

LETTERS TO THE EDITOR

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COMMUNICATIONS

Femtosecond pump-probe spectroscopy of intermolecular vibrations in molecular dimers

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The dynamics of intermolecular vibrations in molecular aggregates can be directly monitored by ultrafast spectroscopic techniques. Starting with the third order response function obtained using the path-integral approach, we calculate the pump-probe spectrum of a molecular dimer, taking into account the effects of an intermolecular vibration coupled to the solvent. The various contributions to the signal which represent distinct Liouville space paths are identified and analyzed. © 1995 American Institute of Physics.

Nonlinear optical spectroscopy of molecular aggregates provides a direct probe for the joint electronic and nuclear dynamics. Various systems such as the photosynthetic reaction center,¹⁻⁴ J aggregates,⁵⁻⁸ and charge transfer aggregates⁹ have been extensively studied. In this letter, we demonstrate how the dynamics of intermolecular vibrations can be observed in a differential absorption (pump-probe) measurement. We consider a dimer made out of a pair of two-level molecules. The ground and the excited states of each molecule are denoted by $|g\rangle_j$ and $|e\rangle_j$ ($j=1,2$). We denote an annihilation and creation operator for an electronic excitation of the j th molecule by B_j and B_j^\dagger (with the Pauli commutation relation $[B_j, B_j^\dagger]=1-2B_j^\dagger B_j$). The total Hamiltonian is

$$H=H_0+H'-\mu E(t)(B_1^\dagger+B_1+B_2^\dagger+B_2), \quad (1)$$

where

$$H_0=\Omega_0(B_1^\dagger B_1+B_2^\dagger B_2),$$
$$H'=J(q)(B_1^\dagger B_2+B_2^\dagger B_1)+\frac{P^2}{2M}+\frac{1}{2}M\omega_0^2 q^2$$
$$+\sum_j\left(\frac{p_j^2}{2m_j}+\frac{1}{2}m_j\omega_j^2 x_j^2\right)+q\sum_j c_j x_j.$$

Here, H_0 is the electronic part of the Hamiltonian of the isolated molecules where Ω_0 is the molecular electronic excitation energy. The electronic coupling and the nuclear degrees of freedom are represented by H' : $J(q)$ is the intermolecular electronic coupling which depends on an intermolecular vibrational mode q with frequency ω_0 , the momentum P , and the mass M . We assume that this mode is coupled to a solvent with an arbitrary spectral density. The solvent is described by a set of harmonic oscillators with

coordinate x_j and momenta p_j . The interaction between the mode and the j th oscillator [the last term in Eq. (2)] is assumed to be linear, with a coupling strength c_j . The third term in the Hamiltonian Equation (1) represents the dipole coupling with an external electronic optical field $E(t)$, and μ is the molecular transition dipole moment. A similar model has been used in the studies of luminescence of excimers in crystals.¹⁰ In bound aggregates, the intermolecular coordinate is restricted to a small amplitude motion. We can then expand $J(q)$ in a Taylor series around the equilibrium configuration $q=0$, and write $J(q)=J+J'q$. In this case we can introduce collective normal modes of the system x'_j which are linear combinations of q and x_j and H' can be recast in the form

$$H'=J(B_1^\dagger B_2+B_2^\dagger B_1)+\sum_j\left[\frac{p_j^{*2}}{2m_j^*}+\frac{1}{2}m_j^*\omega_j^{*2}x_j^{*2}\right]$$
$$+(B_1^\dagger B_2+B_2^\dagger B_1)\sum_j c_j^* x_j^*. \quad (3)$$

This is a reminiscent of the spin-boson Hamiltonian,¹¹ which is commonly used in the description of charge transfer processes. The difference is that here the nuclei couple to the off-diagonal element J (electronic coupling) and not to the diagonal part of the Hamiltonian (nuclear energies). The coupling strength of the electronic degree of freedom is now included in c'_j .

