Ultrafast liquid dynamics studied by third and fifth order three pulse photon echoes

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We report a new spectroscopic measurement based on fifth order nonlinear response from a molecule in a room temperature liquid. In conjunction with conventional three pulse stimulated photon echo, detailed information on solvent–solute dynamics for a wide range of time scales has been obtained. Both the ultrafast inertial components and much slower dynamics of the solvent are found to make important contributions to the solvent relaxation. The potential of the fifth order measurements is discussed via numerical calculations using model solvent spectral densities. © 1995 American Institute of Physics.

INTRODUCTION

The dynamics of the interaction of solutes and solvents plays a key role in a wide range of physical and chemical processes. The interaction occurs over a wide range of time scales and with a variety of coupling strengths. An important theoretical approach to condensed phase dynamics, the spin-boson model, characterizes three time scales and coupling strengths by means of a spectral density, $J(\omega)$. From an experimental perspective the spectral line shape of a dye molecule in a dilute solution provides an accessible system of probing the chromophore–bath interaction that go beyond coupled to a complex bath, and thus allows information to be obtained on the spectral density. In this letter we describe results obtained with a new nonlinear technique, which in combination with conventional photon echo measurements, provides insights into the range of time scales and the type of molecular processes involved in the interaction of a dye molecule with ethylene glycol as a solvent.

In order to describe the reasons for developing the new technique it is necessary to briefly discuss existing methods of probing the chromophore–bath interaction that go beyond linear absorption spectroscopy. Figure 1 shows pulse sequences, time orderings, and double-sided Feynman diagrams for two-pulse photon echo (2PE), three-pulse stimulated photon echo (3PE), and fifth order three-pulse photon echo (F3PE, called FOTS in Ref. 2). In the two- and three-pulse photon echo measurements the time-integrated echo signal (integration over $t'$ in Fig. 1) is measured rather than the actual echo profile. Even though the echo profile itself is very sensitive to the detailed nature of the dynamics, the integrated echo signal is not. In addition, when the inhomogeneous width is not large, the photon echo technique can produce ambiguous results (vide infra). Recently, Cho and Fleming proposed a new technique—here called F3PE—which avoids these difficulties. In the F3PE the system is placed in an electronic coherence by the first pulse and evolves for period $\tau_1$. The second pulse involves two interactions which leave the system in an electronic coherence which is the complex conjugate of the first. During $\tau_2$ the system rephases. The third pulse also interacts twice leaving the system in a coherence which is the same as that following the first pulse. Thus the electronic polarization will fully rephase when $\tau_2=\tau_1+\tau'$, provided the phase memory is not lost. In F3PE both $\tau_1$ and $\tau_2$ are controllable, allowing control over the rephasing process which is not possible in the conventional echo measurements. In F3PE when the signal integrated over $t'$ is measured with $\tau_1$ set equal to $\tau_2$ (diagonal signal), the contribution from slow dynamics can be completely eliminated in the Markov limit. The situation is more complex for non-Markovian dynamics as discussed below. The off-diagonal signal, where $\tau_1 \neq \tau_2$, also provides useful information. To see this consider a system with a large inhomogeneous width. When $\tau_2$ is scanned with $\tau_1$ fixed, there will be no signal until $\tau_2$ is equal to $\tau_1$. That is, the signal will be delayed as much as $\tau_1$. In general, the off-diagonal measurement enables the timing of the echo to be observed directly. This feature gives the technique high sensitivity to the detailed form of the dynamics.

EXPERIMENT

Measurements of the echo signals were made for the cyanine dye HITCI in ethylene glycol solution. The concentration was $1.6 \times 10^{-3}$ M and the solution was flowed in a 30 $\mu$m-thick jet. 20 fs pulses centered at 780 nm from a home-built Kerr lens mode-locked Ti:sapphire laser running at 88.2 MHz and 15 fs pulses from a cavity-dumped version of the same laser running at 300 kHz were used. In both cases pulses are transform limited. No thermal grating was apparent at the higher repetition rate. An important factor in the accuracy of the measurements is the determination of zero time. For F3PE this determined to better than 2 fs by simultaneous measurement of the adjacent third order signal with wave vector $k_1$ and $k_2$ for the F3PE signal at $k_1-2k_2+2k_3$ or wave vector $k_1+k_2-k_3$ for the F3PE signal at $k_1+2k_2-2k_3$. For 3PE, by simultaneous measurement of the two mirror image signals in the $k_1-k_2+k_3$ and $-k_1+k_2+k_3$ phase matching directions, time zero was determined to be ±0.3 fs.
RESULTS AND DISCUSSION

