

Nonlinear Optical Properties of Confined Excitons in Clusters

Jan A. Leegwater, Laurence E. Fried¹, and Shaul Mukamel

Department of Chemistry, University of Rochester, Rochester, NY 14627

¹ Present address: L-277, Chemistry and Materials Science Division,
Lawrence Livermore National Laboratory Livermore, CA 94550.

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Abstract. Size effects in femtosecond photon echo spectroscopy of neat clusters are calculated using a quasiparticle representation of the nonlinear response. We extend our previous study of cooperative effects on the nonlinear response of assemblies of two level molecules [J. A. Leegwater and S. Mukamel, Phys. Rev. A **46**, 452 (1992)] to allow for nuclear motion and to have an s-p model of polarizable atoms. Photon echos in Benzene/Argon clusters are calculated using a semiclassical phase averaging procedure [L. E. Fried and S. Mukamel, Adv. Chem. Phys. (in Press)].

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1 Introduction

In recent years a number of studies have appeared investigating the optical response of molecular and semiconductor nanostructures [1-3]. A main point of focus has been the effects of exciton confinement on the magnitude of the nonlinear optical response [1,4-6].

Femtosecond nonlinear spectroscopy [7-9] of atomic clusters may provide a direct probe for the combined exciton and nuclear dynamics [10].

So far the theories used to study cooperativity concerned themselves with one dimensional regular lattices with nearest neighbor interactions [4,5]. The main purpose of the present work is to remove these limitations by simulating a realistic model for neat atomic clusters which takes into account its geometry, the full dipole-dipole interaction and ultrafast nuclear dynamics.

2 The s-p model of an atomic cluster

We consider the Hamiltonian for an atomic cluster. Each atom is modeled as a four level system representing a ground s state and a triply degenerate excited p state.

We hereafter denote this as the s-p cluster. We assume the following Hamiltonian

$$\begin{aligned}
 H = & \sum_{n\alpha} \Omega_b B^\dagger_{n\alpha} B_{n\alpha} + \sum_{n < m, \alpha\beta} (B_{n\alpha} + B^\dagger_{n\alpha}) \\
 & \times J_{n\alpha, m\beta}(r_{nm})(B_{m\beta} + B^\dagger_{m\beta}) \\
 & - \sum_{n\alpha} \mu_n E_{n\alpha} (B^\dagger_{n\alpha} + B_{n\alpha}) \\
 & + H_{nucl}, \tag{1}
 \end{aligned}$$

where H_{nucl} is the Hamiltonian of the nuclear degrees of freedom

$$H_{nucl} = \sum_n \frac{p_n^2}{2m_n} + \sum_{n < m} V(r_{nm}), \tag{2}$$

the couplings J describe the dipole-dipole interaction between the molecules

$$J_{n\alpha, m\beta}(r_{nm}) = -J \left[\frac{3r_{nm,\alpha}r_{nm,\beta}}{r_{nm}^5} - \delta_{\alpha,\beta} \frac{1}{r_{nm}^3} \right] \xi_{n,m}, \tag{3}$$

where $\xi_{n,m} = 1 - \delta_{n,m}$, with δ the Kronecker delta, and J is a prefactor determining the energy scale of the exciton interactions. In the summation, n runs over the molecules and α over the internal degrees of freedom, $\alpha = x, y, z$. The operators B^\dagger and B are creation and annihilation operators for the s-p system at site n . The commutation relations for these may be found by studying the action of the B 's on the basis $|s\rangle$, $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$. We find that $B^\dagger_x |p_\alpha\rangle = 0$, and, using this, also that $B_x B^\dagger_y = 0$. Combining we obtain

$$[B_\alpha, B^\dagger_\beta] = \delta_{\alpha\beta} - (1 + \delta_{\alpha\beta}) B^\dagger_\beta B_\alpha. \tag{4}$$

We find that an s-p atom is not identical to a collection of three two level molecules on the same site, but that there is an additional nonlinearity in the model since

each atom can carry only one excitation. Using polarized laserbeams these additional nonlinearities can be probed [7]. The results presented here are valid for the simpler two level model as well, the only change is that the vector indices (greek letters) then only take on one value.

