EFFECT OF INHOMOGENEOUS BROADENING ON THE OPTICAL LINE SHAPE OF MOLECULAR AGGREGATES [‡]

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We discuss the effect on the optical spectra of molecular aggregates of inhomogeneous broadening due to inequivalent medium sites. Previous theories, which do not explicitly include this effect, are re-examined, and an alternate approach to the calculation of optical properties is suggested.

1. Introduction

In recent years there has been great interest in the optical line shapes (absorption and circular dichroism, e.g.) of molecular aggregates. The form of the electronic hamiltonian is simple in most cases, so attention has focused on determination of the effects of vibronic interactions. This has been pursued from a number of perspectives, which we briefly summarize:

(1) Numerical calculation of line positions and intensities from a simple microscopic model [1,2].

(2) Formulation of sum rules as moment theorems for the vibronic line shape [2–4].

(3) Classical coupled-oscillator polarizability theory (or, equivalently, time-dependent Hartree theory with a suitable neglect of correlations) [3,5].
Recent work by Hemenger [6], also in the same spirit, uses the monomer absorption envelope as a direct input in the calculations (although the details of the approximations are different).

(4) Treatment of the exciton–phonon interaction as a stochastic time-dependent potential. This procedure starts from a microscopic hamiltonian, but at some point assumes rapid phonon relaxation described by an exponential correlation function [7].

Despite the increasing progress in development of the above theoretical methods, quantitative application to real systems has been problematic. This is particularly true when the aggregate is studied in a relatively disordered medium; liquid, glass, membrane, protein, etc. We suggest that, in such systems, it is necessary to explicitly consider the distribution of inequivalent (on the time scale of the experiment) sites and to average the line shape functions over this distribution. The importance of such inhomogeneous broadening is manifest theoretically (e.g. the rotational diffusion time in a typical liquid is 0.1 ps as compared with 10^{-8} s for the homogeneous linewidth of an optical excitation) and experimentally (e.g. in hole-burning experiments).

This paper is organized as follows. In section 2 we construct a simple conceptual framework for consideration of local inhomogeneity, and write down a formal line shape expression. We then examine the vibronic moment theorems, and show that the above considerations can produce substantial effects. We perform an elementary sample calculation on a linear exciton–phonon hamiltonian to illustrate the results. In section 3 we discuss some of the theories described above, discussing errrors which will occur as a result of neglect of inhomogeneous terms. We propose an alternate program for calculation of aggregate line shapes which we believe will generate correct quantitative results.

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2. Model hamiltonian; general formalism

We consider an ensemble of chemically identical aggregates in a disordered medium. The functional form of the hamiltonian corresponding to each system is uniform, but the parameter values may vary from system to system. We also divide the medium modes which interact with the aggregate into fast and slow modes. Fast modes are treated via the usual exciton–phonon interaction, while slow modes produce the static inhomogeneity. If we include only linear exciton–phonon coupling terms, the hamiltonian becomes

$$H = \sum \epsilon_i A_i^+ A_i + \sum_n \omega_n B_n^+ B_n + \sum_j \sum_i \sum_n g_{ij}^n \omega_n (B_n + B_n^+) A_i^+ A_j, \qquad (1)$$

where ϵ_i are the relevant electronic levels of the aggregate. We have grouped the molecular and medium vibrational modes together in the last two terms; ω_n are the frequencies, while g_{ij}^n is the exciton–phonon coupling parameter for vibrational mode in between levels i and j. A_i, A_i^+, B_i, B_i^+ are the usual exciton and phonon creation and annihilation operators. (Note that in this representation we have assumed the electronic part of the aggregate hamiltonian to be diagonal.)

Because of the inhomogeneous local perturbations, any of the parameters (ϵ, ω, g) can be different for the members of the ensemble: our assumption is that during the time scale of photon absorption the parameters remain constant at each site. Then we can consider a subensemble of aggregates with identical hamiltonians $H(\boldsymbol{p})$, where $\boldsymbol{p} = (\epsilon_1 \dots \epsilon_N, \omega_1 \dots \omega_N, g_{ij}^k, i, j, k)$. The linear response of such a subensemble is

$$R(\omega, \boldsymbol{p}) = \int_0^\infty \langle A(t)\, A(0) \rangle\, \mathrm{e}^{+\mathrm{i}\omega t}\, \mathrm{d}t, \qquad (2)$$

where A is the dynamical variable of interest. $A(t) = \mathrm{e}^{\mathrm{i}H(\boldsymbol{p})t} A\, \mathrm{e}^{-\mathrm{i}H(\boldsymbol{p})t}$ and the average $\langle\ \rangle_{\boldsymbol{p}}$ is a thermal average over the subensemble. The response of the entire system is an integral over the distribution function D of the parameters of $\boldsymbol{p}$;

$$\bar{R}(\omega) = \int_{-\infty}^{\infty} R(\omega, \boldsymbol{p})\, D(\boldsymbol{p})\, \mathrm{d}\boldsymbol{p}. \qquad (3)$$

