Two-Exciton Collective Photon Echoes in Disordered Molecular Nanostructures

Vladimir Chernyak and Shaul Mukamel
Department of Chemistry, University of Rochester, Rochester, New York 14627
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A new disorder-induced two-exciton photon echo and its frequency-domain counterpart, a narrow four-photon extra resonance, are predicted in molecular aggregates. These effects are induced by the combined influence of aggregation and inhomogeneous broadening and provide a direct signature for the strong correlation between one- and two-exciton levels.

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The nature of electronic excitations and of excitonic nanostructures (clusters, quantum wells, and superlattices) are currently drawing considerable attention [1–3]. Some clear optical signatures of geometric confinement include cooperative radiative decay, nonlinear response enhancement, and two-exciton resonances [2–5]. The electronic structure of an assembly of two-level molecules can be described by the Frenkel exciton Hamiltonian: $\hat{H} = \sum_{mn} \hat{h}_{mn} \hat{B}_m^\dagger \hat{B}_n$, with $\hat{h}_{nm} = \Omega_n \delta_{nm} + J_{nm}$ [6]. Here $\hat{B}^\dagger$ ($\hat{B}$) are exciton creation (annihilation) operators which satisfy the Pauli commutation rule $[B_n^\dagger, B_m] = (1 - 2B_n^\dagger B_n)\delta_{mn}$. Ω_n is the excitation energy of the nth molecule and J_{nm} is the hopping matrix element. We assume a dipole interaction with the radiation field, where the dipole operator is $\mu \sum_n (B_n + B_n^\dagger)$ and μ is the molecular dipole moment.

It is possible to derive exact expressions for the optical response functions using Green function techniques. The linear susceptibility of an aggregate with size much smaller than the optical wavelength, determined by properties of one-exciton states alone, is given by $\chi^{(1)}(\omega) = \mu^2 \sum_{mn} [G_{mn}(\omega) + G_{nm}^*(-\omega)]$, and G is the one-exciton Green function $G(\omega) = (\omega - \hat{h} + \frac{1}{2} i\eta)^{-1}$. The width η represents finite exciton lifetime or homogeneous dephasing. The third-order response depends on one- and two-exciton states and is given by

$$\chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) = \mu^4 \sum_{\text{perm}} \sum_{\substack{nm_1m_2m_3 \\ n'n''}} G_{nn'}(\omega_s) G_{n'm_2}^*(\omega_2) G_{n''m_3}(\omega_3) \times G_{n''m_1}(\omega_1) \overline{\Gamma}_{n'n''}(\omega_1 + \omega_3) + \text{c.c.}, \quad (1)$$

where $\omega_s = \omega_1 - \omega_2 + \omega_3$ is the signal frequency and $\overline{\Gamma}$ is the two-exciton scattering matrix

$$\overline{\Gamma}_{mn}(\omega) = -2[F(\omega)^{-1}]_{mn},$$

$$F_{mn}(\omega) \equiv \int \frac{d\omega'}{2\pi i} G_{mn}(\omega') G_{mn}(\omega - \omega'). \quad (2)$$

Disorder often exists in organic molecular assemblies due to their relatively weak intermolecular forces [1,7]. We assume that the two-level molecules form a d-dimensional lattice ($d = 1, 2, 3$) with periodic boundary conditions $\Omega_n = \Omega_n^0 + \delta\Omega_n$ and $J_{nm} = J_{nm}^0 + \delta J_{nm}$, where J_{mn}^0 (which depends only on $m - n$), together with $\Omega_n^0 = \Omega$, correspond to a reference system without disorder, and $\delta\Omega$ and δJ represent diagonal and off-diagonal static disorder, respectively, and have a given statistical distribution. We will denote the averaging over realizations of the disorder parameters $\delta\Omega_n$ and δJ_{mn} by $\langle \cdots \rangle$. We also assume that disorder is sufficiently weak so that the disorder-induced exciton scattering rate Γ_e is small compared with the exciton bandwidth W, and it is sufficiently strong so that Γ_e is larger than the average spacing between exciton levels ΔE, $\Delta E \ll \Gamma_e \ll W$. This condition holds in typical cases: The bandwidth W in molecular aggregates is typically a few hundred cm^{-1} (e.g., 600 cm^{-1} for J aggregates and 1000 cm^{-1} for anthracene) [6(b)]. The spacing between the exciton levels is $\Delta E \sim W/N$, where N is the number of molecules. The exciton scattering rate Γ_e has the magnitude of the inhomogeneous absorption linewidth which usually varies between 1 and 500 cm^{-1}. Hereafter, we shall assume Gaussian diagonal disorder whereby $\delta J_{nm} = 0$, $\langle \delta\Omega_n \rangle = 0$, and $\langle \delta\Omega_n \delta\Omega_m \rangle = \sigma^2 \delta_{nm}$. Weak disorder implies in this case $\sigma/W \ll 1$. However, the following derivation holds for a more general model of disorder, and the final expressions are not sensitive to the particular model of disorder.