The approach to the calculation of the echo signals is via the line broadening function $g(t)$. The response functions for the three experiments shown in Fig. 1 are

$$R_{2PE} = \exp\{-2g^*(\tau) - 2 \text{Re}[g(t')] + g*(\tau + t')\}, \quad (1)$$

$$R_{3PE} = \exp\{-g^*(\tau) - g*(t') + g(T) - g*(t + T) - g(T + t') + g*(\tau + T + t')\}, \quad (2)$$

$$R_{F3PE}(\tau_1, \tau_2, t') = \exp\{-2g(\tau_1) - 4 \text{Re}[g(\tau_2)] - 2 \text{Re}[g(t')] + 2g(\tau_1 + \tau_2) + 2 \text{Re}[g(\tau_2 + t')] - g(\tau_1 + \tau_2 + t')\}. \quad (3)$$

Insight into the microscopic origin of $g(t)$ can be obtained by writing $g(t)$ in one of two ways.

$$g(t) = i\lambda \int_0^t d\tau_1 M(\tau_1) + (\Delta \omega^2) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 M(\tau_2), \quad (4)$$

where

$$M(t) = \frac{\langle \Delta \omega(0) \Delta \omega(t) \rangle}{\langle \Delta \omega^2 \rangle} \quad (5)$$

is a correlation function describing the fluctuations in the transition energy of the two-level system and $\lambda$ is the magnitude of the Stokes shift. Alternatively we may write

$$g(t) = i\lambda t + i2 \int_0^\infty d\omega \sin \omega t \omega - o t \omega^2 \tanh(\beta \omega/2)D(\omega) + 2 \int_0^\infty d\omega \frac{1 - \cos \omega t}{\omega^2}D(\omega), \quad (6)$$

where $D(\omega)$ is a spectral density scaled by the fluctuation amplitude, i.e.,

$$D(\omega) = \frac{\Delta \omega^2}{\omega^2}J(\omega). \quad (7)$$

Considerable progress in understanding the short-to-medium time behavior of $M(t)$ has been made via fluorescence Stokes shift measurements and computer simulations. In highly polar liquids the solvation dynamics are strongly bimodal with an ultrafast initial component accounting for 30%–80% of the response. Simulations and theoretical models suggest this initial component is indeed inertial [Gaussian $M(t)$] rather than some ultrafast diffusive [exponential $M(t)$] process. However, the time resolution and precision of the fluorescence measurements is not sufficient to confirm the Gaussian shape directly. This issue is of importance for the interpretation of the echo measurements since a substantial Gaussian component in $M(t)$ immediately rules out the optical Bloch [M(t) = $i\delta(t)$] and Kubo [M(t) = $\exp(-t/\tau)$] models that have previously been used. The critical point is that, in general, both fast and slow dynamics may be time reversible in striking contrast to the optical Bloch picture where the fast (homogeneous) dephasing is dissipative and not rephasable. The location of the echo, as revealed by off-diagonal F3PE measurements, is very sensitive to this distinction.

In order to provide a flexible basis for modeling and fitting of data we have worked with the spectral density representation of $g(t)$. Our starting point is the Brownian oscillator model which provides a qualitatively correct form of $M(t)$, i.e., an initial Gaussian decay followed by an exponential. The spectral density of a Brownian oscillator is given by

$$D(\omega) = \frac{\Delta^2 \gamma_j \omega^2}{\pi} \times \frac{1}{(\omega^2 - \omega_j^2)^2 + \gamma_j^2 \omega^2}, \quad (8)$$

where $\omega_j$ is the mode frequency, $\gamma_j$ its damping constant, and $\Delta_j$, the coupling strength. (In the high temperature limit $\Delta_j^2 = 2\lambda_j k_B T/\hbar$, where $\lambda_j$ is the optical reorganization energy.) In order to describe our experimental data we have found it necessary to include contributions from much slower degrees of freedom than that can be obtained with parameters consistent with the short-time behavior. We do this somewhat arbitrarily (but in qualitative agreement with the simulation spectral densities) by adding a rapidly decaying exponential component to $D(\omega)$ with the form $A \exp(-\omega/\omega_o)$. For the calculations presented here we set $\omega_o = 6 \text{ cm}^{-1}$.

