ELSEVIER

Journal of Luminescence 76&77 (1998) 359–364

JOURNAL OF
LUMINESCENCE

Optical absorption of molecular aggregates with colored noise

Martijn Wubs, Jasper Knoester*

Institute for Theoretical Physics and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

We study the optical absorption line shape for molecular aggregates in which the effect of the environment is modeled by a stochastic fluctuation of the molecular transition frequencies. We argue that exchange narrowing of this disorder is not only possible in the static limit, but also in the fast-fluctuation limit. The latter is further investigated using numerical calculations for dichotomic noise. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: J-aggregates; Disorder; Exchange narrowing; Excitons

1. Introduction

The collective optical properties of chromophores in molecular J-aggregates have drawn attention for many years already [1,2]. The Frenkel excitons in these systems may be coherently delocalized over a number of molecules that, depending on circumstances, varies from less than 10 to more than 50. The delocalization manifests itself in cooperative properties, like superradiant transitions [3] and exchange narrowing of static disorder [4,5]. The latter effect is generally believed to be responsible for the characteristic sharpness of the absorption band (J-band) of J-aggregates.

Molecular aggregates are far from nicely ordered systems. They are generally studied in solution or in a glass. These hosts induce disorder in the molecular transition frequencies and (or) intermolecular excitation transfer rates. In the case of low-temperature glassy hosts, the disorder may be considered static. Indeed, the linear and nonlinear optical properties of J-aggregates under these circumstances are well-understood now in terms of a Frenkel exciton model with static diagonal disorder [6,7]. Exchange narrowing then reduces the J-band width by a factor $\sqrt{N_{\mathrm{del}}}$, where N_{del} is the typical delocalization length of excitons at the lower band edge.

For aggregates in solution, however, the situation is less clear, as the dynamical nature of the environment then becomes important. This also holds for the biological molecular assemblies, like light-harvesting systems, that recently have attracted a growing interest [8–10]. The dynamics of the Frenkel excitons in these assemblies are affected by the dynamics of the protein environment. Taking the dynamics of the surroundings into account without describing them in full detail, can in a simple but appealing way be done by generalizing the model of static disorder to one of stochastically fluctuating molecular frequencies [11] and (or) transfer rates (dynamic disorder).

---

* Corresponding author. Tel.: + 31-50-3634369; fax: + 31-50-3634947; e-mail: knoester@chem.rug.nl.

0022-2313/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved
PII S0022-2313(97)00156-7

For single molecules in solution, this level of modeling has been well-studied theoretically [12] and it has been used succesfully to describe optical experiments in dilute solutions [13,14]. The theoretical treatment of *coupled* chromophores with stochastic frequency fluctuations, however, is complicated by the fact that three frequency scales play a role: the amplitude Δ and inverse correlation time λ of the fluctuations, and the intermolecular excitation transfer rate J [15]. Only in the simplest case of white noise (λ large compared to both Δ and J), one can obtain exact solutions in closed form by using a cumulant expansion. In this δ-correlated limit, the model reduces to the well-known Haken–Strobl model [16], where the excitons obtain a homogeneous dephasing rate given by $\Gamma = \Delta^2/\lambda$, independent of the aggregate size. Thus, the aggregate absorption spectrum is homogeneous with a width (HWHM) Γ that equals the width of the single-molecule spectrum. For interacting chromophores with colored noise (finite λ), it is much harder to obtain analytical results. Cumulant expansions may still be useful [17] if the fluctuations are not too slow, but they are not exact.

In an analysis of absorption, two-pulse echo, and pump–probe experiments on J-aggregates of TDBC in solution, Van Burgel et al. [18] recently posed the question whether exchange narrowing (i.e., narrowing resulting from intermolecular interactions) of dynamic disorder is possible in the fast-fluctuation limit. From the above, it is clear that in the white-noise limit such narrowing does not occur. In this contribution, we will investigate this issue in more detail, by considering a fluctuation rate that is not necessarily large compared to the intermolecular interactions. In Section 2, we describe the model and give an analysis of the problem based on physical arguments. In Section 3, we present numerical results. Finally, in Section 4 we conclude.