To average Eq. (1) over disorder, we first expand the Green functions G and the scattering matrix $\overline{\Gamma} = -2F^{-1}$ in powers of $\delta\Omega$. Each term in the expansion contains a product of several Green functions G and $\overline{\Gamma}$ calculated for the reference ordered system. These can be represented by the diagrams shown in Fig. 1(a), where the solid single and double lines stand for G and $\overline{\Gamma}$, respectively, and the dashed lines (which connect only the single lines) stand for $\langle \delta\Omega_m \delta\Omega_n \rangle$. The number of loops in a diagram corresponds to the power of δF in the expansion of $\overline{\Gamma} = -2F^{-1}$ in δF, which in turn is related to $\delta\Omega$. The number of dashed lines connected to a loop is equal to the power of $\delta\Omega$ in the expansion of $F(\omega)$ [Eq. (2)] and should be at least one since the expansion of δF starts with the first power of $\delta\Omega$. The number of dashed lines connected to an external line corresponds to the order of the expansion of a one-exciton Green function in Eq. (1) in powers of $\delta\Omega$. It is possible to resum the diagrams by including in a renormalized $\overline{\Gamma}$ all loops not connected to other parts

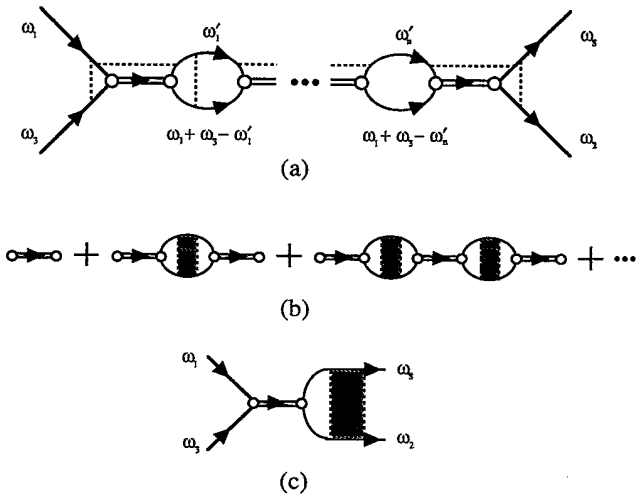

FIG. 1. (a) Diagrams contributing to $\langle\chi^{(3)}(-\omega_s;\omega_1,-\omega_2,\omega_3)\rangle$. Solid lines stand for the one-exciton Green functions G, double lines for the two-exciton scattering matrix $\overline{\Gamma}$, and dashed lines represent the correlation functions of disorder. (b) Diagrams contributing to the renormalized two-exciton scattering matrix. (c) Diagrams contributing to the two-exciton photon echo. Dashed lines connect the Green functions $G^*(\omega_2)$ and $G(\omega_s)$ in all possible ways.

of the diagram with dashed lines [see Fig. 1(b)]. The renormalized $\overline{\Gamma}$ is then given by $\overline{\Gamma}(\omega) = -2\langle F(\omega)\rangle^{-1}$. Using this $\overline{\Gamma}$ for the double line, we should exclude all diagrams containing loops not connected to other parts of the diagram with dashed lines.