The distribution of parameter values in the medium is easily given physical interpretation. The shifts in the energy levels ϵ_i is a result of different local electrostatic interactions with the various levels, while the existence of "local" modes due to different configurations of medium molecules may result in variation of g_{ij}^n and ω_n.

The kth moment of $\bar{R}(\omega)$ is

$$\bar{M}^k = \int_{-\infty}^{\infty} \omega^k\, \bar{R}(\omega)\, \mathrm{d}\omega = \int_{-\infty}^{\infty} D(\boldsymbol{p})\, \mathrm{d}\boldsymbol{p} \int_{-\infty}^{\infty} \omega^k\, R(\omega, \boldsymbol{p})\, \mathrm{d}\omega = \int_{-\infty}^{\infty} D(\boldsymbol{p})\, M^k(\boldsymbol{p})\, \mathrm{d}\boldsymbol{p}, \qquad (4)$$

where $M^k(\boldsymbol{p})$ is the kth moment of the line shape corresponding to $H(\boldsymbol{p})$. The latter are the moments calculated previously by a number of workers [8] and are obtained here if $D(\boldsymbol{p}) = \delta(\boldsymbol{p} - \boldsymbol{p}_0)$, i.e. the ensemble is homogeneous.

It is clear from eq. (3) that the dependence of the vibronic moments on the average microscopic parameters, $\bar{\boldsymbol{p}} = \int_{-\infty}^{\infty} D(\boldsymbol{p}) \cdot \boldsymbol{p}\, \mathrm{d}\boldsymbol{p}$, need not be that given by the homogeneous moment equations, i.e.

$$\bar{M}^k \neq M^k(\boldsymbol{p}). \qquad (5)$$

Thus in the case of inhomogeneous systems the previously derived moment theorems must be re-examined.

To examine this result more explicitly, we consider the hamiltonian for the exciton dimer composed of identical molecules, each with a single excited electronic state and vibrational mode linearly coupled to the excitation. After removal of one vibration via a canonical transformation (see ref. [9]), we have

$$H = J(A_+^* A_+ - A_-^* A_-) + \epsilon_0 (A_+^* A_+ + A_-^* A_-) + \omega B^+ B + g\omega (B + B^+)(A_+^* A_- + A_-^* A_+), \qquad (6)$$

where we utilize the ± electronic representation, ϵ_0 is the separation in energy of the monomer excited states from the ground state and J is the electronic exchange interaction. The parameters which can vary in this simple case are thus J, ϵ_0, ω and g.

The homogeneous moments for absorption, $M^k(\boldsymbol{p})$ are found from

$$M^k(p) = \int \mathrm{d}\omega\, \omega^k \int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} \langle \mu(t)\, \mu(0) \rangle$$

$$= \langle\langle 0 | [H, [H \ldots [H, \mu] \ldots]]\, \mu | 0 \rangle\rangle (-1)^k$$

$$\equiv \langle\langle 0 | \{(H^\times)^k \mu\}\, \mu | 0 \rangle\rangle (-1)^k; \qquad (7)$$

where $H^\times A \equiv [H, A]$ and the outer brackets represent a thermal average over the occupation of the ground vibrational states, $|0\rangle$ is the ground electronic state, and μ is the dipole operator:

$$\mu = \mu_+ (A_+ + A_+^*) + \mu_- (A_- + A_-^*), \qquad (8)$$

where $\mu_\pm = \langle 0 | \Sigma_i \boldsymbol{r}_i e | \pm \rangle$.