2. Model and physical discussion

Our model aggregate is a ring of N identical two-level molecules, with transition dipoles μ pointing in the direction perpendicular to the plane of the ring. The molecules are coupled by nearest-neighbor transfer interactions J and the effect of the environment is modeled by a stochastic modulation of the molecular transition frequencies. In the Heitler–London approximation [19], the Frenkel exciton Hamiltonian for this system reads ($\hbar = 1$),

$$\hat{H}(t) = \sum_{n=0}^{N-1} [(\omega_0 + \Delta_n(t))\hat{b}_n^\dagger \hat{b}_n + J(\hat{b}_n^\dagger \hat{b}_{n+1} + \hat{b}_{n+1}^\dagger \hat{b}_n)]. \tag{1}$$

Here, $\hat{b}_n^\dagger$ and $\hat{b}_n$ denote the Pauli creation and annihilation operator, respectively, for an excitation on molecule n, ω_0 is the average molecular transition frequency, and $\Delta_n(t)$ is the modulation of the frequency of molecule n at time t.

We will assume that each molecule undergoes independent Gaussian frequency fluctuations with correlator

$$\langle \Delta_m(t)\Delta_n(0)\rangle = \delta_{mn}\Delta^2 e^{-\lambda t}. \tag{2}$$

Thus, Δ is the amplitude of the fluctuations, while λ gives their inverse correlation time, which is determined by the frequency width of the bath modes that are responsible for them.

For the case $N = 1$ (the monomer), this model is exactly solvable using the cumulant expansion [11,12]. In the static regime, $\Delta > \lambda$, the spectrum is Gaussian (inhomogeneous) with width Δ. In the fast-fluctuation regime, $\Delta < \lambda$, the spectrum is Lorentzian with width (HWHM) Δ^2/λ. The latter decreases with increasing λ, an effect that is known as *motional narrowing.*

Let us now turn to aggregates ($N \neq 1$). Then, another narrowing effect, namely *exchange narrowing* is well known in the static limit ($\lambda = 0$) [4,5]. In this limit, well-defined Frenkel exciton states exist. For weak disorder (Δ small), the energy of these states may be calculated perturbatively. For $\Delta = 0$, the only exciton state that is observed in absorption is the totally symmetric $|k = 0\rangle$ state,

$$|k = 0\rangle = \frac{1}{\sqrt{N}} \sum_n \hat{b}_n^\dagger |g\rangle, \tag{3}$$

where $|g\rangle$ denotes the aggregate ground state, in which all molecules are in the ground state. To first order in Δ, the energy correction $\Delta_{k=0}$ of this state relative to its zeroth-order value $\omega_0 + 2J$ is simply given by the average over the single-molecule inhomogeneities of the aggregate:

$$\Delta_{k=0}=\frac{1}{N}\sum_{n}\Delta_{n}. \tag{4}$$

As the Δ_n are assumed uncorrelated Gaussian variables, their average also is a Gaussian variable, with a width, however, that is reduced to $\Delta/\sqrt{N}$. This immediately implies that the aggregate absorption line is narrower than the distribution of monomer frequencies by a factor $\sqrt{N}$. In practice, the physical size of aggregates and (or) the disorder is often too large to allow for this perturbative approach, and N should be replaced by the typical band-edge exciton delocalization length N_{del}.

We note that the effect called exchange narrowing here, is often also referred to as motional narrowing in the literature [5,18,20]. In view of the fact that the term motional narrowing is also used for the single-molecule line narrowing in the fast-fluctuation limit (vide supra), we prefer to reserve a different name for the collective narrowing effect, caused by excitation transfer, that we are interested in here. It should be stressed that in the static limit, exchange narrowing preserves the Gaussian shape of the absorption lines (for small Δ), while motional narrowing in a single molecule always leads to Lorentzian lines.

We now turn to dynamic disorder (finite λ) and wonder whether a similar simple picture as above may then be used to find exchange narrowing. The problem faced here, is that in the dynamic case we cannot define proper Frenkel exciton states. Rather, one is forced to work in a density matrix picture. Suppose, however, that $\lambda < J/N$, so that the time scale of the fluctuations is still long compared to the time scale needed for an excitation to travel over the aggregate. Let us further restrict our consideration to the motional narrowing regime, $\Delta < \lambda$, so that the size of the fluctuations is no limitation for the excitation to spread. Thus, while the fluctuations are fast on the scale of $1/\Delta$, they are slow on the scale of excitation transfer. Then we may still consider delocalized Frenkel exciton states, which adiabatically follow the fluctuations. Like in the static case, the exciton states *at each time* average over the molecular fluctuations and one simply finds that the exciton states undergo Gaussian fluctuations with rate λ, just as a molecular excitation, and with the narrowed amplitude $\Delta/\sqrt{N}$.