The most widely used time domain techniques, such as pump-probe, hole burning, or photon echo spectroscopy are related to the third order polarization $P^{(3)}(t)\equiv\text{tr}\{V\rho^{(3)}(t)\}$, where $V\equiv\mu(B_1^\dagger+B_1+B_2^\dagger+B_2)$ is the molecular dipole operator.¹² We then have

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E(t-t_3)E(t-t_2-t_3) \times E(t-t_1-t_2-t_3)R^{(3)}(t_3,t_2,t_1) + c.c. \quad (4)$$

When the nonlinear response function $R^{(3)}(t_3,t_2,t_1)$ is evaluated, we find sixteen distinct Liouville paths which represent all possible time orderings of the interactions with the radiation field. The corresponding double-sided Feynman diagrams are shown in Fig. 1. The various terms can be evaluated using path integral techniques¹³ and we obtain

$$R^{(3)}(t_3,t_2,t_1) \equiv \frac{i\mu^4}{\hbar^3} \sum_{\alpha=1}^8 \exp[Q_\alpha(t)], \quad (5)$$

where

$$\begin{aligned} Q_1(t) &= -i\Omega_+t_1 - i\Omega_+t_3 - g_-(t_1) - g_+(t_3) - [g_+(t_2) - g_+(t_2+t_3) - g_-(t_1+t_2) + g_-(t_1+t_2+t_3)], \\ Q_2(t) &= i\Omega_+t_1 - i\Omega_+t_3 - g_+(t_1) - g_+(t_3) + [g_-(t_2) - g_-(t_2+t_3) - g_+(t_1+t_2) + g_+(t_1+t_2+t_3)], \\ Q_3(t) &= i\Omega_+t_1 - i\Omega_+t_3 - g_+(t_1) - g_-(t_3) + [g_+(t_2) - g_+(t_2+t_3) - g_+(t_1+t_2) + g_+(t_1+t_2+t_3)], \\ Q_4(t) &= -i\Omega_+t_1 - i\Omega_+t_3 - g_-(t_1) - g_-(t_3) - [g_-(t_2) - g_-(t_2+t_3) - g_-(t_1+t_2) + g_-(t_1+t_2+t_3)], \\ Q_5(t) &= -i\Omega_+t_1 + i\Omega_-t_3 - g_-(t_1) - g_+(t_3) - [g_+(t_2) - g_+(t_2+t_3) - g_-(t_1+t_2) + g_-(t_1+t_2+t_3)], \\ Q_6(t) &= i\Omega_+t_1 + i\Omega_-t_3 - g_+(t_1) - g_+(t_3) + [g_-(t_2) - g_-(t_2+t_3) - g_+(t_1+t_2) + g_+(t_1+t_2+t_3)], \\ Q_7(t) &= i\Omega_+t_1 + 2i\Omega_0t_2 + i\Omega_-t_3 - g_+(t_1) - g_-(t_3) + [g_+(t_2) - g_+(t_2+t_3) - g_+(t_1+t_2) + g_+(t_1+t_2+t_3)], \\ Q_8(t) &= -i\Omega_+t_1 - 2i\Omega_0t_2 - i\Omega_+t_3 - g_-(t_1) - g_-(t_3) - [g_-(t_2) - g_-(t_2+t_3) - g_-(t_1+t_2) + g_-(t_1+t_2+t_3)]. \end{aligned} \quad (6)$$

Here

$$g_\pm(t) \equiv \int_0^t dt' \int_0^{t'} dt'' \int \frac{d\omega}{2\pi} C(\omega) \times \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) \cos(\omega t'') \pm i \sin(\omega t'') \right], \quad (7)$$

$\Omega_\pm \equiv \Omega_0 \pm J$, and $\beta \equiv 1/k_B T$ is the inverse temperature. The spectral distribution is defined by

$$C(\omega) = \pi \sum_j \left(\frac{c_j'^2}{2m_j'\omega_j'} \right) \delta(\omega - \omega_j') = \frac{iM\lambda}{2\hbar} \times \int dt (\langle q(t)q(0) - q(0)q(t) \rangle) \sin(\omega t), \quad (8)$$

where λ is the coupling strength and the time evolution of $q(t)$ is with the Hamiltonian $H_0 + H'$. The first four terms in Eq. (6) involve only the ground $|0\rangle$ and the $|1+\rangle$ states and do not depend on the $|2\rangle$ state. After two interactions, the density matrix can be either in the $|1+\rangle\langle 1+|$ state ($\alpha=1,2$) or in the ground state $|0\rangle\langle 0|$ ($\alpha=3,4$). The remaining four terms represent processes where the system ends up in the $|2\rangle\langle 2|$ state. These can be either sequential (passing through

