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Time-resolved Femtosecond Photon Echo Probes Bimodal Solvent Dynamics

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We report on *time-resolved* femtosecond photon echo experiments of a dye molecule in a polar solution. The photon echo is time resolved by mixing the echo with a femtosecond gate pulse in a nonlinear crystal. It is shown that the temporal profile of the photon echo allows separation of the homogeneous from the inhomogeneous contribution to the optical spectrum. A biexponential correlation function for frequency fluctuations is used to simulate the echo.

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Many electronic transitions in the condensed phase are much broader than expected on basis of the excited state lifetime. One of the effects contributing to this excess linewidth is dynamical in origin and arises from fast fluctuations in the chromophore-environment coupling. The width that results from this dynamic effect is known as the *homogeneous* linewidth. A second contribution to the linewidth, denoted *inhomogeneous*, comes from site disorder or slow fluctuations in the coupling between the optical oscillator and its surroundings. In crystalline solids, there is often a distinct separation between the time scales of the fast fluctuations, the optical experiment, and the slow fluctuations. In amorphous solids, like glasses, polymers, and proteins, a strict separation does not exist, due to structural fluctuations over a broad range of time scales. As a consequence the homogeneous linewidth becomes time dependent, meaning that the time scale of the experiment determines what is conceived as homogeneous. This effect is known as spectral diffusion. In liquids, it is not clear whether any separation of time scale exists at all.

In the past decades it has been one of the great challenges of modern laser spectroscopy to probe the underlying dynamical linewidth of electronic spectra in ionic and molecular solids, amorphous materials, semiconductors, photobiological systems, and, recently, in solvents. An assessment of the dynamics of the solute-solvent interaction is of special significance to chemistry, since solvation dynamics plays an essential role in many reactions, especially for those in polar solvents in which a charge rearrangement occurs [1]. Photon echoes [2] and line narrowing [3] (hole burning) have been the most important techniques to separate homogeneous from inhomogeneous broadening. In the case that a clear separation exists between the fast and slow dynamics, either technique is suitable. In systems where dispersive dynamics occurs, the (stimulated) photon echo is superior as it can set a time window in which the system dynamics is probed. Glass dynamics has been thoroughly investigated [4] in this way, and applications in protein dynamics look very promising [5].

It was only after optical pulses of a few femtoseconds became available that the solute-solvent dynamics could be explored by photon echo. The first experiments—by the Shank group [6,7]—showed that the decay of the photon echo in solution occurs on a fs time scale. Modeling of the echo response was performed using theories that treat optical response in the regime between homogeneous and inhomogeneous broadening [8,9]. This is often referred to as non-Markovian dynamics. A successful application of such an approach, clearly demonstrating the link between the decay of the photon echo and the optical line shape, was reported by Nibbering *et al.* [10]. In that particular system the solvent response was shown to occur on a single time scale. This is exceptional since molecular dynamics simulations of solvent motion indicate [11–13] that the dynamics is usually bimodal: First a fast inertial response occurs, followed by a much slower decay. The existence of inertial solvent response and bimodal dynamics has been measured for acetonitrile [14] and recently for water [15], by time-resolved Stokes shift measurements. Molecular dynamics simulations showed that this leads to a very fast decay of the photon echo [16–18] and a non-Markovian absorption line shape [19].

The existence of bimodal solvent dynamics in polar liquids leads us to anticipate that in many solvents the optical line width has contributions from fluctuations on two distinct time scales. This we will call homogeneous and inhomogeneous broadening. In femtosecond photon echo experiments it has not been possible, so far, to separate these contributions in a straightforward manner. The reason is that only the integrated photon echo intensity could be measured. With delta-pulse excitation, the intensity of the integrated echo is

$$S_{2\text{PE}}(\tau) \propto \int_0^{\infty} H(\tau, t) I(\tau, t) dt, \quad (1)$$

where $H(\tau, t)$ and $I(\tau, t)$ are the homogeneous and inhomogeneous echo response functions, and τ and t are the pulse delay and time after the last pulse. In the Markov limit $H(\tau, t) = \exp[-2\Gamma(\tau + t)]$, with Γ the homogeneous dephasing constant, while in the Gaussian static

limit $I(\tau, t) = \exp[-\Delta^2(t - \tau)^2]$, with Δ the inhomogeneous dephasing constant. It is easily derived that the maximum echo signal occurs at a time $t = \tau - \Gamma/\Delta^2$ after the second pulse (only positive times t). This shows that the integrated echo intensity will only probe the homogeneous dynamics when the relation $\Gamma/\Delta^2 \ll \tau$ holds. Otherwise the echo response will be determined by both the homogeneous and inhomogeneous response functions.

