

# Determination of Two-Pulse Photon Echoes from Solvent Spectral Densities

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**Abstract:** Photon echo measurement of a cyanine dye chromophore in acetonitrile solutions are reported. The measured spectral density is used to calculate the 2-pulse photon echo signal.

The nonlinear response function description of third-order polarization,  $P^{(3)}(t_1, t_2, t_3)$ , spectroscopy[1,2] shows that different four wave mixing (FWM) measurements of the time evolution of a solute-solvent system contain complementary information about the time correlation function of solvent fluctuations. In particular, chromophore optical dephasing is determined by the correlation function of the chromophore electronic frequency modulation and the coupling of the chromophore transition dipole to the bath. Solvent fluctuations occur on timescales corresponding to the Fourier transform of its far-infrared or Raleigh-wing spectrum.[3] Experiments that are performed on such short timescales are capable of directly capturing the solvent effect on or response to chemical processes.[4] Photon echo methods are useful for studying optical dephasing of molecules in solution.[5-9]

We describe the results of experimental measurements and numerical calculation of the 2-pulse photon echo of the cyanine dye HITCI in acetonitrile. Analogous measurements have been performed in DMSO and alcohol solutions.[9] The experiments involve the simultaneous measurement of the echo signal in the  $k_3=2k_1-k_2$  and  $k_3'=2k_2-k_1$  phase matched directions for accurate determination of the temporal shift, an important fitting constraint. The short pulse source is a home-built[10] Kerr lens modelocked Ti:Sapphire laser [11] producing transform limited 18-22 fs duration gaussian pulses. The sample is a flowing jet (150 $\mu$ m thick) of the chromophore in solution. Solvent spectral densities,[12] obtained from impulsive optical Kerr effect (OKE) measurements, are used to generate the lineshape function used in the nonlinear response function formalism to simulate the echo signal.

Any FWM signal can be expressed as a convolution of the correct molecular response function,  $R(t, \tau)$  with a sequence of excitation fields.  $R(t, \tau)$  contains the temporal response of the system for pulses separated in time by  $\tau$  and the optical lineshape function  $g(t)$ . We assume a well-separated pulse limit in the calculations. The real part of a lineshape function that allows incorporation of solvent dynamics through a spectral density function,  $C(\omega)$ , is given by [2]

$$g(t) = \int_0^{\infty} \left( \frac{1 - \cos(\omega t)}{\omega^2} \right) C(\omega) d\omega \quad (1)$$

We assume the spectral density to be of the (ohmic) form

$$C(\omega) = N\omega^\alpha \exp\left(-\frac{\omega}{\omega_0}\right) \quad (2)$$

Figure 1 shows the spectral density of acetonitrile obtained as the imaginary part of the deconvoluted Fourier transform of our measured impulsive OKE response. The line through the data is the result of fitting to eqn. (2). The solvent spectral density is assumed to describe the spectrum of solvent fluctuations that contribute to the 2-pulse photon echo signals. The

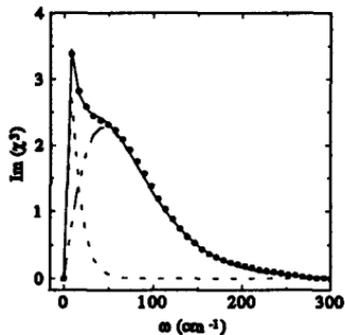


Figure 1

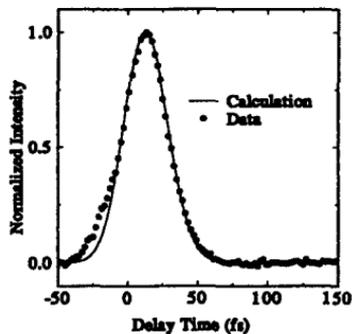


Figure 2

calculated echo signal, shown in Figure 2, is in very good agreement with the experimental signal. A thermal grating contribution to the signal causes a discrepancy at early times.

The observed 2-pulse photon echo signal of this symmetric cationic cyanine dye is similar to the two-pulse echo signals observed in oxazine dyes.[11] The echo shape, the timescale for and nonexponential decay of the echo signal is in agreement with recent calculations [13] and simulations.[14]

The principal result of this study is that the 2-pulse PE signal can be "predicted" from the neat solvent spectral density. This conclusion implies that the solvent spectral density obtained from impulsive OKE measurements accounts for the solvent fluctuations that determine the evolution of optical coherence of HITCI in acetonitrile. Apparently, no frequency-dependent couplings are required. Solvent-dependent studies.[9] show that in the case of HITCI the solute-solvent coupling scales with the solvent polarizability.

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