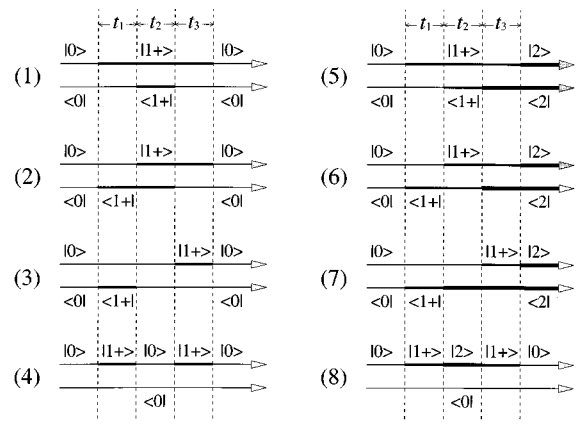


FIG. 1. Double-sided Feynman diagrams for the third order response function. The Hermitian conjugate paths of 1–8, which can be obtained by interchanging all left and right interaction L and R are not shown here.

$|1+\rangle\langle 1+|$ after two interactions $\alpha=5,6$) or coherent, Raman type, which pass through the coherence $|0\rangle\langle 2|$ or $|2\rangle\langle 0|$ ($\alpha=7,8$).

The linear absorption spectrum of this system is given by

$$I(\omega) = \int_0^\infty dt R^{(1)}(t) \exp(i\omega t) + c.c., \quad (9)$$

where

$$R^{(1)}(t) \equiv \frac{i\mu^2}{\hbar} \exp[-i\Omega_+t - g_-(t)]. \quad (10)$$

Hereafter, we assume the Brownian oscillator spectral density

$$C(\omega) = \frac{\lambda\omega_0^2}{\pi} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}. \quad (11)$$

Here, λ , ω_0 , and γ are the coupling strength, oscillator frequency, and the friction constants, respectively.¹⁴ For this model the phase function $g_\pm(t)$ can be evaluated

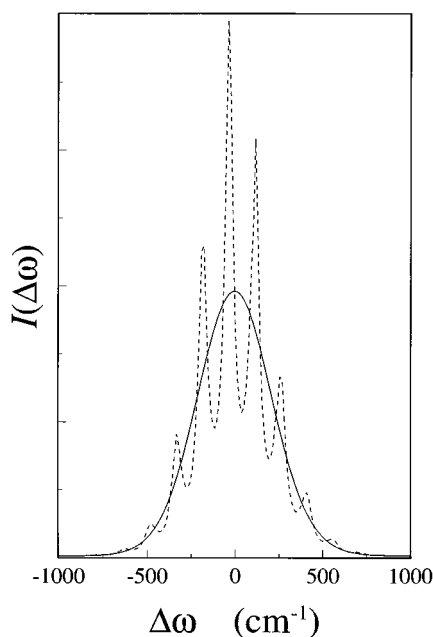


FIG. 2. Linear absorption spectrum for an overdamped intermolecular mode (solid line) and an underdamped mode (dashed line), where $\Delta\omega \equiv \omega - \Omega_0$.

analytically.¹³ Using the electronic eigenstates, $|0\rangle \equiv |g\rangle_1 |g\rangle_2$, $|1+\rangle \equiv |e\rangle_1 |g\rangle_2 + |g\rangle_1 |e\rangle_2$, $|1-\rangle \equiv |e\rangle_1 |g\rangle_2 - |g\rangle_1 |e\rangle_2$, $|2\rangle \equiv |e\rangle_1 |e\rangle_2$, our model with the Brownian spectral density is equivalent to a four-level system. The potentials are given by $U_2(q) = \hbar\omega_0 q^2/2 + 2\hbar\Omega_0$, $U_{1+}(q) = \hbar\omega_0(q+D)^2/2 + \hbar(\Omega_0+J)$, $U_{1-}(q) = \hbar\omega_0(q+D)^2/2 + \hbar(\Omega_0-J)$, and $U_0(q) = \hbar\omega_0 q^2/2$, where q is the dimensionless coordinate and $D = \sqrt{2\lambda/\omega_0}$.

