

phys. stat. sol. (b) **189**, 67 (1995)

Subject classification: 71.35 and 78.20; S12

*Department of Chemistry and Center for Photoinduced Charge Transfer,
University of Rochester¹*

Level Correlations and Dephasing-Induced Resonances in Molecular Aggregates

By

V. CHERNYAK and S. MUKAMEL

Dephasing-induced resonances in the nonlinear optical response of molecular aggregates are expressed in terms of level correlations. The third-order optical response is related to the three-dimensional spectral density function $\chi(\epsilon', \epsilon, \epsilon'')$. Expressions for $\chi(\epsilon', \epsilon, \epsilon'')$ derived using the Frenkel exciton model show the existence of collective (dephasing-induced) resonances.

1. Introduction

Studies of linear and nonlinear optical properties of molecular aggregates and nanostructures are of considerable interest [1]. Properties of electronic states in geometrically confined nanostructures are very different from macroscopic systems. The electronic-state structure of molecular aggregates can be described in terms of the Frenkel exciton model. Since the exciton bandwidth is much smaller than the molecular transition frequency, one can use the Hamiltonian in the Heitler-London approximation [2] where the number of excitons is conserved, the ground state is the vacuum state with no excitons, and the linear optical response is determined by properties of one-exciton states alone. The third-order nonlinear optical response, which controls techniques such as pump probe and hole burning spectroscopy depends on one- as well as two-exciton states. Therefore, if one does not take into account additional degrees of freedom, such as nuclear motions, the optical response becomes a finite-body problem. It is then possible to derive exact expressions for the third-order optical response by means of various methods: diagonalization of the Frenkel exciton Hamiltonian [3], equations of motion for one- and two-exciton variables [4], and Green function techniques [5]. The situation becomes more complicated if we include additional degrees of freedom such as intramolecular, intermolecular, and solvent nuclear motions. In this case the calculation becomes a genuine many-body problem.

In this paper we address the relations between the resonances in the nonlinear optical response functions and collective properties of the aggregate eigenstates. The optical response functions can be expressed using either the global eigenstates of the system containing all degrees of freedom, or using the eigenstates of a reduced system containing the electronic degrees of freedom alone. For the first description one can either start with the time-dependent Schrödinger equation for the wave function or with the Liouville equation for the density matrix. Both approaches give identical expressions for the response functions. However, these expressions contain a large number of terms, and there is no simple correspondence between individual terms obtained using both approaches [6]. If we adopt

¹) Rochester, NY 14627, USA.

a reduced description, we can only use the density matrix since a reduced wave function is not a useful object. Other degrees of freedom show up in the reduced description in the form of dephasing and relaxation superoperator in the equations of motion for the reduced density matrix. The main advantage of the reduced description is that the equations of motion for the reduced density matrix are simpler.

For some applications for many-body systems it may be preferable, however, to adopt the first approach which is based on the global eigenstates of the system. Within this approach we can consider effects of dephasing related to processes which conserve the number of excitons through level correlations, treating the exciton lifetime (exciton annihilation) phenomenologically.

2. Kramers-Kronig Representation of $\chi^{(3)}$

Let E_i be the eigenvalues of the total Hamiltonian and P_{ij} the matrix elements of the polarization operator. The wave function expression for the third-order nonlinear optical susceptibility is (we set $\hbar = 1$) [6, 7]

$$\begin{aligned} \chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) &= \sum_{\text{perm}} \sum_{abcd} P_{ac} P_{cd} P_{ab} P_{ba} Q_{aa} \\ &\times \left\{ \frac{1}{\omega_1 - (E_b - E_a) + i\eta} \frac{1}{\omega_1 + \omega_3 - (E_d - E_a) + i\eta} \frac{1}{\omega_s - (E_c - E_a) + i\eta} \right. \\ &\quad \left. + \frac{1}{\omega_1 - (E_b - E_a) + i\eta} \frac{1}{\omega_1 + \omega_3 - (E_d - E_a) + i\eta} \frac{1}{\omega_2 - (E_c - E_a) - i\eta} \right\} \\ &+ \text{c.c.} \end{aligned} \quad (1)$$

