecules were taken into account; the disorder strength was fixed at $\sigma/|J| = 4.0$. Panels correspond to $\Delta/|J| = 7.6$ (a), 14.4 (b), and 28.7 (c). In order of decreasing (increasing) weight at the high- (low-) energy side, curves within each panel correspond to $c_A = 1.0, \dots, 0.0$ in steps of 0.1. The simulations were averaged over 5000 disorder realizations and their statistics were improved by using the smoothening procedure of Ref. 38. Note the different frequency scales for the three panels.

disorder strength $\sigma/|J| = 4.0$. In order of decreasing (increasing) weight at the high- (low-) energy side, curves within each panel represent correspond to $c_A (= 1 - c_B) = 1.0, \dots, 0.0$ in steps of 0.1. The spectra were calculated using a lattice of 10×10 sites, with geometry characterized by $d/a_1 = 0.2$ and $s/a_1 = 0.4$ (cf. Fig. 1); extended dipole-dipole interactions between all molecules were taken into account, with the size of the dipole characterized by $\lambda = 2/3$. For this geometry, the exciton band width W of the completely homogeneous infinite system (one type of molecules and no disorder) equals $W \approx 24|J|$.

Figure 3 clearly demonstrates the effects of the detuning Δ on the behavior of the spectra upon mixing. In particular, we see the well-known distinction between amalgamation and persistence type spectra.^{9,11} In Fig. 3(a), with $\Delta/|J| = 7.6$, we are in the amalgamation situation. The detuning is considerably smaller than the band width and the spectra of the mixed aggregates maintain a single peak structure at all mixing ratios. Their position interpolates between both extreme positions of the pure A and pure B aggregates; their widths grow somewhat upon mixing (which also symmetrizes the spectra slightly). It is clearly seen that the evolution of the spectra is not symmetric around $c_A = 1/2$. Mixing a small concentration of B molecules into A aggregates diminishes the peak absorption value and increases the width of the absorption band more than mixing in the same amount of

A into B aggregates. This asymmetry arises from the combination of facts that (i) the current geometry gives J aggregates, for which the dipole allowed state lies near the bottom of the exciton band, and (ii) the A molecules have a higher transition energy than the B molecules, leading to a corresponding shift in their unperturbed exciton bands. Thus, upon mixing, the dark states in the middle and upper part of the B band mix easily with the dipole allowed state of the A aggregates and thus steal some of the oscillator strength. This spreads the oscillator strength over a larger frequency interval, giving rise to broader spectra with lower peak intensity. When mixing A molecules into B aggregates, these mixing effects are smaller, because there is no overlap between the A exciton band and the dipole allowed state at the bottom of the B band. This asymmetry is well-known from the case of a dichotomic frequency distribution.¹¹ The presence of additional disorder in our case, makes the effects less dramatic, as this leads to smearing of the exciton band edges and the position of the optically allowed states of the pure A and B aggregates. The asymmetry decreases with decreasing value of Δ/W (not shown), which may be understood from a simple perturbative treatment around the virtual crystal approximation (VCA), which shows that the effect is second order in Δ/W .¹¹

In Fig. 3(b), with $\Delta/|J| = 14.4$, we are in the intermediate regime. In the strict sense, this is still an amalgamation-type system, as no gaps are seen to emerge in the spectra and the density of states (not shown) still shows a continuous rather structureless band. Yet, there is a clear tendency to create a double-peak structure in the absorption spectrum. The above mentioned asymmetry is very clear. Finally, in Fig. 3(c), with $\Delta/|J| = 28.7$, we have entered the persistence regime, where both types of aggregates are seen to persist at all concentrations, albeit that they still affect each other, as is clear from the changes that both lines undergo when changing the mixing ratio. Again, as we are dealing with the additional disorder σ , a real gap never arises in the spectra, in contrast to the dichotomic case,¹¹ but we may clearly distinguish a pseudogap between both peaks.

The above observations agree with the general picture that the transition between amalgamation and persistence type systems is governed by the value of Δ/W and that the critical value of this parameter is in the order of unity. For model calculations in one dimension⁹ and three dimensions,¹¹ the critical value of this parameter was found to be of the order unity at $c_A = 1/2$ ($1/\sqrt{2}$ in one dimension and $1/2$ in three dimensions).