A realistic simulation of resonant femtosecond nonlinear spectroscopy must incorporate the coupled dynamics of disordered excitons as well as nuclear motions. The effect of nuclear motion on the optical nonlinearities is a complicated problem even for the simplest case of a single chromophore in a medium (Sec. 6). First we use a semi-classical approach. We also assume that the electronic degrees of freedom do not affect the nuclear motion.

Using the Heisenberg equation of motion for an operator $A(t)$, $\hbar dA(t)/dt = i[A, H]$, we find the equation of motion for B

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} B_{n\alpha} = & -(\Omega_n - i\gamma) B_{n\alpha} - \sum_{m\beta} J_{n\alpha, m\beta}(t) B_{m\beta} \\ & + \frac{\mu_n}{\hbar} E_{n\alpha}(t) \\ & + \sum_{m\beta\gamma} (1 + \delta_{\alpha\beta}) J_{n\alpha, m\beta}(t) B_{n\beta}^\dagger B_{m\gamma} B_{m\alpha} \\ & - \frac{\mu_n}{\hbar} \sum_{\beta} (1 + \delta_{\alpha\beta}) E_{n\beta}(t) B_{n\beta} B_{n\alpha}. \end{aligned} \quad (5)$$

Here $J(t)$ is the exciton coupling matrix for particles at certain sites $r_n(t)$, and $1/\gamma$ is the exciton lifetime. For the nuclear degrees of freedom we have $\dot{r}_n = v_n$, $\dot{v}_n = -\sum_m \nabla_n V(r_{nm})$, where $V(r)$ is the ground state interaction. We will use the Lennard-Jones form $V(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$ below.

3 Green function expression for the third order response

We shall be interested in calculating the third order nonlinear polarization under uniform excitation

$$P = \sum_n \mu_n (\langle B_n(t_1 + t_2 + t_3) \rangle + \langle B_n^\dagger(t_1 + t_2 + t_3) \rangle). \quad (6)$$

which can be expanded in the form [11]

$$P(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 R(t_3, t_2, t_1) E(t - t_3) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1). \quad (7)$$

The three-time response function $R(t_3, t_2, t_1)$ gives the polarization resulting from three very short pulses (Fig. 1). It contains all the information necessary for calculating any third order experiment.

We have shown previously [6] that the calculation of R requires the dynamics of B as well as the two exciton variable BB . For the two exciton operator BB we find the time evolution equation (neglecting terms of normally ordered products of three and four B 's which are

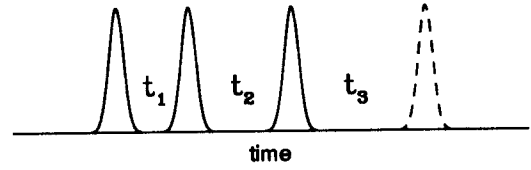


Figure 1: The delay times occurring in the three time response function $R(t_3, t_2, t_1)$ illustrated. The solid lines are the applied fields, and the dashed line is a hypothetical third order response. A realistic response is graphed in Fig. 3

irrelevant for the third order response)

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} B_{n\alpha} B_{m\beta} = & -(\Omega_n + \Omega_m - 2i\gamma) B_{n\alpha} B_{m\beta} \\ & - \xi_{n,m} \sum_{i\gamma} J_{n\alpha, i\gamma}(t) B_{i\gamma} B_{m\beta} \\ & \xi_{n,m} \sum_{i\gamma} J_{m\beta, i\gamma}(t) B_{n\alpha} B_{i\gamma} \\ & + \xi_{n,m} \frac{\mu_n}{\hbar} E_{n\alpha}(t) B_{m\beta} + \xi_{n,m} \frac{\mu_m}{\hbar} E_{m\beta}(t) B_{n\alpha} \end{aligned} \quad (8)$$

The solution can be written in terms of the following Green functions evaluated in the absence of the field

$$B_{n\alpha}(t) = G_{n\alpha, n'\alpha'}(t_1, t) B_{n'\alpha'}(t_1), \quad (9)$$

(we adopt the convention that repeated indices are summed over) and the two exciton Green function

$$B_{n\alpha} B_{n'\alpha'}(t) = D_{n\alpha n'\alpha', n''\alpha'' n'''\alpha'''}(t_1, t) B_{n''\alpha''} B_{n'''\alpha'''}(t_1). \quad (10)$$

The time arguments are given explicitly to remind us that we take the average over the nuclear degrees of freedom of the final expressions.