$\chi^{(3)}$ has resonances related to the vanishing of the denominators in the right-hand side of (1). These resonances, related to specific energy levels, are the only resonances which can exist in a small system, and will be denoted ‘‘simple resonances’’. However, systems with a very large number of degrees of freedom such as an aggregate in a solvent, can have resonances of a very different origin: the infinite sums in the right-hand side of (1) can diverge for certain values of the frequencies $\omega_1, \omega_2, \omega_3$. We will denote resonances of this type which cannot be attributed to a particular pair of levels as ‘‘collective’’. These resonances originate from specific correlations between energy levels, i.e., from energy level statistics. The properties of level statistics which affect the third-order nonlinear optical response can be expressed in terms of a multi-dimensional spectral density $\varkappa(\varepsilon', \varepsilon, \varepsilon'')$, which depends on three energy variables

$$\varkappa(\varepsilon', \varepsilon, \varepsilon'') = (2\pi)^3 \sum_{abcd} Q_{da} P_{da} P_{ac} P_{cb} P_{bd} \delta(\varepsilon' - E_b) \delta(\varepsilon - E_c) \delta(\varepsilon'' - E_a), \quad (2a)$$

\varkappa can also be defined in operator form,

$$\varkappa(\varepsilon', \varepsilon, \varepsilon'') = (2\pi)^3 \text{Tr} \{ Q \hat{P} \delta(\varepsilon'' - \hat{H}) \delta(\varepsilon - \hat{H}) \hat{P} \hat{P} \delta(\varepsilon' - \hat{H}) \hat{P} \}. \quad (2b)$$

Using this spectral density, we can then recast (1) as²⁾

²⁾ For clarity, we consider an aggregate with size much smaller than the wavelength. In this case we can make the dipole approximation and the polarization \hat{P} is given by the dipole operator $\hat{P} \equiv \int d\mathbf{r} \hat{P}(\mathbf{r})$. All our expressions can be easily generalized for an aggregate with arbitrary size; the spectral density \varkappa will then be also a function of four coordinates.

$$\begin{aligned} \chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) &= \sum_{\text{perm}} \int \frac{d\varepsilon'}{2\pi} \frac{d\varepsilon''}{2\pi} \frac{d\varepsilon}{2\pi} \kappa(\varepsilon', \varepsilon, \varepsilon'') \\ &\times \left\{ \frac{1}{\omega_1 - \varepsilon' + i\eta} \frac{1}{\omega_1 + \omega_3 - \varepsilon + i\eta} \frac{1}{\omega_s - \varepsilon'' + i\eta} \right. \\ &\quad \left. + \frac{1}{\omega_1 - \varepsilon' + i\eta} \frac{1}{\omega_1 + \omega_3 - \varepsilon + i\eta} \frac{1}{\omega_2 - \varepsilon'' - i\eta} + \text{c.c.} \right\}. \end{aligned} \quad (3)$$

Equation (3) is a Kramers-Kronig representation for the third-order response function. It guarantees the correct analytical properties of $\chi^{(3)}$ for arbitrary spectral density functions $\kappa(\varepsilon', \varepsilon, \varepsilon'')$. All properties of the level statistics are now incorporated in this function.

The time-domain correlation functions which are useful in the description of femtosecond measurements [8] can be obtained using a Fourier transform

$$\begin{aligned} \kappa(\varepsilon', \varepsilon, \varepsilon'') &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\tau_1 d\tau_2 d\tau_3 \text{Tr} [\hat{P}(\tau_1 + \tau_2 + \tau_3) \hat{P}(\tau_1 + \tau_2) \hat{P}(\tau_1) \hat{P}(0) \hat{\rho}] \\ &\quad \times \exp(i\varepsilon'\tau_1 + i\varepsilon\tau_2 + i\varepsilon''\tau_3), \end{aligned} \quad (4)$$

where $\hat{\rho}$ is the equilibrium density matrix.