Figure 2 compares calculated 2PE and diagonal F3PE signals for two model $D(\omega)$: a Brownian oscillator and the Brownian oscillator plus slow modes. The two 2PE signals clearly differ although the “homogeneous” (the Brownian oscillator) contribution is the same in both cases. The two diagonal F3PE signals are indistinguishable and show that this technique’s ability to completely remove the effects of slower dynamics, which occurs analytically in the optical Bloch limit, carries over into the non-Markovian case, at least when the time scales are well separated. However, by
FIG. 2. Model calculation for the 2PE and F3PE diagonal. (a) $t'$ integrated 2PE signal intensity vs $\tau$: Solid line, a Brownian oscillator (model A); dashed line, a Brownian oscillator with an exponential spectral density (model B). Parameters used are $\omega_0=160$ cm$^{-1}$, $\gamma=260$ cm$^{-1}$ and $\Delta_{s}=250$ cm$^{-1}$ for the Brownian oscillator; $A=1000$, $\omega_0=6$ cm$^{-1}$ for the exponential spectral density. (b) $t'$ integrated F3PE diagonal signal intensity. Parameters are the same as (a).

FIG. 3. (a) Calculated peak positions of F3PE off-diagonal and 2PE signals vs $\tau_1$ and $\tau$ respectively. Parameters are the same as those in Fig. 2. The solid line, for model A; the dashed line, model B. (b) Calculated peak shifts from zero in 3PE vs $T$, the population period. Solid line, model A; dashed line, model B.

This shift as function of $T$ for the two models over a 2 ps range. It is ironic that extremely high time resolution is required to observe the small shifts characteristic of the slow dynamics.

Figures 4(a) and 4(b) present experimental diagonal and off-diagonal F3PE data, respectively, for HITCI in ethylene glycol. The diagonal F3PE signal is clearly asymmetric and demonstrates the ability of this technique to remove contributions from slow dynamics. The decay, however, is ultrafast and accurate extraction of the early time dynamics requires consideration of the pulse field envelope and inclusion of contributions from diagrams that are not properly time ordered. These latter contributions (referred to as $R_1$ and $R_4$ in Ref. 2) give a “coherence artifact” around zero time delay. This coherence artifact is also present in the off-diagonal data, but in this case it is temporally distinct from the signal peak. A complete calculation of the fifth order diagonal signal is underway and will be presented elsewhere.

In Figs. 5(a) and 5(b) the off-diagonal F3PE peak positions and the time shifts in the 3PE experiment are plotted. The off-diagonal F3PE data clearly show an initial offset in the peak position. In addition, no plateau in the peak position vs $\tau_1$ is evident up to $\tau_1=80$ fs. The peak position shifts roughly with a slope of about $\sim 0.5$. The 3PE peak position vs $T$ requires a minimum of three exponentials to give a good fit. We found components of 43 fs, 2.6 ps, and 100 ps with relative amplitudes of 1, 0.35, and 0.75, respectively.

An issue that may complicate the interpretation of our
data is the involvement of intramolecular vibrational modes. The presence of a strong modulation in the signal can significantly alter the decay of an echo. Intrinsic vibrations will generally lead to oscillations in the transient absorption signal and the shift vs $T$ curve in 3PE. In the current measurements intramolecular vibrational contribution to the signal was found to be minimal and was therefore ignored. We found very small oscillations in the transient absorption signal measured under the same experimental conditions and no oscillations were detectable in the 3PE data for HITCI. Oscillations are evident for the dye IR144 under the same conditions. A second issue that needs to be addressed is the role of finite pulse duration. We have carried out a series of simulations of 3PE experiments including realistic pulse shapes and find that the time constants obtained from fits of 3PE data vs $T$ are essentially unaffected.