The solution to third order in the applied electric fields of Eq. (5) yields $R(t_3, t_2, t_1) = R_l + R_{nl} + c.c.$, where the local nonlinearity [the fourth term on the right hand side of Eq. (5)] contributes

$$\begin{aligned} R_l = & \sum_{n\alpha} G_{n\alpha, n'''\beta}(t_1 + t_2, t_1 + t_2 + t_3) (1 + \delta_{\alpha'''\beta}) \\ & \left[G_{n'''\alpha''', n''\alpha''}(t_1, t_1 + t_2) G_{n'''\beta, n'\alpha'}(0, t_1 + t_2) \right. \\ & \left. + G_{n'''\alpha''', n'\alpha'}(0, t_1 + t_2) G_{n'''\beta, n''\alpha''}(t_1, t_1 + t_2) \right], \end{aligned} \quad (11)$$

and the nonlocal nonlinearity [the last term of Eq. (5)] contributes

$$\begin{aligned} R_{nl} = & - \sum_{n\alpha} \int_0^{t_3} d\tau G_{n\alpha, n_1\alpha_1}(t_1 + t_2, t_1 + t_2 + t_3 - \tau) \\ & (1 + \delta_{\alpha_1\tilde{\alpha}_1}) (\delta_{n_1\alpha_1, n'_1\alpha'_1} J_{n_1\tilde{\alpha}_1, n'_1\alpha'_1}(t_1 + t_2 + \tau) \\ & + \delta_{n_1\alpha_1, n'_1\alpha'_1} J_{n_1\tilde{\alpha}_1, n'_1\alpha'_1}(t_1 + t_2 + \tau)) \end{aligned}$$

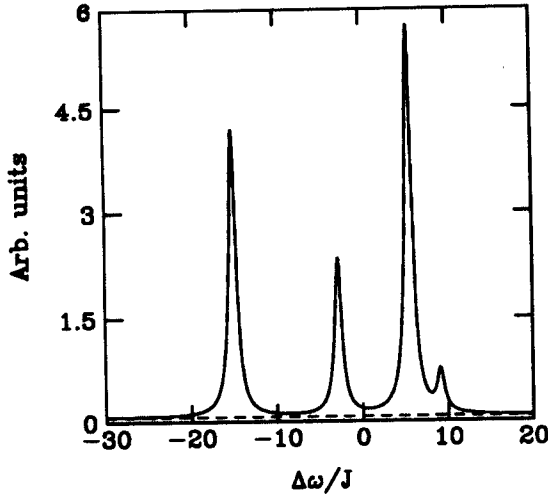


Figure 2: Two photon absorption $Im\chi^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1)$. The solid lines are numerical results for a $3 \times 3 \times 3$ cluster, the dashed line is the local field approximation. Here we have taken $\omega_1 = 0.7\Omega_s + \Delta\omega$, and $\omega_2 = 1.3\Omega_s$. For these frequencies the one photon frequencies are non resonant, but the two exciton term in the cooperativity enhancement factor is resonant, giving rise to resonances. The signal is given for dephasing rate $\gamma/J = 0.5$. The TPA probes the two exciton resonances which are missed completely by the local field approximation.

$$\left\{ \begin{aligned} & D_{n'_1\alpha'_1 n''_1\alpha''_1, n''\alpha'' k\beta}(t_1, t_1 + t_2 + \tau)(1 - \delta_{n''k}) \\ & G_{n_1\tilde{\alpha}_1, n''\alpha''}^*(t_1 + t_2, t_1 + t_2 + \tau) G_{k\beta, n'\alpha'}(0, t_1) \\ & + D_{n'_1\alpha'_1 n''_1\alpha''_1, n''\alpha'' k\beta}(t_1 + t_2, t_1 + t_2 + \tau) \\ & (1 - \delta_{n''k}) \left[G_{n_1\tilde{\alpha}_1, n''\alpha''}^*(t_1, t_1 + t_2 + \tau) \right. \\ & \quad G_{k\beta, n'\alpha'}(0, t_1 + t_2) \\ & \quad \left. + G_{n_1\tilde{\alpha}_1, n'\alpha'}^*(0, t_1 + t_2 + \tau) \right. \\ & \quad \left. G_{k\beta, n''\alpha''}(t_1, t_1 + t_2) \right] \end{aligned} \right\}. \quad (12)$$

As the motion of the particles is taken into account implicitly through the Green functions, effects related to nuclear motions such as pure dephasing are still being treated here, and will show up after these expressions are averaged over the ensemble of nuclear degrees of freedom.