The first and second moments are

$$M^1(p) = \epsilon_0 (\mu_+^2 + \mu_-^2) + J(\mu_+^2 - \mu_-^2),$$

$$M^2(p) = [(\epsilon_0^2 + J^2) + g^2 \omega^2 (2\bar{n} + 1)(\mu_+^2 + \mu_-^2)$$

$$+ 2\epsilon_0 J (\mu_+^2 - \mu_-^2)], \qquad (9)$$

where $\bar{n} = (\mathrm{e}^{\beta\omega} - 1)^{-1}$. For notational convenience, we assume $\mu_+^2 + \mu_-^2 = 1$ and define $\hat{\mu} = \mu_+^2 - \mu_-^2$. Now, we assume that $D(p) = \Pi_i d(p_i)$ and we will evaluate the effect of the inhomogeneity in each of the parameters

$$\bar{M}^1 = \bar{\epsilon}_0 + \bar{J}\hat{\mu},$$

$$\bar{M}^2 = \overline{\epsilon_0^2} + \overline{J^2} + \overline{g^2}\, \langle (2\bar{n} + 1)\omega^2 \rangle + 2\bar{\epsilon}_0 \bar{J}\hat{\mu}, \qquad (10)$$

where the averages are taken over the separate distributions of the parameters.

These results indicate that, in general, there is no simple set of relations connecting even the lowest moments $\bar{M}^k$ of the aggregate with those of the monomer, as is the case for the homogeneous moments, M^k.

Suppose, for example, that $\bar{\epsilon}_{0_\mathrm{d}} = \bar{\epsilon}_{0_\mathrm{m}} = \bar{\epsilon}_0$ (the subscript d will denote dimer parameters while the subscript m will denote monomer parameters), and there is no distribution in J, g, or ω for either the monomer or dimer. The homogeneous monomer moments are

$$M_\mathrm{m}^1 = \bar{\epsilon}_0, \quad M_\mathrm{m}^2 = g^2 (2\bar{n} + 1). \qquad (11)$$

(Note that we assume ω, g are identical for monomer and dimer.)

The relation between the *homogeneous* monomer and dimer moments is

$$M_\mathrm{d}^2 - (M_\mathrm{d}^1)^2 - J^2 (1 - \hat{\mu}) = M_\mathrm{m}^2 - (M_\mathrm{m}^1)^2, \qquad (12)$$

while for an inhomogeneous distribution of ϵ_0, we have instead

$$M_\mathrm{d}^2 - (M_\mathrm{d}^1)^2 - J^2 (1 - \hat{\mu})$$

$$= \overline{\epsilon_{0_\mathrm{d}}^2} + g^2 \omega^2 (2\bar{n} + 1) - (\bar{\epsilon}_0)^2,$$

$$M_\mathrm{m}^2 - (M_\mathrm{m}^1)^2 = \overline{\epsilon_{0_\mathrm{m}}^2} - (\bar{\epsilon}_0)^2 + g^2 \omega^2 (2\bar{n} + 1). \qquad (13)$$

Thus if $\overline{\epsilon_{0_\mathrm{d}}^2} \neq \overline{\epsilon_{0_\mathrm{m}}^2}$ (quite likely in real systems, as the distribution of environmental configurations will be different for the dimer), the moment theorem of eq. (11) is no longer valid.

A second point is that the functional form of the temperature dependence of the second moment will be affected by the inhomogeneous distribution. Instead of

$$M_\mathrm{d}^2 \propto (\mathrm{e}^{\beta\omega} - 1)^{-1}, \qquad (14)$$

we have

$$M_\mathrm{d}^2 \propto \int \mathrm{d}\omega (\mathrm{e}^{\beta\omega} - 1)^{-1} \omega^2 \qquad (15)$$

Similarly, attempts to determine $\bar{J}$ from eq. (10) may produce erroneous results if J^2 is replaced by $(\bar{J})^2$ in eq. (10).

The full absorption spectrum of the exciton dimer described by the above hamiltonian is in general complex, and the line shape is qualitatively affected by many higher moments than the second. For these moments, failure to include inhomogeneous broadening leads to important effects. As an illustration of this, we consider the following two sets of monomer parameters;

(1) $g/2^{1/2} = 0.1, \quad \omega = 1,$

$$d_\mathrm{m}(\epsilon_0) = (\pi/\Delta_1) \exp(-\epsilon_0^2/\Delta_1^2),$$

$$\Delta_1 = 3.6, \quad \beta = 1/RT = 0.1;$$

(2) $g/2^{1/2} = 0.5, \quad \omega = 1,$

$$d_\mathrm{m}(\epsilon_0) = (\pi/\Delta_2) \exp(-\epsilon_0^2/\Delta_2^2),$$

$$\Delta_2 = 2.0, \quad \beta = 1/RT = 0.1.$$

Each of these will yield the same monomer absorption spectrum. Now consider the dimer spectra that may arise from each of these two systems, which we com-