It follows that, under the conditions considered, the aggregate has a Lorentzian absorption spectrum of width $\Delta^2/(N\lambda)$, which is seen to be narrowed by a factor of N compared to the monomer case. In other words, the motionally narrowed monomer line is further narrowed because of the interactions between the molecules: exchange narrowing. The effect is even stronger than in the static regime, where we found a narrowing factor of $\sqrt{N}$.

It is clear that, even in the motional narrowing regime (where Δ is necessarily restricted in size), the aggregate length and (or) the value of λ/J for which the above picture holds is restricted. If the aggregate becomes too large or the fluctuations are too frequent, the excitation cannot sample all N molecules before fluctuations take place. The $1/N$ narrowing should then be expected to break down. Increasing N while keeping λ/J constant, the amount of narrowing should be expected to saturate at some aggregate length. As we noted in the Introduction already, it also is clear that if $\lambda \gg J$, no exchange narrowing of the motional narrowing line can occur, i.e., the saturation occurs at $N = 1$ already. Our numerical results presented in the next section confirm these expectations.

3. Numerical results

In this section, we report results of numerical simulations that illustrate the effect of exchange narrowing of fast fluctuations. Instead of Gaussian noise, we will consider dichotomic fluctuations [21,22]. For this type of fluctuations, $\Delta_n(t)$ stochastically switches between two discrete values, $+\Delta$ and $-\Delta$, with average jump rate λ. Thus, its two-time correlation function decays according to Eq. (2). Higher correlation functions for fluctuations on one molecule vanish for an odd number of fluctuations and for an even number they read

$$\langle\Delta_n(t_1)\Delta_n(t_2)\cdots\Delta_n(t_{2\nu-1})\Delta_n(t_{2\nu})\rangle=\langle\Delta_n(t_1)\Delta_n(t_2)\rangle\cdots\langle\Delta_n(t_{2\nu-1})\Delta_n(t_{2\nu})\rangle \tag{5}$$

$(t_1 > t_2 > \cdots > t_{2\nu-1} > t_{2\nu})$. The advantage of dichotomic noise is that the linear absorption spectrum, in principle, may be calculated from a finite hierarchy of linear equations of motion, while in the motional narrowing limit ($\Delta \ll \lambda$) it gives the same line shapes as the full Gaussian model.

Reineker, Barvík and co-workers [21,22] have shown that a closed hierarchy of $N2^N$ linear equations of motion can be derived that describes the absorption spectrum for an aggregate of N molecules. The variables in this hierarchy are stochastic averages of the product of a one-particle Green function at time t and an arbitrary number of molecular fluctuations at t. The hierarchy closes, because for any n and any t, $(\Delta_n(t))^2 = \Delta^2$. The steep increase of the size of this set with growing N strongly restricts the possibility to investigate the dependence of the spectrum on N, which is required to study the effect of exchange narrowing. Calculations published thus far have been restricted to hexamers ($N = 6$) and smaller. By taking advantage of our ring structure (periodic boundary conditions) and the translational invariance of stochastic averages, this hierarchy may be reduced to a set of 2^N equations [23]. Using this smaller set, we have studied aggregates upto the nonamer ($N = 9$).

Fig. 1 shows the numerically calculated absorption spectra for the nonamer with $\Delta = 0.5J$ and λ/J from left to right taking the values 0.003, 0.03, 0.5, and 2. At small λ we are in the static regime (both relative to Δ and to J). The spectrum then simply shows the dense collection of discrete peaks due to the various optically allowed exciton states that are possible in aggregates with two randomly distributed types of molecules ($\omega_0 \pm \Delta$). For larger λ the discrete lines broaden and merge into one peak, which gets narrower with growing λ as soon as the motional narrowing regime ($\lambda > \Delta$) is entered. For other values of N or Δ, similar effects are seen [21–23]. Here, we focus completely on the behavior of the line width of the spectrum in the motional narrowing regime.