4 Frequency domain response

The expressions of the previous section have to be Fourier transformed to give the frequency domain response. This constitutes a generalization of the expressions derived before for a system of coupled two level molecules [6]. Here we apply these calculations to ordered cubic nanocrystals.

In order to directly observe the cooperative enhancement factor we consider a two color experiment for two

photon absorption. We took frequencies such that single photon transitions are off resonant so we see only the two photon resonances in the cooperative enhancement factor (Fig. 2). Notice in particular the complete absence of a resonance in the local field approximation, so that this two color experiment provides direct information on the two exciton Green function.

5 Photon echos in small clusters

As another application of the formal expressions derived in section 2 we studied the photon echo (described below) of a small s-p cluster in a Monte Carlo study. The prime motivation was that for the frequency domain response cooperative effects were found to have a considerable effect on the magnitude of optical nonlinearities, and now we can address this question in the time domain. For this we first consider the static approximation (mass $m = \infty$) so that the Green's functions are exponentials of matrices. Though there are many analytical approaches for the one exciton Green function we did here the simplest possible: we calculated the Green function by numerically diagonalizing the matrix J . While this limits us to studying small clusters it is guaranteed to produce reliable results.

The two exciton Green function is considerably more difficult to evaluate. For lattice calculations it was found useful to use the scattering, or T matrix representation. While this reduces the number of degrees of freedom from $9N^2$ to $9N$ we have found that calculating the T matrix numerically to be unreliable. Instead we diagonalized the two exciton coupling matrix ($9N^2$) numerically.

In a photon echo experiment a short pulse is applied at a time $t = -\tau$ (we take all the pulses and signal polarized along the x -axis here). Due to the inhomogeneous broadening the polarization will rapidly dephase. At $t = 0$ a second pulse interacts with the system, initializing, among other effects which are not important here, a rephasing which causes the polarization to reappear at time $t = \tau$, an echo. In terms of the three time response function R the echo appears as a distinct peak of $R(t, 0, \tau)$ whenever $t \simeq \tau$. In the theory of photon echos the system is assumed to consist of noninteracting inhomogeneously broadened two level atoms. It is not clear that this model applies here since the broadening of the linear absorption line is caused entirely by the intermolecular interactions and also the transition dipole has to be considered. We reverted to simulations to study the question whether there is an echo in clusters of s-p atoms.

In Fig. 3 a typical result is presented for the intensity, the polarization squared. Here we studied an ensemble of clusters consisting of 8 s-p atoms interacting through the Lennard-Jones interaction. As is clear there is an echo even for this very small cluster. Separating contributions into one originating from the local nonlinearity [the first

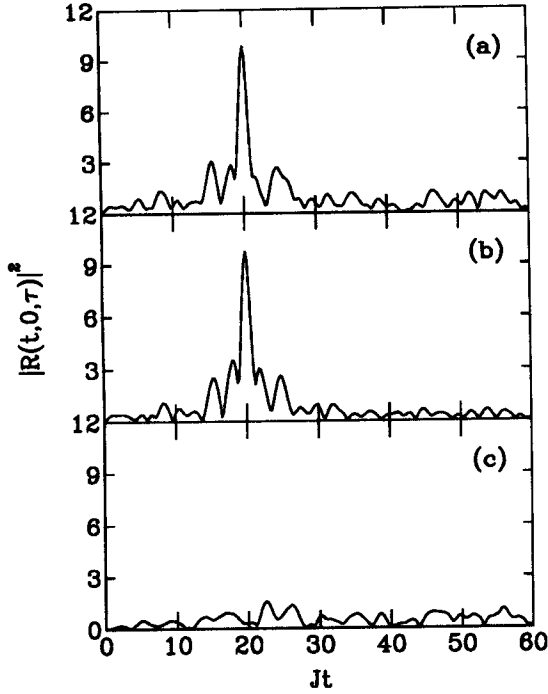


Figure 3: The photon echo signal for a cluster of 8 Lennard-Jones *s-p* atoms prepared at temperature $T = 0.2\epsilon$. We plotted $|R(t, 0, \tau)|^2$ as a function of the observation time t . The average is over 570 configurations of clusters. The first pulse is for $\tau = 20/J$. $1/J = 5fs$ is a reasonable value for Argon. For other delay times essentially identical, but shifted, curves are found. (a): total, (b): contribution of the local nonlinearity (see text). (c): nonlocal nonlinearity. There is an additional cross contribution, which is not plotted.