Finally, we turn to the comparison of the CPA results to those obtained from numerical simulations, performed on the same system of 10×10 molecules. In Fig. 3, these simulated spectra are represented by dashed curves. Clearly, for all situations that we have considered, excellent agreement exists between both approaches. The deviations between them were found to be smaller than 5% for c_A close to zero or unity, and smaller than 10% for intermediate concentrations. Close inspection reveals that noise in the numerical simulations is the main limiting factor in these larger deviations. These results clearly demonstrate the validity of the CPA in the presence of long-range dipole-dipole interactions and

FIG. 4. Molecular structure of the dye molecules used in the mixed aggregate absorption experiments on AgBr surfaces.

bi-Gaussian diagonal disorder in the amalgamation as well as persistence case. This conclusion justifies the use of the CPA to fit experimental spectra in Sec. IV. This will be done using much larger lattices of 200×200 molecules, in order to avoid finite size effects. Indeed, increasing the lattice size from 10×10 to 200×200 gives observable effects on the spectra, mostly in the form of peak shifts that probably originate from the long-range interactions (see end of Sec. IV).

IV. COMPARISON TO EXPERIMENTS

In this section, we present and analyze experimental results for the absorption spectra of mixed two-dimensional aggregates of two similar nearly planar thiacyanine dyes adsorbed on the $\{100\}$ surfaces of AgBr microcrystals. The two dyes are shown in Fig. 4. The upper one, which we will refer to as A, absorbs at a higher frequency than the lower one (B). Dye A is well-known in the literature^{16,39–41} and is sometimes referred to as Thia(et),¹⁶ THIATS,⁴¹ or Dye 1.⁴²

Samples were prepared as follows. Cubic $\{100\}$ AgBr microcrystals with 0.2 mm edge length suspended in aqueous gelatin solution were kindly provided by Dr. Tani. The dye molecules were adsorbed on the AgBr grains during agitation at 40 °C for 3 h, to which end methanol solutions of dye mixtures were added to the emulsion in a similar manner as in Ref. 42. The AgBr grains were suspended in a 3% gelatin solution. For all samples, the surface coverage was about 60% of the monolayer. All emulsions with different molar ratios of dyes A and B, as well as the reference sample without dyes, were prepared and measured under the same conditions. Assuming that both dyes have equal equilibrium constants for aggregation, we thus end up with two-dimensional randomly mixed binary aggregates adsorbed on the AgBr substrates.

Room temperature reflection spectra $[R_\infty(\omega)]$ of the optically thick emulsions were recorded using a Jasco spectrophotometer. From these spectra, the absorption spectrum was obtained using the Kubelka–Munk equation,⁴³

$$I(\omega) = S(\omega) \frac{(1 - R_\infty(\omega))^2}{2R_\infty(\omega)}, \quad (15)$$

FIG. 5. Absorption spectra of mixed two-dimensional aggregates of the cyanine molecules A and B in Fig. 4 measured at room temperature. From left to right, the spectra correspond to $c_A (= 1 - c_B) = 0, 0.09, 0.18, 0.36, 0.55, 0.73, 0.91$, and 1.0 , respectively.

where $S(\omega)$ denotes the scatter coefficient, which was determined using the reference sample.