We shall consider the third-order nonlinear optical response function averaged over disorder $\langle\chi^{(3)}\rangle$ in the vicinity of $\omega_s \approx \omega_2$. We assume that the frequencies ω_1 and ω_3 are tuned off resonance (i.e., the detunings of ω_1 and ω_3 from the exciton band are larger than the bandwidth W), so that the Green functions $G(\omega_1)$ and $G(\omega_3)$ can be factorized from the averaging and that ω_2 is inside the exciton band but not too close to the band edge; i.e., the detuning is larger than σ^2/W, which corresponds to the weak disorder limit. The diagrams contributing to $\langle\chi^{(3)}\rangle$ [see Fig. 1(a)] are given by averaged products of the advanced Green function $G^*(\omega_2)$ and the retarded Green functions $G(\omega_s)$, $G(\omega_j')$, and $G(\omega_1+\omega_3-\omega_j')$, where ω_j' and $\omega_1+\omega_3-\omega_j'$ are the frequencies of the Green functions corresponding to internal lines in the diagrams. For weak disorder, the only case when this product may not be factorized into a product of averaged one-exciton Green functions is when the frequency ω_2 of the advanced Green function $G^*(\omega_2)$ is close to one of the frequencies ω_j in the retarded Green functions. This leads to a large resonant factor $(\omega_2-\omega)^{-1}$ coming from the average $\langle G(\omega)G^*(\omega_2)\rangle$, which can compensate for the small weak disorder parameter. Since the internal lines contain integrations over the frequencies ω_j', which eliminate the resonant factors when disorder is weak and the states are delocalized, the only way to obtain this resonant factor is by retaining $\langle G(\omega_s)G^*(\omega_2)\rangle$ and factorizing the other Green functions $G(\omega)$. This factorization [which is equivalent to taking into account the diagrams presented in Fig. 1(c)] results in

$$\langle\chi^{(3)}(-\omega_s;\omega_1,-\omega_2,\omega_3)\rangle = -2\mu^4 \sum_{\substack{nm_1m_2\\ m_3n'n''}} \langle G_{nn'}(\omega_s)G^*_{n'm_2}(\omega_2)\rangle \langle G_{n''m_3}(\omega_3)\rangle \langle G_{n''m_1}(\omega_1)\rangle [\langle F(2\omega_2)\rangle^{-1}]_{n'n''}. \tag{3}$$

Making use of time-reversal symmetry and the Ward identity [8], we can express the product in terms of the averaged one-exciton Green function

$$\sum_{n'}\langle G_{nn'}(\omega_s)G^*_{n'm_2}(\omega_2)\rangle = \frac{1}{\omega_s-\omega_2+i\eta}[\langle G^*_{nm_2}(\omega_2)\rangle - \langle G_{nm_2}(\omega_s)\rangle]. \tag{4}$$

Using Eqs. (2) and (4), the identity $\sum_n[\langle F(2\omega_2)\rangle^{-1}]_{nm} = [\sum_n\langle F_{nm}(2\omega_2)\rangle]^{-1}$ and the analog of the Ward identity for the function F, $\sum_m\langle G_{mn}(\omega')G_{mn}(\omega'')\rangle = [\langle G_{nn}(\omega')\rangle - \langle G_{nn}(\omega'')\rangle]/(\omega''-\omega')$. We finally recast Eq. (3) in the form

$$\langle\chi^{(3)}(-\omega_s;\omega_1,-\omega_2,\omega_3)\rangle = \kappa(\omega_1,\omega_2,\omega_3)\frac{1}{\omega_1+\omega_3-2\omega_2+i\eta}, \tag{5a}$$

with

$$\kappa(\omega_1,\omega_2,\omega_3) = 4i\mu^4 G(\omega_1)G(\omega_3)\left(\int d\mathbf{q}\, G(\omega_2,\mathbf{q})\right)^{-1}\mathrm{Im}[G^*(\omega_2)]. \tag{5b}$$