term in Eq. (11)] and nonlocal nonlinearity [the term with the time integral in Eq. (11)] we find that the local nonlinearity produces the echo, whereas the nonlocal nonlinearity gives a background type signal. Apparently the local nonlinearity is dominating the photon echo.

The most interesting aspect of the photon echo experiment is that it eliminates inhomogeneous broadening, so that the homogeneous broadening caused by the nuclear motion becomes observable. In a semiclassical approximation the following expression for the Green function can be derived [12]

$$G_{n\alpha, n'\beta}(t) = \sum_k \psi_{n\alpha}^{(k)} \exp\left(i\omega_k t - \frac{k_B T t^4}{m} \lambda_{k,k}\right) \psi_{n'\beta}^{(k)*}, \quad (13)$$

where $\psi_{n'\beta}^{(k)}$ is an eigenvector of the coupling matrix J , k_B is the Boltzmann constant, T is the temperature, and

$$\lambda_{k,k} = \sum_{i\alpha\beta} \left| \sum_{j\gamma} (\nabla_{i\alpha} T_{i\beta, j\gamma}) \psi_{j\gamma}^{(k)} \right|^2. \quad (14)$$

Substituting this Green function in the expression for

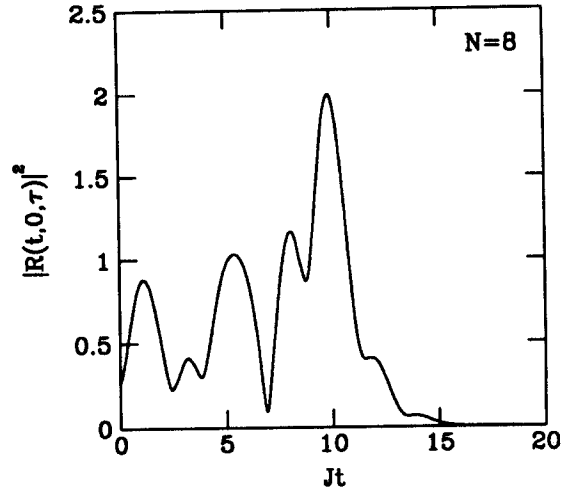


Figure 4: As in Fig. 3, for a delay time $\tau = 10/J$, treating the nuclear motion semiclassically using Eq. (13). Parameters appropriate for Argon were used here. For this delay an echo is still distinguishable, which no longer is the case for a delay of $\tau = 20/J$.

the nonlinear response Eq. (11), ignoring the nonlocal contribution which we have shown to be small, we have a practical way of obtaining results for the effect of nuclear motion on the photon echo signal. A typical result is shown in Fig. 4.

6 Single chromophore in a cluster

In the previous sections we discussed neat clusters. Here we study a single chromophore in a cluster. This is a much simpler model since it involves only two electronic levels (instead of an exciton band), which allows us to investigate the ground state and the excited state dynamics more rigorously. In particular we have included the effect that a localized chromophore excitation has on the time dependence of $r_n(t)$.

We assume that the chromophore has an electronic transition frequency Ω well separated from the electronic transition frequencies of the medium. In this case the exciton is completely localized at the chromophore, which can be treated as having two electronic states $|g\rangle$ and $|e\rangle$. The corresponding Hamiltonian is

$$H = H_g + B^\dagger U B - \mu E(t)(B^\dagger + B). \quad (15)$$

Here, the annihilation-creation operators for the chromophore electronic states (B, B^\dagger) obey the same commutation relation as Eq. (4) with $\alpha = \beta$. H_g is of the form:

$$H_g = \sum_n \frac{p_n^2}{2m_n} + \sum_{n < m} V_g(r_{mn}), \quad (16)$$

where the summations are over all the atoms in the chromophore-medium system. U is the difference be-

tween the ground and excited state Born-Oppenheimer potential energy surfaces:

$$U \equiv \sum_{n < m} V_e(r_{nm}) - V_g(r_{nm}). \quad (17)$$

Many-body nuclear potentials can easily be included in the present formalism by generalization of the form of U and V_g .