In the following calculations, we chose $J = 600 \text{ cm}^{-1}$, $\lambda = 37 \text{ cm}^{-1}$, $\omega_0 = 150 \text{ cm}^{-1}$, and $T = 150 \text{ K}$ which are typical for J aggregates. The corresponding dimensionless displacement of the oscillator is $D = 0.7$. We used two values of the friction; $\gamma = 500 \text{ cm}^{-1}$ for which the oscillator is overdamped and $\gamma = 10 \text{ cm}^{-1}$ (coherent, underdamped oscillation). The linear absorption spectra for these two cases [Eq. (10)] are displayed in Fig. 2. Only the $|0\rangle$ and $|1+\rangle$ states participate in the linear absorption and the center of the lineshape is blue shifted with respect to Ω_0 because of the coupling J .

We next turn to the pump-probe experiment. Here, the system is first subjected to a short pump pulse, followed by a second probe pulse. We assume that the pump and the probe are impulsive with a relative delay time τ , and the pulse carrier frequency is taken to be $\Omega_p = -\Omega_0 + 400 \text{ cm}^{-1}$. The probe absorption spectrum at ω_2 is expressed in terms of the third order response function by¹⁵

$$S(\omega_2 - \Omega_p) = 2 \text{Re} \int_0^\infty dt \exp[i(\omega_2 - \Omega_p)t] R^{(3)}(t, \tau, 0). \quad (12)$$

We have calculated the differential probe absorption spectrum using Eqs. (5)–(7) and (11) and (12) for different pump-probe delay periods τ , and detunings $\Delta\omega_2 \equiv \omega_2 - \Omega_0$. Figures 3(a) and 3(b) show the signal for the overdamped and the underdamped case, respectively. An oscillatory structure with frequency ω_0 is observed in the underdamped case

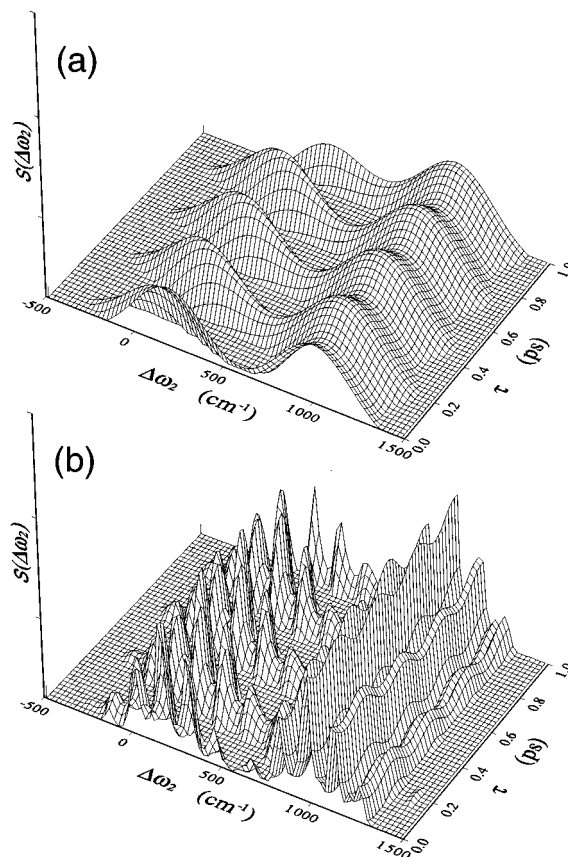


FIG. 3. Impulsive pump-probe spectrum for (a) an overdamped intermolecular mode ($\gamma = 500 \text{ cm}^{-1}$) and (b) underdamped mode ($\gamma = 10 \text{ cm}^{-1}$) for different delays τ between the pump and the probe. For other parameters, see text.