In this Letter we show that *time-resolved* femtosecond photon echo experiments *can* unequivocally separate the homogeneous and inhomogeneous contributions to an optical spectrum. Time resolving of the echo was done by up-conversion [20]. Figure 1(a) depicts how the temporal shape of the photon echo is mapped out when a gating pulse is mixed with the echo in potassium dihydrogen phosphate (KDP). The shapes of the excitation pulses and echo in Fig. 1(a) reflect the actual situation (*vide infra*) in our experiments. Cho and Fleming have recently shown [21] that two-dimensional six-wave mixing spectroscopy in the sample [22] could also be used to distinguish homogeneous from inhomogeneous broadening in solution. However, this six-wave mixing technique has limited value when the optical dynamics is non-Markovian [7,10]. Echo up-conversion has no limitations related to the dynamics, since the response of KDP can be taken as instantaneous.

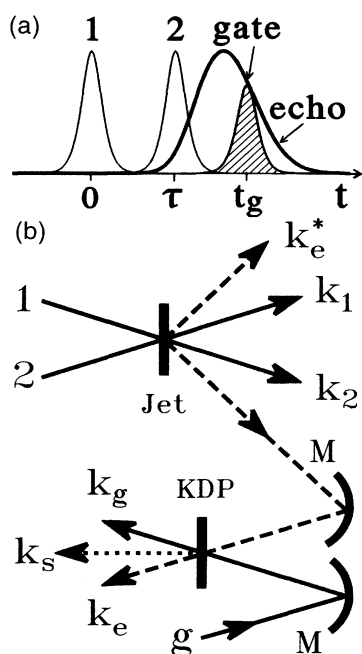


FIG. 1. Echo pulse sequence (a) and layout of the setup (b) for the generation and detection by up-conversion of the photon echo. The excitation pulses are denoted by 1 and 2, while g stands for gate pulse. In (a) the actual pulse shapes and echo signal are depicted for a delay between pulses of 53 fs. In (b), M = mirror, and KDP is potassiumdihydrophosphate.

The experiments were performed by using a cavity-dumped Ti:sapphire laser [23] for excitation and gating of the echo. The output of the laser was split in three parts: The energy of the excitation pulses (1 and 2 in Fig. 1) was 4 nJ each; the gate pulse (g in Fig. 1) was 7 nJ. The cross correlation of the pulses could be well described with a $\text{sech}^2(1.76t/\delta t)$ pulse shape with a pulse length δt (FWHM) of 14.5 fs. The sample consisted of a 100 μm thick jet containing HITCI (1,1',3,3',3',3'-hexamethylindotricarbocyanine iodide) in ethylene glycol, with a peak optical density of about 0.3. The *integrated* intensities of the echoes were detected with photodiodes in both phase-matched directions simultaneously, to accurately determine the zero delay point. The *time-resolved* intensities were measured by recollimating the echo with a curved mirror, and combining it with the gate pulse in a 300 μm thick KDP crystal. This setup is shown schematically in Fig. 1(b). The use of reflective optics is essential to prevent distortion of the echo profile. Type-I phase matching was employed in order to reduce dispersive lengthening of the pulses in the nonlinear crystal. Use of a 100 μm thick KDP crystal gave identical results. The signal at the sum frequency was spectrally and spatially filtered and detected with a photomultiplier.

Figure 2(a) shows a plot of the *integrated* photon echo intensity of HITCI in ethylene glycol as a function of delay between the excitation pulses. Figure 2(b) presents a series of *time-resolved* photon echo signals at different delays. It is clear that the temporal shape of the echo changes as a function of the delay between the excitation pulses. Note that the temporal width of the echo considerably exceeds the gate-pulse width. Results of numerical integration of the echo signals, measured by up-conversion, are also displayed in Fig. 2(a), and match perfectly those obtained by direct integration of the echo signal on a slow detector. The inset in Fig. 2(b) gives the measured maxima of the echo profiles.