For the single chromophore problem, it is possible to include the change in nuclear dynamics brought on by electronic excitation in a semiclassical framework. Below, we will use \mathbf{Q} to denote the positions of all the atoms, and \mathbf{P} to denote the momenta of all the atoms. We introduce two trajectories $\mathbf{Q}_1(t)$ and $\mathbf{Q}_2(t)$. Each trajectory begins from the same initial condition (\mathbf{Q}, \mathbf{P}) when $t = 0$. $\mathbf{Q}_1(t)$ is the coordinate of the initial condition propagated with H_g . The other trajectory $\mathbf{Q}_2(t)$ is run on the ground state for the t_1 period and on the excited state for the t_2 and t_3 periods. Associated with $\mathbf{Q}_1(t)$ and $\mathbf{Q}_2(t)$ are the energy gap functions: $U_j(t) = U[\mathbf{Q}_j(t; \mathbf{Q}, \mathbf{P})]$, ($j = 1, 2$)

In terms of these quantities, a semiclassical phase averaging approach [13–16] yields

$$\begin{aligned} R(t_3, t_2, t_1) = & \\ & i \left\langle \exp \left(-i \int_{t_1+t_2}^{t_1+t_2+t_3} U_2(t') dt' \right) \exp \left(-i \int_0^{t_1} U_2(t') dt' \right) \right. \\ & + \exp \left(-i \int_{t_1+t_2}^{t_1+t_2+t_3} U_2(t') dt' \right) \exp \left(i \int_0^{t_1} U_2(t') dt' \right) \\ & + \exp \left(-i \int_{t_1+t_2}^{t_1+t_2+t_3} U_1(t') dt' \right) \exp \left(i \int_0^{t_1} U_1(t') dt' \right) \\ & \left. + \exp \left(-i \int_{t_1+t_2}^{t_1+t_2+t_3} U_1(t') dt' \right) \exp \left(-i \int_0^{t_1} U_1(t') dt' \right) \right\rangle \\ & + c.c. \quad (18) \end{aligned}$$

Eq. (18) has been applied to the nonlinear spectroscopy of liquid water [15] and benzene- Ar_N clusters [16]. In Fig. 5 we show the photon echo signal

$S(\tau) = \int_0^\infty |R(t, 0, \tau)|^2 dt$ of benzene- Ar_N clusters as a function of N . Lennard-Jones interactions were used for V_g and V_e . In the present calculation the photon echo signal is entirely due to nuclear motion, whereas the many chromophore calculations shown above contain both nuclear motion and exciton dynamics.

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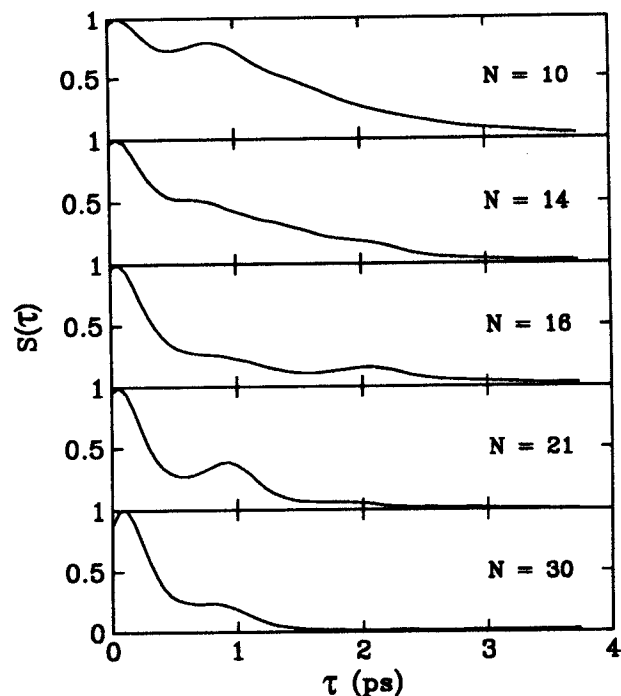


Figure 5: The photon echo signal $S(\tau)$ for benzene- Ar_N clusters as a function of the delay time τ .

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