Consider, for example, the third panel of Fig. 1 ($\Delta = \lambda = 0.5J$). The HWHM of this peak can be estimated to be $0.1J$, which is a factor of 5 smaller than the monomer width of Δ^2/λ. This clearly indicates exchange narrowing. We have investigated this more systematically, by measuring (in the motional narrowing regime) the width W (HWHM) of numerically obtained spectra as a function of λ/J and N. Let us define an exchange narrowing factor F_e through the relation

$$W = \frac{1}{F_e}\frac{\Delta^2}{\lambda}. \tag{6}$$

Thus, F_e indicates how much the peak width is decreased due to the intermolecular transfer interactions.

Fig. 2 shows a plot of the thus obtained narrowing factor for aggregates of $N = 3$, 6, and 9 molecules as a function of λ/J, while keeping the ratio Δ^2/λ (the monomer line width) constant at $0.5J$. As is observed, for all three values of N, the narrowing factor equals unity for $\lambda/J \gg 1$. This is what we expected (white-noise limit). If λ/J is decreased, however, the narrowing factor increases and this growth is faster for larger aggregates. In the case of

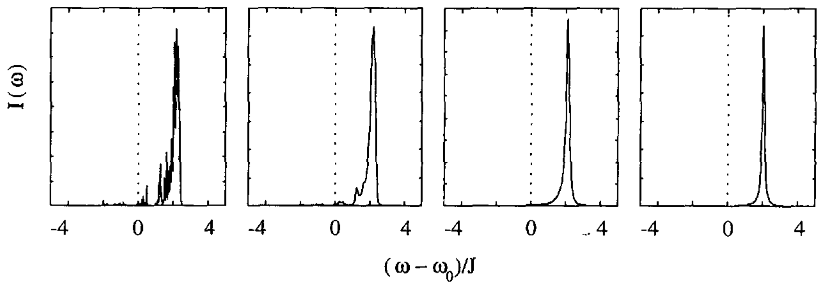

Fig. 1. Numerically obtained absorption line shapes for a ring aggregate of $N = 9$ molecules, all of which undergo independent dichotomic frequency fluctuations. The amplitude of the fluctuations is kept constant at $\Delta = 0.5J$, while the fluctuation rate increases from left to right through the values $\lambda/J = 0.003$, 0.03, 0.5, and 2.

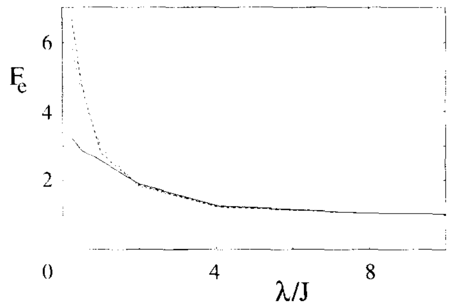

Fig. 2. The exchange narrowing factor as a function of λ/J, obtained by measuring the absorption line width W in numerically calculated spectra and using Eq. (6). At each value of λ, Δ was chosen such that $\Delta^2/\lambda = 0.5J$, giving a constant monomer line width (HWHM) of $0.5J$ in the motional narrowing regime. The solid line refers to $N = 3$, the dotted line to $N = 6$, and the dashed line to $N = 9$.

the trimer ($N = 3$), the narrowing factor is close to 3 for the smallest λ/J values, which agrees with our predictions in Section 2 [24]. In the case of the hexamer and the nonamer, the narrowing factor does not quite reach the value N: the aggregates are still too large for the considered λ/J values to use the adiabatic exciton picture for the entire aggregate. Still further decreasing λ/J, however, would move us out of the motional narrowing regime for the Δ^2/λ value of $0.5J$ that we consider. Nevertheless, Fig. 2, clearly demonstrates that exchange narrowing in the motional narrowing regime is possible and suggests that, indeed, the narrowing factor for small aggregates and small λ/J values tends to the aggregate size N.

Analytical results, derived by truncating the hierarchy of equations of motion, confirm the $1/N$ narrowing for small aggregates and small λ/J values and show how the exchange narrowing factor F_e saturates if N gets too large. These results, as well as a full account of the hierarchy of 2^N equations of motion that we used in the numerical calculations, will be published elsewhere [23].