In order to model the various experimental results with a constant set of parameters we return to the model spectral density. The form of the spectral density used has five parameters: $A_1/A_2$, the ratio of the amplitude of the exponential component to the amplitude of the Brownian oscillator component; $(A_1+A_2)$, the coupling strength; $\omega_o$, the exponential cutoff frequency; $\omega_j$, the Brownian oscillator frequency; and $\gamma_j$, the Brownian oscillator damping constant. With these variables we have to fit (1) the decay rate (width) of the various echo signals, (2) the fast and slow components and their relative amplitudes in the 3PE peak position measurements and (3) the position of the off-diagonal F3PE signal as a function of $\tau_1$. These different quantities exhibit strongly varying sensitivities to the various parameters and—within our model spectral density—strongly constrain the parameters. For example, the width of the echo signals is largely controlled by the coupling strength, but this has little effect on the other two measurements. As has been noted recently in connection with the solvated electron, if the coupling strength is large, the decay of the 2PE signal carries no dynamical information. Within our model the peak position decay in the 3PE measurements can be well fit by two exponential components. The longer lifetime is controlled in large measure by the exponential cutoff frequency, $\omega_o$, the smaller $\omega_o$ is, the longer the slow decay is. The decay time of the short component is determined by $\omega_j$ and $\gamma_j$. The relative amplitude of the two exponential components in the 3PE fits are strongly influenced by the ratio $A_1/A_2$. The larger the exponential contribution to $D(\omega)$ is, the larger is the amplitude of slow decay component. Finally, we consider the dependence of the off-diagonal F3PE peak position vs $\tau_1$. The slope depends strongly on the relative amplitude of the fast to slow components—it increases as $A_1/A_2$ decreases. For fixed amplitudes the shape of the off-diagonal F3PE peak positions vs $\tau_1$ depends on $\omega_j$ and $\gamma_j$. As $M(t)$ gains diffuse character, i.e., as $\gamma_j/\omega_j$ increases towards the underdamped limit, the shape becomes linear with increasing slope. As $\gamma_j/\omega_j$ decreases towards underdamped regime, the curvature of the plot increases, resulting in a decreased slope over a range of $\tau_1$ 20–80 fs. The initial offset of the peak position for a fixed Brownian oscillator frequency $\omega_j$ depends on $\gamma_j$, the damping constant. The initial offset increases as the oscillator becomes progressively more
strongly damped. The existence of a plateau in the peak position depends strongly on both $\gamma_j$ and the weight of slow (low frequency) modes in $D(\omega)$. Increasing either parameter decreases the curvature, but $A_1/A_2$ has no influence on the initial offset. The other parameters have little or modest effect on the off-diagonal peak position confirming its sensitivity to the presence of slow modes and to the degree of inertial motion in the initial solvent response.

Given these widely varying sensitivities, we find that the parameters required to fit all the data are quite constrained. The best set of parameters are those already used for illustration in Figs. 2 and 3 with one addition. For HITCI in ethylene glycol the 3PE reveals a second very slow component (~100 ps) which we model as a static inhomogeneous component with an rms width of 240 cm$^{-1}$. This additional component increases the slope of the off-diagonal F3PE peak position vs $\tau_i$ plot but has a negligible effect on the other features of the signals.

The solid lines in Figs. 5(a) and 5(b) are calculated with $A_1 = 1000$ cm$^{-1}$, $\omega_j = 6$ cm$^{-1}$, $A_2 = 202$ cm$^{-1}$ corresponding to $\Delta_r = 250$ cm$^{-1}$, $\omega_l = 160$ cm$^{-1}$, $\gamma_j = 260$ cm$^{-1}$, and a static inhomogeneous rms width of 240 cm$^{-1}$. It can be seen that both the 3PE peak shift and the off-diagonal F3PE peak position are consistently described by the parameter set. In addition the 2PE and diagonal F3PE signals are consistent with these parameters.

Before commenting on the significance of the parameters listed above we briefly discuss whether the data are consistent with simpler models. For example, it has been shown that Kubo model [exponential $M(t)$] can be used to simulate the spectral diffusion process in 3PE.\textsuperscript{9,31} The ultrafast 43 fs component in our 3PE data can be modeled as a Kubo process in the intermediate modulation regime. In this case 3PE signals alone uniquely determine the parameters: the coupling strength is largely determined by the relative amplitude of the fast to slow component and the time constant $\tau_i$ is determined by the 3PE shift decay time. The measured off-diagonal F3PE peak position, however, cannot be fitted with these parameters. Purely inertial motion, i.e., a Gaussian $M(t)$, can also be used to model the fast process. Again the parameters are uniquely determined by the 3PE signals alone. For this model the calculated off-diagonal F3PE peak positions are in close agreement with the measured values indicating that the fast process has indeed significant inertial character. Thus, as recently discussed by Stratt and Cho,\textsuperscript{32} during this initial period each solvent molecule responds to the perturbation independently without feeling the presence of other solvent molecules. This remark must be clarified, however, by noting that the solvent/solute configuration at the moment of the perturbation is a result of complex interactions in the solvent–solute system.