3. Multidimensional Spectral Density of a Molecular Aggregate

We adopt a model of a molecular aggregate with exciton–phonon interaction, and size smaller than the optical wavelength but sufficiently large so that the separation between exciton states is much smaller than the absorption linewidth. The Hamiltonian can be written in momentum space in a form

$$\begin{aligned} \hat{H}_{\text{mat}} &= \int d\mathbf{q} \{ \varepsilon(\mathbf{q}) \hat{B}_{\mathbf{q}}^+ \hat{B}_{\mathbf{q}} + \Omega(\mathbf{q}) \hat{b}_{\mathbf{q}}^+ \hat{b}_{\mathbf{q}} \} \\ &\quad + \int d\mathbf{q} d\mathbf{p} \{ V(\mathbf{q}, \mathbf{q} - \mathbf{p}) \hat{B}_{\mathbf{p}}^+ \hat{B}_{\mathbf{q}} \hat{b}_{\mathbf{q}-\mathbf{p}}^+ + V^*(\mathbf{q}, \mathbf{q} - \mathbf{p}) \hat{B}_{\mathbf{q}}^+ \hat{B}_{\mathbf{p}} \hat{b}_{\mathbf{q}-\mathbf{p}} \}, \end{aligned} \quad (5)$$

where B , B^+ and b , b^+ are the the Frenkel exciton and phonon operators, respectively.

The four-point correlation function in (4) can be evaluated using the Green function technique on a four-component time loop introduced in [8] (generalization of the Keldysh time loop). For an arbitrary set of operators $\hat{Q}^{(1)}, \dots, \hat{Q}^{(n)}$ in the system described by (5) we introduce the chronologically ordered Green functions on the four-component time loop as follows:

$$\langle \hat{Q}_{\alpha_1}^{(1)}(\tau_1) \dots \hat{Q}_{\alpha_n}^{(n)}(\tau_n) \rangle \equiv \text{Tr} \{ T[\hat{Q}_{\alpha_1}^{(1)}(\tau_1) \dots \hat{Q}_{\alpha_n}^{(n)}(\tau_n)] \hat{\rho} \}, \quad (6)$$

where the Greek indices α assume the values $\alpha = 1, 2, 3, 4$ and T is the ordering operator which puts the operators $Q^{(1)}(\tau_1), \dots, Q^{(n)}(\tau_n)$ in the following order, from the right to the left (i.e., in the order of acting on $\hat{\rho}$): first operators \hat{Q}_{α} with $\alpha = 1$ chronologically ordered then operators with $\alpha = 2$ antichronologically ordered, then operators with $\alpha = 3$ chronologically ordered, and finally operators with $\alpha = 4$ antichronologically ordered. The Green functions in (6) are chronologically ordered with respect to a “time” parameter on a four-component time loop shown in Fig. 1, which makes it possible to use perturbative

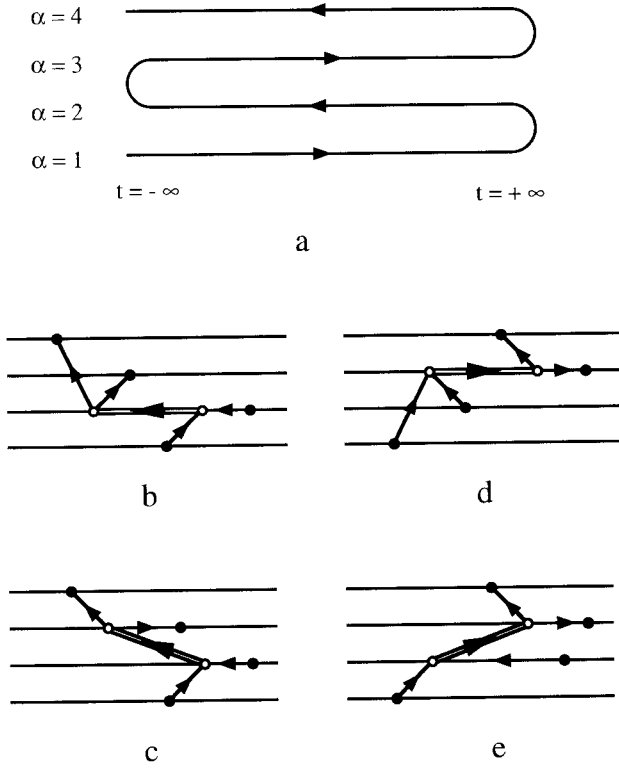


Fig. 1. a) The four-component time loop which makes the Green functions in (6) chronologically ordered. b) to e) All possible skeleton diagrams (i.e., without phonon lines) contributing to the Green function in (7) with respect to positions of time arguments on the four-component time loop