Figure 5 displays the thus obtained aggregate absorption spectra as a function of mixing ratio. The rightmost spectrum corresponds to a pure A aggregate, and the leftmost to the pure B case. A couple of observations can readily be made. First, the molecules form J aggregates. Monomers of dye A on AgBr surfaces absorb at approximately $\omega_A = 17\,280\text{ cm}^{-1}$ (579 nm),⁴⁴ while the pure A aggregate is found to absorb at $15\,250\text{ cm}^{-1}$ (656 nm). Thus, aggregation leads to a redshift of 2030 cm^{-1} , which also gives a rough measure of the exciton band width W . The second observation is that over the entire range of mixing ratios, only one absorption peak is observed. We are thus in the amalgamation situation. This is immediately clear from an estimate of parameters. The pure B aggregate has its peak at $14\,590\text{ cm}^{-1}$, which is 660 cm^{-1} redshifted compared to the A aggregate. Assuming, as we do throughout this paper, that A and B species do not differ in their intermolecular transfer interactions, this implies that $\Delta = \omega_A - \omega_B = 660\text{ cm}^{-1}$, which is considerably less than W , and leads to amalgamation type spectra, as we discussed in the previous section. We also see that the absorption lines are strongly asymmetric for all mixing ratios (Fig. 5); the line width is large (hundreds of wave numbers), as is typical for two-dimensional aggregates, and is largest close to equal mixing, similar to Fig. 3(a). A more detailed discussion of the shape of the absorption line, its position, and width as a function of mixing ratios will be given below, together with the theoretical results.

We now turn to a more quantitative analysis and try to fit the spectra using our model with extended dipole-dipole interactions and bi-Gaussian diagonal disorder. To this end, we need to fix as many parameters in the model as possible, before actually attempting to make a fit. Two important parameters have been discussed above already. First, the detuning between A and B monomers is taken $\Delta = 660\text{ cm}^{-1}$. Second, the redshift from the A monomer band to the pure A aggregate band is 2030 cm^{-1} . This parameter in the end serves to establish the value of $|J|$ (which throughout the analysis we use as free unit of energy) in wave numbers. Finally, the third energy parameter is the disorder strength σ , which will be used to obtain a best fit of the shape of the absorption band to experiment.

Next, we have to fix the aggregate geometry (cf. Fig. 1).

This is of crucial importance to express the transfer interactions $J(\mathbf{n})$ in terms of the energy unit $|J|$ [cf. Eq. (4)]. The parameters involved are the ratio a_2/a_1 , the slip angle α , and the electronic parameter λ that fixes the length of the dipole relative to a_1 . Many studies have been done on the geometry of cyanine aggregates on silver halides (see, e.g., Refs. 39 and 40), but as far as we know, direct microscopic information of aggregates on actual silver halide crystals is lacking. Only relatively recently have STM and AFM techniques been used to visualize cyanine aggregates on “imitated” AgBr surfaces, created by the formation of a Br adlayer on a sputtered Ag {111} film.^{45,46} The following is well-established: the nearly planar thiacyanines tend to form aggregates in which they are standing (almost) upright on their long edge on the AgBr surface. This long edge gives the direction of the dipole and is parallel to the lattice vector $\mathbf{a}_1$ in Fig. 1. The length a_1 is roughly equal to the length of the molecules, which for our case is $\sim 19\text{ Å}$.³⁹ The length a_2 is not known from direct measurement, but information exists on the distance between two consecutive rows of molecules, $d = a_2 \sin \alpha$ (cf. Fig. 1). This distance is determined by a combination of optimal packing of the cyanine molecules and the geometry of the underlying AgBr lattice. There is ample spectroscopic evidence that the long edges of the cyanine molecules line up making a very small angle ($< 10^\circ$) with the $\langle 110 \rangle$ rows on the AgBr {100} surface.⁴⁰ As the distance between successive $\langle 110 \rangle$ rows is 4.083 Å , one arrives at $d = a_2 \sin \alpha \approx 4.0\text{ Å}$. Thus, we have $a_2/a_1 \approx 0.2(\sin \alpha)^{-1}$. This leaves us with the unknown quantities α and λ . The latter has been studied in detail by Kuhn and co-workers,^{32,33} who concluded that for these types of dye molecules the value $\lambda = 2/3$ gives an accurate representation of the intermolecular interactions as compared to quantum chemical calculations. Finally, as far as we know the parameter α is the most elusive one characterizing the aggregate structure.^{39,40} The angle should be rather small, in order to yield a J aggregate²⁹ (also see below); the STM studies of cyanine aggregates on “imitated” silver halide {111} surfaces confirm this.^{45,46} As direct information on actual (cubic) AgBr crystals is not available, we will, in addition to the interaction unit J and the disorder strength σ , treat the angle α as fit parameter. Thus, our model contains three free parameters.