We have assumed that after averaging over disorder, the system possesses a translational symmetry $G(\omega,\mathbf{q}) \equiv \sum_n e^{-i\mathbf{q}\cdot\mathbf{n}}\langle G_{n0}(\omega)\rangle$ and $G(\omega) \equiv G(\omega,\mathbf{q}=0)$. Provided ω_2 is not too close to the band edge (i.e., the detuning is comparable to the bandwidth W), we obtain the resonant (peak) value of $\langle\chi^{(3)}\rangle \sim [\mu^4/W(\Delta\omega)^2]\Gamma_e/\eta$, where $\Delta\omega$ is the detuning of ω_1 (ω_3) from the band edge and $\Gamma_e \sim \sigma^2/W$, which shows a large resonant enhancement Γ_e/η, compared to the first factor which represents the background susceptibility of an ordered system.

Equations (5) express the nonlinear optical susceptibility in terms of the one-exciton Green function $G(\omega, \mathbf{q})$ averaged over disorder. The elementary one-photon and two-photon resonances in Eq. (1) and in $\kappa(\omega_1, \omega_2, \omega_3)$ are all related to specific pairs of levels. The four-photon resonance at $\omega_1 + \omega_3 = 2\omega_2$, which is the main result of this Letter, is of a very different nature. The existence of this new resonance is not apparent by inspection of Eq. (1) since this is a *collective* resonance resulting from the integration over the continuous distribution of levels. It is closely related to the dephasing induced resonances observed in near degenerate four wave mixing [9(a)]. The linear absorption linewidth is dominated by inhomogeneous broadening coming from the distribution of energies $\delta\Omega_n$; this new resonance, however, is much narrower, and its width (η) is purely homogeneous. In this respect this is a four-photon analog of hole burning (which is a two-photon resonance). This resonance does not exist for noninteracting two-level systems or in the absence of disorder.

The present Green function form of $\chi^{(3)}$ is very different (though identical) to the standard sum over state expression [9(b)] and has numerous advantages: it is more compact, it does not contain large cancellations among almost identical terms [2,4], and it offers an oscillator (quasiparticle) picture of the nonlinear response. To make a connection with standard treatments, it will be instructive to identify the terms in the sum over states that are responsible for the new resonance. To that end, we consider the level scheme, which consists of a single ground state $|g\rangle$, a one-exciton manifold $|e\rangle$, and a two-exciton manifold $|f\rangle$. We assume that the polarization operator couples only $|g\rangle$ to $|e\rangle$ and $|e\rangle$ to $|f\rangle$ and that the energy spacings between the manifolds $|g\rangle$ and $|e\rangle$ and $|e\rangle$ and $|f\rangle$ are very similar. The simplest system which may show the new resonance has one $|g\rangle$ level, two $|e\rangle$ levels ($|e\rangle$ and $|e'\rangle$), and one $|f\rangle$ level with $\varepsilon_{e'} = \omega_{e'g}$, $\varepsilon_e = \omega_{eg}$, $\varepsilon_f = 2\omega_{eg}$, and an inhomogeneous distribution of ω_{eg}. Using the sum over states expression for the third-order nonlinear optical response function $\chi^{(3)}$, and introducing the inhomogeneous distribution $S(\omega_{eg})$, we obtain

$$\chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) = \mu_{ge}\mu_{ef}\mu_{fe'}\mu_{e'g} \int \frac{d\omega_{eg}}{2\pi} \times S(\omega_{eg}) \frac{1}{\omega_1 - \omega_{e'g} + i\eta} \frac{1}{\omega_3 - \omega_{e'g} + i\eta} \frac{\omega_1 + \omega_3 - 2\omega_{e'g}}{\omega_1 + \omega_3 - 2\omega_{eg} + i\eta} \frac{1}{\omega_2 - \omega_{eg} - i\eta}, \quad (6a)$$

where μ_{ij} are the matrix elements of the polarization operator. Integrating over ω_{eg} under the assumption that the distribution $S(\omega_{eg})$ is much broader than the homogeneous width η, we recover Eq. (5a) with

$$\kappa(\omega_1, \omega_2, \omega_3) = -i\mu_{ge}\mu_{ef}\mu_{fe'}\mu_{e'g} \frac{\omega_1 + \omega_3 - 2\omega_{e'g}}{(\omega_1 - \omega_{e'g} + i\eta)(\omega_3 - \omega_{e'g} + i\eta)} S(\omega_2). \quad (6b)$$