techniques based on the Wick theorem [9, 10]. In the notation of (6), (4) becomes

$$\begin{aligned} \kappa(\varepsilon', \varepsilon, \varepsilon'') = & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \langle \hat{P}_4(\tau_1 + \tau_2 + \tau_3) \hat{P}_3(\tau_1 + \tau_2) \hat{P}_2(\tau_1) \hat{P}_1(0) \rangle \\ & \times \exp(i\varepsilon'\tau_1 + i\varepsilon\tau_2 + i\varepsilon''\tau_3). \end{aligned} \quad (7)$$

If phonons are neglected the Green function in (7) can be written in a form of a sum of four contributions [8, 11] presented diagrammatically in Fig. 1b to e, where a solid line stands for the one-exciton Green function G and a double line denotes the two-exciton scattering matrix \bar{F} . We can take into account exciton-phonon interaction perturbatively, including higher-order contributions only if they are compensated by large resonant factors in the frequency domain calculations [11]. This means that all diagrams in Fig. 1b to e should be „dressed” with wavy lines which denote the bare phonon Green functions as shown in Fig. 2a. The sum of the ladder diagrams in Fig. 2a presented in Fig. 2b can be expressed in terms of the Green function of the Boltzmann equation. After some tedious but straightforward calculations, we obtain the following expression for the spectral density³⁾:

$$\kappa = \kappa_1 + \kappa_2 + \kappa_3 \quad (8)$$

with

$$\kappa_1(\varepsilon', \varepsilon, \varepsilon'') = 4\pi\mu^4 \text{Im } G(\varepsilon') \text{Im } G(\varepsilon'') \{G(\varepsilon - \varepsilon') G(\varepsilon - \varepsilon'') \bar{F}(\varepsilon) - \text{c.c.}\}, \quad (9a)$$

³⁾ There is an additional term in κ which does not contribute to the optical response and was neglected.

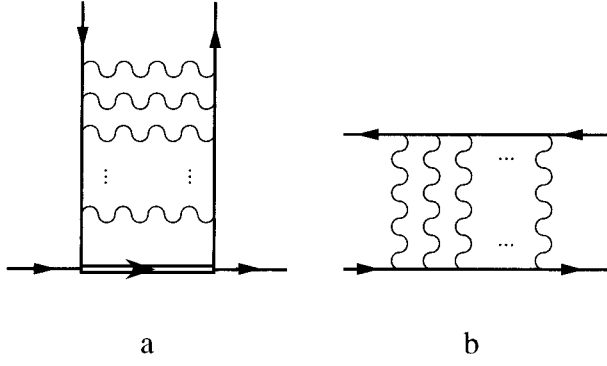


Fig. 2. a) "Dressing" a skeleton diagram with phonon (wavy) lines. b) Ladder diagrams which appear in a) and yield the Green function of the Boltzmann equation

$$\begin{aligned} \kappa_2(\varepsilon', \varepsilon, \varepsilon'') &= 4\pi\mu^4 C \int d\mathbf{p} g(\mathbf{p}, 0; \varepsilon') \frac{\Gamma_0}{(\varepsilon'' - \varepsilon')^2 + \Gamma_0^2} \\ &\times \left\{ G(\varepsilon') G^*(\varepsilon'') G(\varepsilon - \varepsilon') G(\varepsilon - \varepsilon'') \right. \\ &\times \left. \int d\mathbf{q} \exp\left[-\frac{\varepsilon(\mathbf{q})}{kT}\right] \bar{\Gamma}(\varepsilon - \varepsilon' + \varepsilon(\mathbf{q}), \mathbf{q}) - \text{c.c.} \right\} \end{aligned} \quad (9b)$$