It is useful to consider first some of the general effects of the slip angle on the exciton band structure of a two-dimensional aggregate consisting of just one type of molecules (A) and without disorder ($\sigma = 0$), but in the presence of extended dipole-dipole interactions between all molecules. To this end, we give in Table I the frequencies of the lower and upper band edges, the band width W , and the frequency $\Omega_{\mathbf{k}=0}$ of the optically allowed transition for $\cot \alpha = 0, \dots, 2.5$ in steps of 0.5. For our value of d this corresponds to lattice shifts $s = 0, \dots, 0.5a_1$ in steps of $0.1a_1$. This covers the entire range of independent values of s (or α); any other value can always be mapped to one within this interval. We observe that varying α has a strong effect on both band edges, in particular on the upper one, and that the total band width may vary by more than a factor of 2. We remind the reader that in all cases the nearest-neighbor interaction along

TABLE I. Characteristics of the exciton band for two-dimensional aggregates, with lattice structure as depicted in Fig. 1, existing of one type of molecules ($c_A=1$) in the absence of disorder ($\sigma=0$), as a function of the slip angle α . In all cases, the distance between adjacent rows of molecules was taken $d=0.2a_1$, as argued in the text. Extended dipole-dipole interactions between all molecules were taken into account ($\lambda=2/3$) and the band structure was calculated using a lattice of 200×200 sites. For each value of $\cot \alpha$, we give the equivalent value of the lattice shift s , the position of the lower exciton band edge ω_l , the upper band edge ω_u , the total band width W , and the position of the $\mathbf{k}=\mathbf{0}$ transition. The transition frequency of a single molecule, ω_A , was taken as the zero of energy.

$\cot \alpha$	s/a_1	$\omega_l/ J $	$\omega_u/ J $	$W/ J $	$\Omega_{\mathbf{k}=\mathbf{0}}/ J $
0.0	0.0	-12.35	39.18	51.53	8.01
0.5	0.1	-10.75	30.91	41.66	3.03
1.0	0.2	-9.19	20.16	29.35	-4.42
1.5	0.3	-8.86	16.24	25.10	-8.80
2.0	0.4	-9.53	14.42	23.95	-9.51
2.5	0.5	-8.83	13.85	22.68	-8.80

the $\mathbf{a}_1$ direction is equal to $J/(1-\lambda^2)=1.8J$. This is not necessarily the largest interaction in the system; depending on α some of the interactions between neighbors in adjacent rows may be larger. In addition to the strong effects on the band edge positions, we also see that α has a very strong effect on $\Omega_{\mathbf{k}=\mathbf{0}}$. For large slip angles (small lattice shifts), this frequency lies inside the band, above the molecular transition frequency, implying that the monolayer is an H aggregate. If α decreases, $\Omega_{\mathbf{k}=\mathbf{0}}$ shifts more and more towards the lower band edge and the system becomes a J aggregate. This general effect is well known;²⁹ the details depend on the aspect ratio a_2/a_1 of the lattice and the choice of λ . For our choice of parameters, it appears that for $\cot \alpha=2.0$ (i.e., $\alpha \approx 26^\circ$, or $s=0.4a_1$), the $\mathbf{k}=\mathbf{0}$ transition lies closest to the lower band edge, and in fact almost coincides with it, turning it into an ideal J aggregate case.

The fact that the experimental aggregate spectra reveal a J aggregate, sets an upper bound to the slip angle. For our geometry and choice of λ , this boundary lies around $\alpha = 53^\circ$ ($s=0.15a_1$). This still leaves a large range of possible values for α . The strong asymmetry of the experimental line shapes (Fig. 5) allows us, however, to considerably narrow down this range. In models of disordered Frenkel excitons, asymmetry of the absorption line naturally arises if the optically allowed transition of the ordered aggregate is close to the lower band edge. Then, upon switching on the disorder, the red side of the line acquires a rather sharp, Gauss-type shape, while the blue side gets a long tail. This tail arises from the fact that the higher lying, originally dark, exciton transitions get oscillator strength due to their disorder-induced mixing with the $\mathbf{k}=\mathbf{0}$ transition. The further $\Omega_{\mathbf{k}=\mathbf{0}}$ lies inside the band, the less this asymmetry becomes, as dark states will be available on both the red and the blue side of the allowed transition. When $\Omega_{\mathbf{k}=\mathbf{0}}$ lies in the upper half of the exciton band, the situation is reversed. These features are clearly observed in Fig. 6, where we plot the absorption spectra (still consisting of only A molecules) for a range of α values, in the presence of disorder with strength $\sigma=4.0|J|$. The spectra were calculated using the CPA, on a lattice of 200×200 sites. Again, it is clearly observed that with de-