This derivation illustrates the origin of the $\omega_1 + \omega_3 = 2\omega_2$ resonance. (The sharp resonance predicted in Eq. (5a) is a direct consequence of the Ward identity [Eq. (4)]. Equations (6) show that in the eigenstate picture this resonance originates from strong correlations between one- and two-exciton states. In either case, this prediction should hold regardless of the specific model of static disorder (be it diagonal, off-diagonal, or both).)

The new resonance has a clear analog in time-domain spectroscopy, where it shows up as a two-exciton photon echo. To demonstrate that, we consider a time-resolved four wave mixing conducted using three pulses with wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$. The time-dependent polarization with wave vector $\mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ can be calculated using a triple Fourier transform of the averaged susceptibility

$$P(\mathbf{k}_s, t) = \int \frac{d\omega_1\, d\omega_2\, d\omega_3}{(2\pi)^3} \langle \chi^{(3)}(-\omega_s; \omega_1, -\omega_2, \omega_3) \rangle \times E_1(\omega_1) E_2^*(\omega_2) E_3(\omega_3) \times \exp[-i(\omega_1 - \omega_2 + \omega_3)t]. \quad (7)$$

We assume that pulse 2 comes first, and its envelope $\mathcal{E}_2(t + \tau)$ is centered around the time $-\tau$. Pulses 1 and 3, with envelopes $\mathcal{E}_1(t)$, $\mathcal{E}_3(t)$, are simultaneous and centered around time 0.

In order to probe specifically the two-exciton transition and to avoid interference with the single-exciton resonance, we take ω_1 and ω_3 to be off resonant, with $\omega_1 \neq \omega_3$, and ω_2 is tuned inside the one-exciton band so that $\omega_1 + \omega_3 = 2\omega_2$. Assuming that the pulses are short compared with η^{-1} but with a spectral width narrower than the bandwidth W, and substituting Eqs. (5) into Eq. (7), we obtain the nonlinear polarization $P(\mathbf{k}_s, t) = P_s(\mathbf{k}_s, t) \exp(-i\omega_s t)$, with

$$P_s(\mathbf{k}_s, t) = \kappa(\omega_1, \omega_2, \omega_3) \exp(-\eta t) \times \int d\tau' \mathcal{E}_1\left(\frac{\tau'}{2}\right) \mathcal{E}_3\left(\frac{\tau'}{2}\right) \mathcal{E}_2^*(\tau' + \tau - t). \quad (8)$$

For short pulses the last factor in Eq. (8) yields $\delta(t - \tau)$, and the signal is peaked at $t = \tau$. This constitutes a two-exciton photon echo where decay as a function of the delay gives the homogeneous linewidth η. (A two-exciton echo, as well as the sharp resonance, is not expected in the limit $\Delta E \gg \Gamma_e$ considered in [7(b)], where the width of the exciton level distribution and the width of the correlations are comparable.)