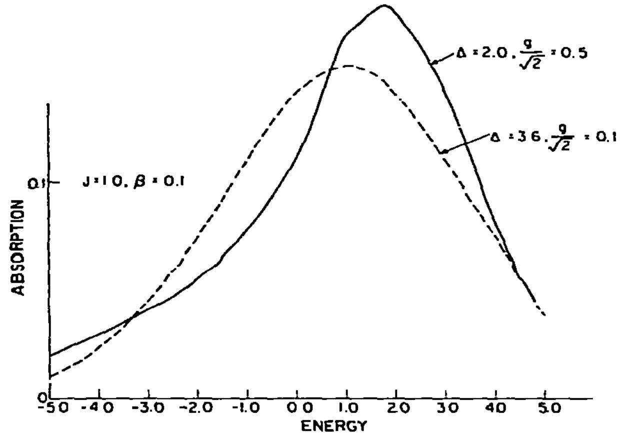

Fig. 1. Comparison of dimer absorption spectra generated from two sets of monomer parameters. The absorption is normalized to 1; energy is in units of $\hbar\omega$.

pute via numerical diagonalization of eq. (6). We take $J = 1.0$, $\omega = 1.0$, $g_d = g_m$, $|\mu_+|^2 = 1$, $|\mu_-|^2 = 0$, and $\Delta_d = \Delta_m$ in each case. In fig. 1 we compare the resultant dimer spectra for each case. Even here, where the first and second moments are identical, the spectra are qualitatively different. Independent variation of Δ_d would produce an entire range of possible dimer spectra from a single set of monomer parameters. Thus, from one monomer spectrum, quite different dimer spectra can be generated, depending on the analysis of the monomer spectrum into vibronic and inhomogeneous contributions to the linewidth, and the choice of Δ_d. These calculations show clearly that, even for this very simple system, theories which fail to consider monomer and aggregate inhomogeneous distributions explicitly are incapable of reliably predicting aggregate spectra from monomer spectra.

3. Discussion

We will now discuss some of the approaches to actual line shape calculations described in section 1. The most elementary is simple exciton theory; line spectra are calculated from the electronic hamiltonian, and convoluted with broadening functions. It can be seen that in our formalism this corresponds to the limit $g_{ij}^n \to 0$, all i, j, n, so that the entire linewidth is due to inhomogeneous broadening of the electronic levels ϵ_i.

Polarizability theory has been shown to be inadequate in the strong coupling regime even within the context of the physical model [6,8]. Our criticism here, though, is of a basic feature of the method; use of the monomer absorption spectrum to directly compute aggregate optical properties. This procedure requires that both the monomer and aggregate be subject to negligible inhomogeneous broadening, an assumption which is clearly invalid without suitable experimental demonstration. The observed monomer spectrum is unlikely to reasonably represent the polarizability of the monomers in every aggregate. Furthermore, the ensemble of aggregates itself has an inhomogeneous distribution which must be properly averaged over.

The DGS theory proposed by Hemenger [6] is subject to the same criticism. It also takes the experimental monomer spectrum to accurately reflect a sum over Franck–Condon factors in the aggregate. A particularly problematic application of the theory has been to chlorophyll aggregates in a medium (protein) quite different from the one in which monomer spectra have been measured [10]. Here, there is no reason to believe in the equivalence of inhomogeneous effects.

Thus the two procedures described above represent opposite extreme limits of eq. (3); one in which $g_{ij}^n \to 0$, the other in which $D(p) \to \delta(p - p_0)$. As neither of these approximations is likely to be satisfactory, we propose an alternative program in which an attempt is made to realistically evaluate eq. (3).

(1) Determine the molecular exciton–phonon constants from monomer spectra via temperature dependence and/or matrix isolation spectroscopy which resolves vibronic peaks.

(2) Treat medium phonons stochastically or with a mean field approximation.

(3) Determine the aggregate inhomogeneous broadening from a study of temperature dependence of various experiments and from details of the aggregate optical line shape.

(4) Use an approximate analytic theory to obtain vibronic levels for the molecular exciton–phonon hamiltonian [9].

(5) Combine (1)–(4) to calculate a final, temperature-dependent line shape which can be compared with experiment [11].

This is a complicated and difficult set of tasks which may at first be practicable only with dimers.

However, we believe it to be the only approach which is likely to produce quantitatively accurate interpretations of experimental data.

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