FIG. 6. Linear absorption spectra according to the CPA for two-dimensional aggregates consisting of one type of molecule ($c_A=1.0$) with extended dipole-dipole interactions ($\lambda=2/3$) and with a disorder strength $\sigma=4.0|J|$ for various values of the slip angle α . From bottom to top, the curves correspond to $\cot \alpha=0.0, \dots, 2.5$ in steps of 0.25 (corresponding to a lattice shift $s/a_1=0.0, \dots, 0.5$ in steps of 0.05). Vertical offsets were used to separate the spectra from each other. The distance between adjacent rows of molecules was taken $d=0.2a_1$, as argued in the text. The lattice size used in the calculations was 200×200 sites, which for all practical purposes may be considered infinite.

creasing α , the absorption line shifts through the exciton band from higher to lower frequencies. Due to the disorder, the line positions are shifted relative to the unperturbed values of $\Omega_{\mathbf{k}=\mathbf{0}}$ given in Table I. Most importantly, we indeed clearly observe the above described effect of the line position on the disorder-induced asymmetry. For large α values, the aggregate is an H aggregate and the line acquires a long tail on the low-energy side, while for smaller α values, the asymmetry is reversed.

From the above it is clear that a good fit to the very asymmetric experimental spectra is only possible for values of the lattice shift close to $s/a_1=0.4$. Indeed, it turns out that this value gives the best possible comparison to experiment. The value of the disorder strength σ can be fixed by fitting the width of the absorption band. This is done as follows: For a given value of the disorder strength $\sigma/|J|$ we calculate the spectrum for the pure A case ($c_A=1$). We then know for this value of σ the shift of the aggregate-A absorption band relative to the monomer absorption in terms of the as yet unknown unit $|J|$. This shift should equal the experimental value of 2030 cm^{-1} , which allows us to calculate J and then to compare the entire calculated spectrum with the observed one. This procedure has been repeated for several σ values and the results for three values ($\sigma/|J|=3.5, 3.7$, and 4.0) are given in Fig. 7, together with the experimental spectrum for $c_A=1$.

We first note that, though the general shape of the line is recovered closely, none of the parameter sets gives an ideal fit. In particular, it turned out impossible within our model to generate a spectrum that was as asymmetric as the measured one. We will briefly return to this point in Sec. V. The three values for the disorder in Fig. 7 were chosen for the following reason: for $\sigma/|J|=3.5$ a reasonable fit to the red side of the band is obtained, for $\sigma/|J|=3.7$ the overall width of the band seems best recovered, but neither of the two sides has an ideal fit, while for $\sigma/|J|=4.0$ the blue side is fitted very well, without deteriorating too much the red side. Picking the best fit may be a matter of taste to some extent, but with the

FIG. 7. Absorption spectra for pure A aggregates. The symbols (+) give the experimental spectrum, while the curves have been calculated using the CPA on a lattice of 200×200 sites, with a lattice shift of $s = 0.4a_1$, a row-to-row distance of $d = 0.2a_1$, and including extended dipole-dipole interactions between all molecules ($\lambda = 2/3$). Parameters characterizing the different curves are: dotted: $J = -179 \text{ cm}^{-1}$, $\sigma = 627 \text{ cm}^{-1}$ ($\sigma/|J| = 3.5$); dashed: $J = -178 \text{ cm}^{-1}$, $\sigma = 657 \text{ cm}^{-1}$ ($\sigma/|J| = 3.7$), and solid: $J = -174 \text{ cm}^{-1}$, $\sigma = 700 \text{ cm}^{-1}$ ($\sigma/|J| = 4.0$).

rather small differences in the above σ values the typical magnitude of the disorder is rather clear. We have chosen to proceed with the value $\sigma/|J| = 4.0$.