Figure 3 presents a plot of the echo maximum as a function of delay between the excitation pulses. For short delays the echo maximum remains stationary in time, while for longer delays it shifts linearly with time. The *relative* uncertainty in determining the position of the echo maxima is less than a few femtoseconds. The *absolute* position of the echo signal with respect to the gate pulse, however, could only be determined with an accuracy of about 20 fs. In the analysis this problem was dealt with by comparing the whole set of echo profiles (16, taken at 5 fs intervals for the delay time τ) with calculated profiles, and to shift the whole set along the time axis until the best global fit was achieved.

To simulate the photon echo response, a stochastic modulation model [8,10] was used. In this model the electronic transition frequency varies randomly by fluctuations in the solute-solvent interaction: $\omega(t) = \omega_0 + \delta\omega(t)$. Anticipating a bimodal solvent response, we assume that the transition frequency correlation function is

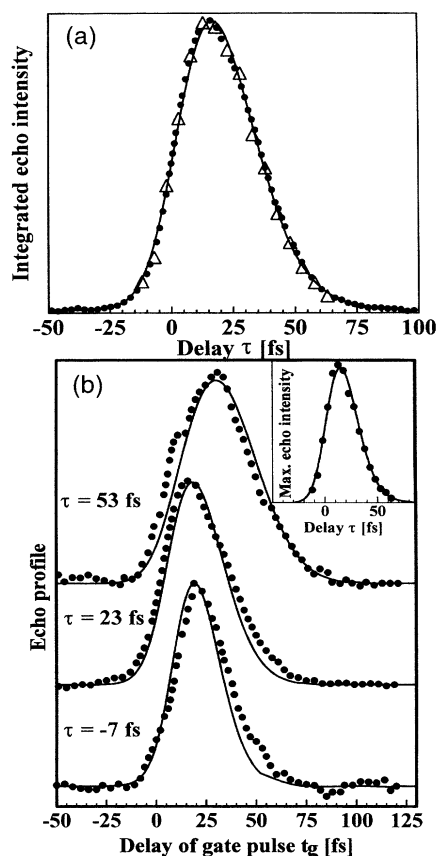


FIG. 2. Integrated (a) and time-resolved (b) two-pulse photon echo intensities. The data in (a) were obtained with a slow detector (dots), and by numerical integration of time-resolved data (triangles). In (b) the echo profiles (dots) are normalized, the actual maxima are given in the inset. The delay t_g is with respect to the second excitation pulse. The solid lines in (a) and (b) are based on the stochastic modulation model discussed in the text.

of the form

$$\langle \delta\omega(t) \delta\omega(0) \rangle = \Delta_f^2 \exp(-\Lambda_f t) + \Delta_s^2 \exp(-\Lambda_s t). \quad (2)$$

Here, $\Delta_{f,s}$ are the root mean square amplitudes and $\Lambda_{f,s}$ the inverse correlation times of the fast and slow fluctuations of the transition frequency around the average value ω_0 . With Eq. (2), the photon echo signal intensity $S_{2PE}(t, \tau)$ for delta-pulse excitation is calculated to be [10]

$$S_{2PE}(t, \tau) \propto \exp\{-2[2g(t) + 2g(\tau) - g(t + \tau)]\}, \quad (3)$$

where the line broadening function $g(t)$ is given by

$$g(t) = \frac{\Delta_f^2}{\Lambda_f^2} [\exp(-\Lambda_f t) + \Lambda_f t - 1] + \frac{\Delta_s^2}{\Lambda_s^2} [\exp(-\Lambda_s t) + \Lambda_s t - 1]. \quad (4)$$

If the fast process occurs in the Markov limit ($\Lambda_f t \gg 1$) and the slow one in the static limit ($\Lambda_s t \ll 1$), Eq. (3) assumes the form discussed in connection with Eq. (1).

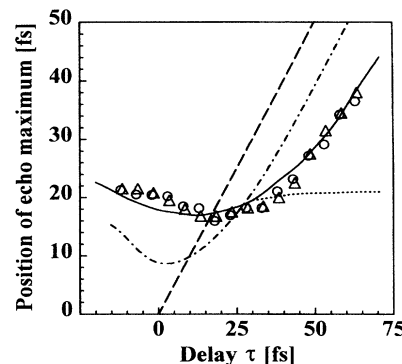


FIG. 3. Position of echo maximum vs delay between excitation pulses. Triangles and circles are measurements with KDP crystals of 100 and 300 μm . The solid line is based on the stochastic modulation model discussed in the text. The dot-dashed curve is calculated for shorter pulse duration. The long-dashed line gives the maximum for infinite inhomogeneous broadening, the short-dashed line for stochastic fluctuations on a single time scale.