The parameters obtained in our analysis carry several implications for the solvation dynamics in ethylene glycol. First the initial dynamics of the solvent response is mostly inertial. The decay of $M(t)$ obtained from the Brownian oscillator parameters is estimated to have ~75% inertial character with time constant of 70 fs. This initial phase presumably results from OH librational motion in analogy to simpler protic solvents.\textsuperscript{17,18} The inertial character is clearly evident in the calculated diagonal F3PE signal in Fig. 2(b). The signal is flat for ~20 fs. Considering the factor of 4 arising from the two coherence periods ($\tau_1$ and $\tau_2$) as well as the measurement of the squared modulus of the response function, Fig. 2(b) shows that for 80 fs the electronic phase memory is essentially retained. After 80 fs the response becomes diffusive and no longer time reversible. If this were an adequate description of the whole behavior, the off-diagonal F3PE signal would go to a plateau value at ~40 fs. That this does not occur, coupled with the slow time constants observed in the 3PE data clearly indicates the presence of slow motions. These slower components arise, at least in part, from diffusive reorientational motions and should give rise to a Lorentzian contribution to the liquid spectral density at low frequencies as recently described by Chang and Castner.\textsuperscript{33} Our exponential model for the low frequency region could also include slow interconversions between different sites in the liquid. For example, the response functions in Eqs. (1)–(3) may arise from convolutions of distribution functions $W(\Gamma)$, i.e.,

$$R_i(t_3,t_2,t_1) = \int d\Gamma W(\Gamma) R_{ij}(t_3,t_2,t_1;\Gamma),$$

where $\Gamma$ is the set of parameters, e.g., $\omega_a$, $\omega_j$, $\gamma_j$, $\Delta_r$ on which $R_i$ depends. Our experiment is not capable of distinguishing whether the spectral density itself is homogeneous or not. The electronic energy gap may be sufficiently more sensitive to such sites than the bare spectrum of nuclear motions so that use of an optical Kerr spectral density to model echo data\textsuperscript{11} may not capture the full range of time scales.

To conclude we briefly discuss the relationship of our results with those of other groups. A more extensive discussion along with data in several other solvents will be presented elsewhere.\textsuperscript{29} Vöhringer et al.\textsuperscript{11} describe 2-pulse echo data for HITCI in several solvents using a spectral density obtained by Fourier transformation of optical Kerr measurements on the pure solvents. This approach is similar in spirit to that used by Cho et al.\textsuperscript{34} to model fluorescence Stokes shift data in acetonitrile and is likely to give a reasonable description of the short time dynamics if the spectrum of coupling constants to the underlying liquid modes is either frequency independent or very similar for the observables of interest. We have previously discussed cases (e.g., water) where this is not likely to be true for optical Kerr and solvation dynamics.\textsuperscript{35} No additional slow motions were included by Vöhringer.\textsuperscript{11} Bardeen and Shank used a correlation function of the form $M(t) = \text{sech}^2(t/\tau_s)$ for their analysis of echo data in several alcohols.\textsuperscript{10b} The sech$^2$ form appears quite arbitrary, although it does contain an initial Gaussian decay followed by an exponential tail. The authors concluded that the dynamics were described by a rapid process followed by longer time scale dynamics. The value of $\tau_s$ obtained was ~20 fs and was assumed constant in the different solvents. Boeij et al.\textsuperscript{5} modeled their 2PE signal for HITCI in ethylene glycol using two processes. As in this work, the short time behavior was modeled through an $M(t)$ which is Gaussian at short times and has an exponential tail. In addition, an overdamped Brownian oscillator was used to introduce slow dynamics. The correlation time of the fast process was found to be ~10 fs. Correlation times in the 10–20 fs range do not
seem reasonable for the inertial time scale expected for polar liquids, except perhaps water. The approach by Maroncelli,17b,36 which was recently supported by a more formal approach,37 gives Gaussian time scales $(1/2\omega_0)$ in the 100–200 fs range for typical polar liquids. As described in the previous paragraph, the parameters used in this work are consistent with an inverse Gaussian frequency in this range rather than 1 order of magnitude shorter. Finally, we note the work of Cong et al.38 who investigated dephasing of HITCI in ethylene glycol through modelling of the coherence spike. As discussed by Boeij et al.,8 the parameters obtained from the analysis by Cong et al.38 do not seem to be consistent with their echo data nor with ours.

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