$$\begin{aligned} \kappa_3(\varepsilon', \varepsilon, \varepsilon'') &= 4\pi\mu^4 \sum_{\alpha \neq 0} \int d\mathbf{p} \varphi_\alpha^{-1}(\mathbf{p}) g(\mathbf{p}, 0; \varepsilon') \frac{\lambda_\alpha}{(\varepsilon'' - \varepsilon')^2 + \lambda_\alpha^2} \\ &\times \left\{ G(\varepsilon') G^*(\varepsilon'') G(\varepsilon - \varepsilon') G(\varepsilon - \varepsilon'') \right. \\ &\times \left. \int d\mathbf{q} \varphi_\alpha(\mathbf{q}) \bar{\Gamma}(\varepsilon - \varepsilon' + \varepsilon(\mathbf{q}), \mathbf{q}) - \text{c.c.} \right\}. \end{aligned} \quad (9c)$$

In (9) μ is the molecular dipole moment, $G(\omega) \equiv G(\omega, \mathbf{q} = 0)$, $\bar{\Gamma}(\omega) \equiv \bar{\Gamma}(\omega, \mathbf{q} = 0)$, $G(\omega, \mathbf{q})$ and $\bar{\Gamma}(\omega, \mathbf{q})$ are the exciton Green function and two-exciton scattering matrix,

$$G(\omega, \mathbf{q}) = \left[\omega - \varepsilon(\mathbf{q}) + \frac{i}{2} \int d\mathbf{p} f(\mathbf{p}, \mathbf{q}) \right]^{-1}, \quad (10a)$$

$$\bar{\Gamma}(\omega, \mathbf{q}) = -2 \left\{ \int \frac{d\omega'}{2\pi i} d\mathbf{p} G(\omega', \mathbf{p}) G(\omega - \omega', \mathbf{q} - \mathbf{p}) \right\}^{-1}. \quad (10b)$$

Γ_0 is the inverse exciton lifetime, T the temperature, and C is given by

$$C \equiv \int d\mathbf{p} \exp\left[-\frac{\varepsilon(\mathbf{p})}{kT}\right]. \quad (10c)$$

φ_α are the eigenmodes of the operator L , with eigenvalues λ_α defined as

$$Ln(\mathbf{p}) \equiv \left\{ \int d\mathbf{p}' f(\mathbf{p}, \mathbf{p}') n(\mathbf{p}') - n(\mathbf{p}) \int d\mathbf{p}' f(\mathbf{p}', \mathbf{p}) \right\}, \quad (10d)$$

$\varphi_x(\mathbf{p})$ are the matrix elements of the transformation from $|\mathbf{p}\rangle$ to $|\alpha\rangle$ modes, $\varphi_x^{-1}(\mathbf{p})$ are the matrix elements of the inverse transformation. The functions f and g are

$$f(\mathbf{p}, \mathbf{p}') = |V(\mathbf{p}', \mathbf{p}' - \mathbf{p})|^2 (1 + N_{\Omega(\mathbf{p}' - \mathbf{p})}) \delta[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}') - \Omega(\mathbf{p}' - \mathbf{p})] \\ + |V(\mathbf{p}, \mathbf{p} - \mathbf{p}')|^2 N_{\Omega(\mathbf{p} - \mathbf{p}')} \delta[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}') - \Omega(\mathbf{p} - \mathbf{p}')], \quad (10e)$$

$$g(\mathbf{p}, \mathbf{q}_0; \Omega) = |V(\mathbf{q}_0, \mathbf{q}_0 - \mathbf{p})|^2 (1 + N_{\Omega(\mathbf{q}_0 - \mathbf{p})}) \delta[\Omega - \varepsilon(\mathbf{p}) - \Omega(\mathbf{q}_0 - \mathbf{p})] \\ + |V(\mathbf{p}, \mathbf{p} - \mathbf{q}_0)|^2 N_{\Omega(\mathbf{p} - \mathbf{q}_0)} \delta[\Omega - \varepsilon(\mathbf{p}) + \Omega(\mathbf{p} - \mathbf{q}_0)], \quad (10f)$$

where N_Ω are the Bose occupation numbers

$$N_\Omega = \left[\exp\left(\frac{\Omega}{kT}\right) - 1 \right]^{-1}. \quad (10g)$$