The origin of the echo can be rationalized as follows: We denote the ground, single-exciton, and two-exciton states as $|g\rangle$, $|e\rangle$, and $|f\rangle$. The ordinary photon echo [1(d)] of a two-level system is related to the polarization $P_s(\mathbf{k}_s, t) = P_0 \exp[-i\omega_{eg}(t - \tau)]$. The phase factor reflects the time evolution of the coherence $|g\rangle\langle e|$ for a period τ, and the conjugate coherence $|e\rangle\langle g|$ for a period t. If the two-level molecules have a broad distribution of transition energies ω_{eg}, the signal will be peaked at $t = \tau$, since at other times contributions from different molecules cancel due to their different phases, but for $t = \tau$ all phases coincide, and we obtain an echo. The presence of the f levels gives rise to an additional pathway that is responsible for the new echo: The density matrix changes from $|g\rangle\langle g|$ via $|g\rangle\langle e|$ to $|f\rangle\langle e|$, and the contribution to the polarization from this pathway is $P_s(\mathbf{k}_s, t) = P_0' \exp(-i\omega_{fe}t + i\omega_{eg}\tau)$. Here the phase factor reflects the evolution of $|g\rangle\langle e|$ for a period τ followed by $|f\rangle\langle e|$ for a period t. If the fluctuations of these levels are strongly correlated, the contribution from this pathway will show an echo at $t = \tau$. Moreover, assuming that the 1 and 3 pulses are off resonant, with $\omega_1 + \omega_3 = 2\omega_2$ being on resonance with the f levels, the contribution from the first pathway vanishes, and only the contribution from the second pathway can give an echo. We will call this a two-exciton echo since it necessarily involves the $|f\rangle$ two-exciton states. Like its frequency-domain counterpart, the extra resonance, the two-exciton echo does not exist in assemblies of noninteracting two-level molecules or in the absence of disorder.

Photon echo experiments can be effectively used to distinguish between almost harmonic systems (our four-level scheme in which $|g\rangle$, $|e\rangle$, and $|f\rangle$ form a harmonic ladder, and anharmonicity is induced by the $|e'\rangle$ level) and strongly anharmonic systems (such as noninteracting two-level molecules). Let us consider the three-pulse echo setup when pulses 2, 1, and 3 are centered at times $-\tau_2$, 0, and τ_3, respectively. For our four-level scheme there are three pathways in Liouville space contributing to the echo (the pathways describe the density matrix at three time intervals $[-\tau_2, 0]$, $[0, \tau_3]$, and $[\tau_3, t]$ where t is the time of the measurement). These pathways are $|g\rangle\langle e|$, $|g\rangle\langle g|$, $|e\rangle\langle g|$; $|g\rangle\langle e|$, $|e\rangle\langle e|$, $|e\rangle\langle g|$, and $|g\rangle\langle e|$, $|e\rangle\langle e|$, $|f\rangle\langle e|$. The first and second pathways describe the contribution of a two-level system. The third pathway is related to the two-exciton echo. If levels $|g\rangle$, $|e\rangle$, and $|f\rangle$ are equally spaced and the dipole moments scale as $\mu_{fe}/\mu_{ge} = \sqrt{2}$, then the model represents a linearly driven harmonic oscillator for which the system is linear and all nonlinear response functions vanish. The three terms then cancel, and the echo disappears. (The pathways involving the state $|e'\rangle$ certainly contribute to the nonlinear response; however, in the present model they do not generate an echo, either due to a rapid dephasing factor $\exp[-i(\omega_{e'g} - \omega_{eg})\tau']$ (where τ' is one of the time intervals) or because of the absence of inhomogeneous broadening of the $|e'\rangle$ level in our model.) In summary, both almost harmonic and strongly anharmonic systems with inhomogeneous broadening show ordinary echo. The two-exciton echo shows up in almost harmonic systems but not in strongly anharmonic systems. The three-pulse echo exists in strongly anharmonic systems but is canceled in almost harmonic systems. Photon echoes in harmonic systems have been predicted recently for intermolecular vibrations in liquids [10]. The almost harmonic character of electronic elementary excitations in aggregates results in a close formal analogy between the two effects.

In weakly disordered molecular aggregates one-exciton states are delocalized, and, therefore, the anharmonicity in the system which is due to Pauli exclusion is much weaker than for noninteracting two-level molecules. Therefore, an aggregate behaves as a system of weakly coupled almost harmonic oscillators, and one expects molecular aggregates to show the two-exciton echo but not the three-pulse echo. When Eqs. (5) for $\langle\chi^{(3)}\rangle$ are extended to the case when ω_1 and ω_3 are both on resonance, we find that the echo vanishes, unless pulses 1 and 3 overlap temporally. Finally, we note that exciton localization (e.g., in low dimensional systems) should lead to an enhanced anharmonicity, which would decrease the correlation between one- and two-exciton states and destroy the echo.

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