4. Concluding remarks

We have studied the absorption spectrum of molecular aggregates in which the molecules undergo stochastic frequency fluctuations. We have argued and shown by numerical calculations that exchange narrowing of the absorption line shape (i.e., collective narrowing due to the intermolecular transfer interactions) occurs not only in the static limit ($\lambda < \Delta$), but also in the motional narrowing regime ($\lambda > \Delta$). In the latter case, the fluctuations should not be fast compared to the excitation transfer (J), in order to see exchange narrowing. Even for $\lambda/J = 1$, however, this type of narrowing still plays a role, as is clear from Fig. 2. Our results answer affirmatively the question recently put forward by the authors of Ref. [18], namely whether exchange narrowing can occur in the fast-fluctuating limit.

The arguments presented in Section 2 show that for small aggregates the exchange narrowing in the fast-fluctuation limit occurs with a factor N, whereas in the static limit, the narrowing factor is $\sqrt{N}$. In both limits, however, this may be traced back to the same reduction of the fluctuation amplitude experienced by the excitons by a factor of $\sqrt{N}$. The difference is that in the static limit the line width eventually is proportional to the amplitude itself, while in the fast limit it is proportional to the amplitude squared. It should be noted that this $1/\sqrt{N}$ scaling of the average fluctuation amplitude only holds if the frequency fluctuations (static or dynamic) on different molecules are uncorrelated [4,5,25].

References

[1] E.E. Jelley, Nature 139 (1937) 631.
[2] G. Scheibe, Angew. Chem. 50 (1937) 212.
[3] S. de Boer, D.A. Wiersma, Chem. Phys. Lett. 165 (1990) 45.
[4] E.W. Knapp, Chem. Phys. 85 (1984) 73.
[5] J. Knoester, J. Chem. Phys. 99 (1993) 8466.
[6] H. Fidder, J. Knoester, D.A. Wiersma, J. Chem. Phys. 95 (1991) 7880.
[7] H. Fidder, J. Knoester, D.A. Wiersma, J. Chem. Phys. 98 (1993) 6564.
[8] T. Pullerits, M. Chachisvilis, V. Sundström, J. Phys. Chem. 100 (1996) 10 787
[9] K. Sauer et al., Photochem. Photobiol. 64 (1996) 564.
[10] T. Renger, V. May, Phys. Rev. Lett. 78 (1997) 3406.
[11] R. Kubo, M. Toda, N. Hashitsume, Statistical Physics II, Springer, Berlin, 1992.
[12] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford University Press, Oxford, 1995.
[13] E.T.J. Nibbering, D.A. Wiersma, K. Duppen, Phys. Rev. Lett. 66 (1991) 2464.

[14] E.T.J. Nibbering, D.A. Wiersma, K. Duppen, Phys. Rev. Lett. 68 (1992) 514.

[15] P. Reineker, in: G. Höhler (Ed.), Exciton Dynamics in Molecular Crystals and Aggregates, Springer, Berlin, 1988 and references therein.

[16] H. Haken, G. Strobl, Z. Phys. 262 (1973) 135.

[17] A. Blumen, R. Silbey, J. Chem. Phys. 69 (1978) 3589.

[18] M. van Burgel, D.A. Wiersma, K. Duppen, J. Chem. Phys. 102 (1995) 20.

[19] L.D. Bakalis, J. Knoester, J. Chem. Phys. 106 (1997) 6964.

[20] F.C. Spano, J. Phys. Chem. 96 (1992) 2843.

[21] P. Reineker, Ch. Warns, Th. Neidlinger, I. Barvik, Chem. Phys. 177 (1993) 715.

[22] I. Barvík, P. Reineker, Ch. Warns, Th. Neidlinger, J. Lumin. 65 (1995) 169.

[23] C.M. Wubs, J. Knoester, Chem. Phys. Lett., accepted for publication.

[24] At the smallest λ value for $N = 3$, the narrowing factor is slightly larger than 3, due to the fact that we have run out of the motional narrowing regime.

[25] J.R. Durrant, J. Knoester, D.A. Wiersma, Chem. Phys. Lett. 222 (1994) 450.