κ_1 is related to contributions of one-exciton states with energies ε' and ε'' not too close. κ_2 describes the contribution when these two states coincide (self-correlation), in the absence of damping, i.e., for $\Gamma_0 = 0$ the contribution is proportional to $\delta(\varepsilon' - \varepsilon'')$. The third term κ_3 is important when $|\varepsilon' - \varepsilon''|$ is comparable to the exciton-phonon dephasing rate, and describes the correlation between one-exciton levels in the multi-dimensional spectral density function κ .

These three terms in κ , when substituted into the Kramers-Kronig representation (3) give three contributions to the optical response function $\chi^{(3)}$. The first contribution contains simple resonances only, related to one- and two-exciton states. The second contribution has a sharp collective resonance with respect to $\omega_1 - \omega_2$:

$$\chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) \propto \frac{\Gamma_0}{(\omega_1 - \omega_2)^2 + \Gamma_0^2}.$$

This degenerate four-wave mixing resonance is related to the self-correlation of the level with the width determined by the lifetime. The third contribution is responsible for a resonance in $\omega_1 - \omega_2$ with a width given by the dephasing rate. This is an additional collective resonance related to one-exciton level correlation.

4. Summary

In summary, there are two types of resonances in the optical response function of aggregates: simple and collective. Collective resonances are not related to individual pairs of states, but originate from specific level correlations which are described by resonances in the multi-dimensional spectral density function κ . This picture provides a new way of describing dephasing-induced resonances in aggregates. In disordered molecular aggregates there is an additional contribution to κ which gives resonances at $\varepsilon = 2\varepsilon'$ and $\varepsilon = 2\varepsilon''$ and describes correlations between one- and two-exciton states (for each one-exciton state with energy ε' there is a two-exciton state with energy $\varepsilon = 2\varepsilon'$). This correlation leads to a resonance at $2\omega_2 = \omega_1 + \omega_3$ in $\chi^{(3)}$, which is related to a two-exciton photon echo, and may be observed in time domain nonlinear spectroscopy [11].

Acknowledgement

The support of the NSF Center for Photoinduced Charge Transfer at the University of Rochester is gratefully acknowledged.

References

- [1] J. ZYSS and D. S. CHEMLA, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, Academic Press, Orlando (Florida) 1987 (p. 23).
- [2] A. S. DAVYDOV, *Theory of Molecular Excitons*, Plenum Press, New York 1971.
- [3] V. A. AGRANOVICH, *Soviet Phys. — Solid State* **12**, 430 (1970).
- [4] F. C. SPANO and S. MUKAMEL, *Phys. Rev. Letters* **66**, 1197 (1991).
J. A. LEEGWATER and S. MUKAMEL, *Phys. Rev. A* **46**, 452 (1992).
- [5] V. CHERNYAK and S. MUKAMEL, *J. chem. Phys.* **100**, 2953 (1994).
- [6] N. BLOEMBERGEN, H. LOTEM, and R. T. LYNCH, *Indian J. pure appl. Phys.* **16**, 151 (1978).
- [7] S. MUKAMEL, *Principles of Nonlinear Optical Spectroscopy*, Oxford/New York 1995.
- [8] N. WANG, V. CHERNYAK, and S. MUKAMEL, *J. chem. Phys.* **100**, 2465 (1994).
- [9] A. A. ABRIKOSOV, L. P. GORKOV, and I. YE. DZYALOSHINSKII, *Quantum Field Theoretical Methods in Statistical Physics*, Oxford/New York 1965.
- [10] E. M. LIFSHITS and L. P. PITAEVSKII, *Physical Kinetics*, Pergamon Press, Oxford/New York 1981.
- [11] V. CHERNYAK, N. WANG, and S. MUKAMEL, *Physics Rep.*, in the press.

(Received November 21, 1994; in revised form February 22, 1995)