From this point on, all parameters in the model are set and we are left to compare the spectra as a function of mixing ratio to experiment. We do this in Fig. 8, where we plot the position and the full width at half maximum (FWHM) as a function of c_A ($= 1 - c_B$). For both observables we find good agreement between theory and experiment. The position follows an almost straight interpolation between the two extrema (virtual crystal), with a slight S-shaped deviation in experiment and a small downward curved deviation in the theoretical curve. The latter is a well-known effect that may be understood already from a perturbative correction to the VCA.¹¹ An experimental S-shaped deviation has also been observed in Ref. 16. However, given the error in the experimental peak positions, it is not clear whether this deviation

FIG. 8. Position (a) and FWHM (b) of the absorption band as a function of mixing ratio, expressed through $c_A (= 1 - c_B)$. Symbols (+) give the experimental values (size indicative of error) and curves are obtained from CPA calculations using the same geometry as in Fig. 7 and the parameter set with $\sigma/|J| = 4.0$.

has significance. The width as a function of mixing ratio is well-described, even at the quantitative level, by the model calculations. In particular the asymmetry around the point $c_A = 1/2$, which was addressed in Sec. III already, is nicely recovered. The origin of the anomalous value of the experimental width at $c_A \approx 0.5$ is not clear.

From the above we conclude that our model with the chosen parameters gives a good description of the experiments. To end this section, it is useful to discuss the values of the parameters that are obtained from this fit. First, we have found that the lattice shift is $s = 0.4a_1$, which gives a slip angle $\alpha = 26.5^\circ$. This is in good agreement with the general expectation that this angle is small^{39,40} and with the STM measurements on “imitated” silver halide surfaces.^{45,46} Second, the value of the interaction unit is found to be $J = -174 \text{ cm}^{-1}$. This gives a nearest-neighbor interaction in the $\mathbf{a}_1$ direction of $1.8J \approx -310 \text{ cm}^{-1}$. The strongest interaction is the one between nearest neighbors separated by $\pm(\mathbf{a}_1 - \mathbf{a}_2)$ and equals $2.66J \approx -460 \text{ cm}^{-1}$. These values are very typical for interactions between cyanine dye molecules. In fact, having established the magnitude of J in cm^{-1} , we may now calculate the molecular transition dipole strength μ by using the known distance between the molecules. Setting the index of refraction $\sqrt{\epsilon}$ equal to unity, we arrive at $\mu \approx 11$ Debye, which is in excellent agreement with dipole strengths that have been calculated for similar thiacyanine molecules.³² Finally, the value of $\sigma = 4.0|J| \approx 700 \text{ cm}^{-1}$ is high, as is typical two-dimensional cyanine aggregates. For example, our value agrees well with the 750 cm^{-1} disorder strength found for LB films of similar cyanine dyes in Ref. 16. To put this disorder strength into better perspective, it is useful to point out that the total exciton band width for our geometry is $\sim 24|J|$ (cf. Table I). Thus, we are still in the rather weak disorder regime. This is also clear from the fact that the excitons are still delocalized over a number of molecules. Using the participation ratio,^{19,22} we find for the case $c_A = 1$, the average number of molecules participating in the exciton wave function at energies coinciding with the peak of the absorption band to equal $N_{\text{del}} = 8.3$. It is worth mentioning that this number nicely agrees with the one obtained from the exchange narrowed linewidth, $\text{FWHM} = 2.35\sigma/\sqrt{N_{\text{del}}}$,^{47,48} which gives $N_{\text{del}} = 7.4$. These numbers also demonstrate that the sensitivity of the absorption spectrum to the system size for a lattice of 10×10 sites derives mostly from the long-range nature of the dipole-dipole interactions and can hardly be effected by the extent of the wave functions of the optically dominant states anymore.