Fig. 3(b). In Figs. 3(a) and 3(b), the peak near 1000 cm^{-1} corresponds to the $|0\rangle$ to $|1+\rangle$ transition, whereas the peak near 200 cm^{-1} represent $|1+\rangle$ to $|2\rangle$ transition. This can be seen from Figs. 4(a) and 4(b), where we show separately the contribution of pathways 1 and 2 (solid line), 3 and 4 (dashed-dot line), 5 and 6 (long dash line), and 7 and 8 (short dash line). The contributions of the $|1+\rangle$ particle (solid line) and the hole (dot dash line) peak near 1000 cm^{-1} . As indicated earlier, our model is equivalent to a three displaced harmonic oscillator system with the displacement $q = 0$, $q = D$, and $q = 0$. For a coordinate-independent dipole interaction (the Condon approximation), the impulsive pulse creates a particle without changing the Gaussian shape of the wave packet in the $|0\rangle$ state (paths 1 and 2). Since the wave packet created in the $|0\rangle$ state represents its equilibrium state, it does not move when subjected to the ground potential and its contribution to the absorption spectrum is, therefore, time independent. The wave packet created in the $|1+\rangle$ state (paths $\alpha = 2$ and 3) does evolve in time. Since the potential is displaced from with respect to the $|0\rangle$ state, we can observe that motion through a redshift of the absorption. Apart from a shift, the absorption between $|1+\rangle$ and $|2\rangle$ (long dash line) is similar to the $|1+\rangle$ contribution. This is because state $|2\rangle$ is not displaced with respect to the $|0\rangle$ state, and we observe the motion of $|1+\rangle$ in the same manner of paths 1 and 2. The coherent contribution (paths 7 and 8) is, however, quite dif-

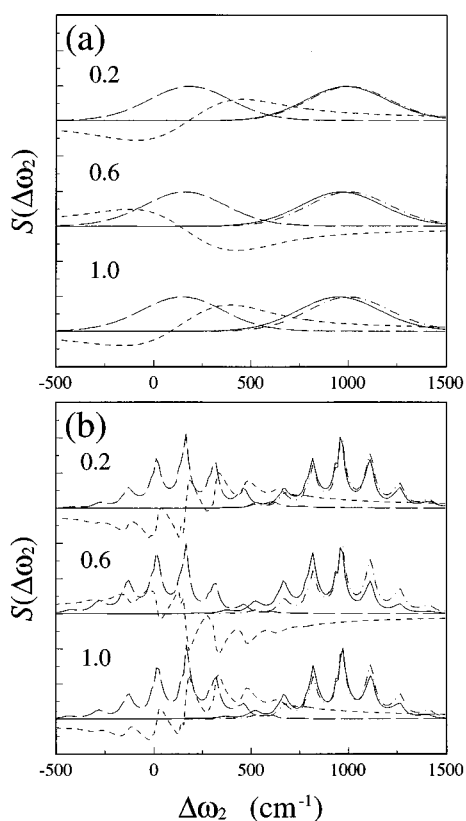


FIG. 4. Contribution of the spectrum of Fig. 3 for delays $\tau=0.2, 0.6,$ and 1.0 ps as indicated. (i) contribution from the $|1+\rangle$ state particle corresponding to the Liouville paths $\alpha=1$ and $\alpha=2$ (solid line), (ii) the hole $\alpha=3$ and $\alpha=4$ (dash dot line), (iii) the $|2\rangle$ state particle $\alpha=5$ and $\alpha=6$ (long dash line), and (iv) the coherent contribution $\alpha=7$ and $\alpha=8$ (short dash line).

ferent. The coherence between the $|0\rangle$ and $|2\rangle$ results in the phase factors $i\Omega_0 t_2$ [see $\alpha=7$ and 8 of Eq. (6)]. For resonant

excitation this contribution will be canceled by the field induced factors ($i\Omega_2 t_2$). For off-resonant excitation, however, this factor shows an oscillatory feature with the delay τ . Thus, the total spectrum also becomes oscillatory as well, as is seen in Fig. 3(a).

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