The photon echo signal was simulated for different sets of parameters. In the actual calculations the effect of finite pulse duration was taken into account by numerical evaluation of the third-order polarization (a threefold integral), including “nonrephasing” contributions which vanish for impulsive excitation [24]. This leads to a more complex expression for the photon echo intensity than is presented in Eq. (3); the physics of the problem is, of course, unaltered. The calculated echo profiles were numerically convoluted with the gate pulse, to simulate the experimental up-converted echo signals. The solid lines in Figs. 2 and 3 present results of the calculations with the parameters: $\Delta_f = 55$ THz, $\Lambda_f = 110$ THz, and $\Delta_s = 55$ THz, $\Lambda_s < 0.5$ THz. The first three parameters are determined to within 5%. The excellent agreement for the integrated echo intensities, profiles, maxima, and shift of the maxima strongly supports the analysis. For the dash-dotted curve in Fig. 3 the same parameters were used, but now for a pulse length of 5 fs. This curve shows that it is essential to take the pulse length explicitly into account in the calculations.

The dotted curve in Fig. 3 presents the result expected when a single stochastic process is used to fit the optical dynamics. Although a single stochastic process with parameters $\Delta = 52$ THz, $\Lambda = 27$ THz provides an excellent fit to the *integrated* echo intensity [24], it fails to describe the shift of the echo maximum with delay time (the echo time profiles are also not correctly predicted). Finally, the dashed line in Fig. 3 gives the calculated response for very large inhomogeneous broadening: The echo appears at a delay time τ after the second pulse.

As a further test of the model, we also calculated the absorption spectrum $S_A(\omega)$, which is the Fourier-Laplace transform of the linear response function $\exp[-g(t)]$

[10]. With the same dynamical parameters as for the echo simulations, the spectrum displayed in Fig. 4 is obtained. The agreement with the experiment is found to be quite satisfactory. The stick spectrum is the assumed vibrational structure (the feature at $13\,800\text{ cm}^{-1}$ is derived from beats in pump-probe spectroscopy [24]). Figure 4 also displays the underlying "homogeneous" line shape, which deviates from a Lorentzian particularly in the wings. The homogeneous width is calculated to be 250 cm^{-1} , while the inhomogeneous contribution to the line shape is 800 cm^{-1} . As these contributions to the linewidth are of the same order, they cannot be separated in an echo experiment when only the integrated intensity is measured.

It is clear from the analysis that there is a distinct separation of time scales in the solvent dynamics of HITCI in ethylene glycol. The ratio $\Delta_f/\Lambda_f = 0.5$ shows that the fast optical dynamics is non-Markovian. The correlation time of the slow solvent fluctuations cannot be determined accurately in these fs experiments. Yu and Berg [25] showed that in ethylene glycol hydrogen-bond formation breaking occurs on a 40 ps time scale; it is quite possible that this effect is responsible for the slow solvent motions probed in the echo.

What remains is to speculate about the physical meaning of the parameters of the stochastic model, in particular the fast correlation time of about 9 fs. Is it due to multiple-particle interactions that each occur on a much slower time scale, or is the stochastic approach inadequate for a description of the echo response at this time scale? Whatever the situation, it is clear that time-resolved (stimulated) femtosecond photon echo experiments on a variety of solutions hold the clue to finding out.

Summarizing, we have shown that *time-resolved* femtosecond photon echo experiments can separate contributions to the optical spectrum that displays dynamics

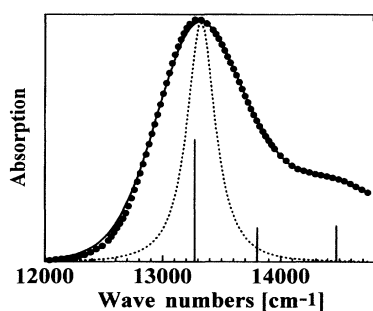


FIG. 4. Absorption spectrum of HITCI in ethylene glycol (solid dots). The solid line is based on the stochastic modulation model discussed in the text. The dotted curve presents the homogeneous line shape as derived from the time-resolved photon echo experiments. The stick spectrum shows the underlying vibrational spectrum.

on different time scales. For the system HITCI in ethylene glycol the transition frequency correlation function is found to be distinctly bimodal.

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