V. CONCLUSIONS

In this paper, we studied the linear absorption spectra of mixed two-dimensional molecular aggregates. The disorder in such aggregates is described by a bi-Gaussian distribution of the molecular transition frequencies. We have used the CPA to calculate the absorption spectra and shown, by comparison to exact numerical simulations for small lattices (up to 20×20 sites), that this approach works well for all cases tested. Of particular interest is that we found excellent agreement between CPA and exact results in both the amalgam-

ation and persistence situation; the agreement persists for detunings between both types of molecules of more than the exciton bandwidth [Fig. 3(c)]. In our calculations, the dipole–dipole transfer interactions between all molecules on the lattice were taken into account; they were calculated using the extended-dipole representation, as for two-dimensional aggregates the point-dipole approximation is rather poor.

We have used our iterative CPA approach to model the absorption spectra of mixed aggregates, consisting of the thiocarbocyanine dyes A and B (Fig. 4) adsorbed on AgBr {100} surfaces as a function of the mixing ratio. We have found good agreement between theory and experiment for the general spectral line shape and for the position and line-width as a function of the mixing ratio. Our modeling involved three fit parameters: the unit of interaction energy J , the disorder strength σ , and the slip angle α . These parameters were all fixed by considering the absorption spectrum of the pure A aggregate and were subsequently found to give good quantitative agreement between theory and experiment for all mixing ratios.

The values obtained for the fit parameters are all very reasonable. The value for J could be translated into a molecular dipole moment of ~ 11 Debye, which agrees well with values quoted in the literature.³² The value for the disorder strength of 700 cm^{-1} is in good agreement with the one reported for two-dimensional cyanine aggregates created via the LB technique,¹⁶ and gives a typical exciton extent of the order of 10 molecules. Finally, for the slip angle we found $\alpha \sim 26^\circ$. This angle, has never been directly measured on AgBr microcrystals, which makes its determination via this fitting procedure of extra interest. The value does agree with general expectations^{39,40} and with STM experiments on “imitated” silver halide films.^{45,46}

Refinement of the model by, e.g., allowing for different disorder strengths and (or) different dipole magnitudes for both types of molecules, or by incorporating off-diagonal disorder, are in principle straightforward, but the present data and already existing agreement between theory and experiment do not warrant this increase of the number of free parameters. In particular, the above extensions will not make the theoretical lineshape more asymmetric, as would be necessary to obtain a yet better fit. Possibly, such an increased asymmetry may be achieved by incorporating the effect of phonons, which leads to intraband relaxation and gives the excitons at the high-energy side of the absorption band a larger homogeneous band width. We also note in passing that we have checked that a quasi-one-dimensional model is not at all able to fit the observed spectra. The combination of large disorder and one-dimensional exciton band structure turns out to make the spectra very symmetric, contrary to the observations.

Finally, it is useful to stress the physics underlying the behavior of the experimental mixed aggregate spectra reported and modeled by us. As it turns out, for the two dyes A and B the detuning Δ is so small compared to the total exciton band width, that the mixed aggregate may be considered almost as if it exists of one type of molecule whose transition frequency is the weighted sum of the two molecu-

lar frequencies, $\bar{\omega} = c_A \omega_A + c_B \omega_B$. This approximation is known as the VCA (Refs. 35 and 36) and it yields for the position of the absorption line as a function of mixing ratio a linear interpolation between the two extreme values. Indeed, the experimental data as well as the theoretical results show that the system is close to this ideal VCA limit. It should be noted that the presence of Gaussian disorder of the same order of magnitude as Δ around both ω_A and ω_B washes out even more of the difference between both species, thus allowing the peak position to be even better described by the VCA. At the same time, this disorder adds to the width of the absorption line, whose evolution with changing mixing ratio cannot be described by the VCA, because this approximation does not add an imaginary part to the self-energy. As we have demonstrated, the CPA captures this evolution very well. The underlying physics is simple: In the two extreme situations ($c_A = 1$ or $c_B = 1$), the absorption peaks have the smallest width, dictated by the competition between disorder strength σ and exciton band width W . Upon mixing, an extra source of disorder is added, namely the configurational disorder of how the A and B molecules are distributed over the lattice. This broadens the spectrum and, as expected, the widest spectrum is reached close to (but not exactly at—see discussion in Sec. III) equal occupation of both dyes.

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