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Phase-locked heterodyne-detected stimulated photon echo. A unique tool to study solute–solvent interactions

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Abstract

Heterodyne-detected phase-locked femtosecond stimulated photon echo (HSPE) and pump–probe (PLPP) experiments were accomplished on a dye dissolved in ethylene glycol. It is shown that all four Liouville pathways are needed in a proper description of the observed phenomena. By measurement of the real and imaginary part of the PLPP signal the short-time (≤ 60 fs) solvation dynamics can be probed, but none was found in ethylene glycol. Time-resolved and conventional stimulated photon echo experiments were also performed. The fastest solvation step in ethylene glycol seems to occur on a time scale of 300 fs.

1. Introduction

There is currently great theoretical and experimental activity in the field of femtosecond reaction dynamics [1–4]. While in the gas phase the chemistry is dictated by the intramolecular potential, in solution collisions have a major impact on the reaction path. Consequently detailed study of solvent and solution dynamics is essential to a grasp of chemical reactivity in the condensed phase. For instance, it is well known that for electron-transfer reactions the reaction rate is directly related to the time scale of solvation. Mukamel and co-workers [5] laid an explicit connection between these entities in the so-called multimode Brownian oscillator (MBO) model. This model provides also a direct link between solvation and optical dynamics [6]. In MBO theory a major role is played by the so-called line broadening function $g(t)$, whose imaginary part is directly related to solvation dynamics. In the past decade vari-

ous time-resolved four-wave mixing techniques [7–13] have been employed to detail the nonlinear optical response function [6,14,15], which directly relates to $g(t)$.

Solvation dynamics covers, of course, a wide range of time scales, and each technique has its own relevant time scale. For instance, the two-pulse photon echo is particularly sensitive to ultrafast solvation dynamics, while the stimulated photon echo probes both the fast and the slow solvent motions. We showed recently [13] that by time-resolving the temporal shape of the fs echo transient in solution a better grip can be obtained on $g(t)$ than by time-integrated photon echo experiments. Pump–probe measurements are in principle open to solvent dynamics on all time scales [14], but the achievable dynamical information depends crucially on the excitation pulse parameters.

The nonlinear optical response function probed by any four-wave mixing experiment has both a real

Fig. 1. Pulse sequence for heterodyne detection of stimulated photon echo (HSPE) (a) and the basic double-sided Feynman diagrams used for a perturbative description of the third-order polarization with a wavevector $\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ or $\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{k}_3$ in a two-level system with ground $|g\rangle$ and excited $|e\rangle$ states (b). Wavevectors of the field pairs E_1 and E_2 and E_3 and E_4 are equal: $\mathbf{k}_1 = \mathbf{k}_2$ and $\mathbf{k}_3 = \mathbf{k}_4$, while the difference between their phases is: $\phi_{12} = \phi_1 - \phi_2$, $\phi_{34} = \phi_3 - \phi_4$. In (a) the dashed line represents the stimulated photon echo polarization (described by diagrams R_1 and R_2). The dotted curve is the tail of the virtual photon echo (R_3 and R_4). For zero delay τ' phase-locked pump-probe (PLPP) is probed.

and imaginary part. However, conventional photon echo techniques probe only the *absolute square* of the third-order polarization while pump-probe measures a *combination* of the real and imaginary part of it. It is well-known that by optical-phase sensitive detection of the polarization, the *real* and *imaginary* part of the nonlinear optical response function can be separated [15–17].

In this Letter we report on phase-locked heterodyne detected stimulated photon echo (HSPE) and phase-locked pump-probe (PLPP) experiments on a solution of 3,3'-diethylthiatricarbocyanine iodide (DTTCI) in ethylene glycol (EG) at room temperature. The pulse sequence for HSPE is displayed in Fig. 1a. The HSPE experiments reported in this paper clearly demonstrate that the phase-locked echo

signals are dependent on the phase differences ϕ_{12} and ϕ_{34} separately, and not only on their difference ($\phi_{12} - \phi_{34}$) as has been suggested [16,17]. This marks the importance of taking all four Liouville pathways into account (Fig. 1b). From PLPP experiments direct information on the short-time dynamics of $g(t)$ is obtained. Time-resolved photon echo and time-integrated stimulated photon echo experiments were also performed to determine $g(t)$.

The potential of femtosecond phase-locked photon echo to the study of solvent dynamics has been explored theoretically in some detail [16,17], but no experiments have been reported. Yet, time-resolved spectroscopic experiments with femtosecond phase-locked pulses demonstrating wavepacket interferometry, have been performed before [18,19]. There is currently much interest in phase-locked excitation pulse schemes because of their potential in coherent control experiments [20]. The only demonstration of an echo effect based on optical-heterodyne detection is the accumulated photon echo (APE) [21]. The APE is a high repetition rate stimulated photon echo experiment, but with heterodyne detection of the echo polarization. The phase differences between the pulses in each pair of excitation pulses are identical by nature of the APE design. APE therefore probes only the real part of the nonlinear optical response function [15], averaged over the lifetime of the bottleneck state [21].

2. Experimental

The phase-locked femtosecond HSPE experiments were performed with pulses from a home-built cavity-dumped Ti:sapphire laser [22], whose spectral output is centred around 780 nm. The dumped laser pulses, after passing through a four-prism compressor are split by a 50% beamsplitter, whereby one of the beams is directed to a variable optical delay that provides a delay time T (Fig. 1a). Both the normal as well as the delayed beams are directed to two Mach-Zehnder interferometers. Each interferometer produces a sequence of two interferometrically stable laser pulses (pulse pair 1 and 2 with delay τ and pair 3 and 4 with delay τ'). A precision translation stage in combination with a ceramic piezo transducer en-

able accurate control of the delay between the pulses of a pulse pair.

Phase-locking of the femtosecond laser pulses is achieved in a similar fashion as described by Scherer et al. [18,19]. Since in the HSPE experiment two independent phase-locked pulse pairs with full and continuous control over the phase-delay in each pulse pair are needed, a double phase-lock loop arrangement is incorporated in the experimental setup. To this end the idler output beams of both Mach–Zehner interferometers are focused on the entrance slit of a monochromator by a cylindrical lens. Since both reference beams are traversing the same monochromator (double image on the entrance slit), both interferometers are phase-locked to exactly the same wavelength. The absorption maximum of the dye solution at 770 nm is chosen as the phase-lock wavelength. This particular choice compensates for a phase factor introduced in the polarization by a slight detuning between the pulse carrier frequency and the absorption maximum of the dye [19].

In the HSPE experiment the two independently phase-locked pulse pairs were focused in the sample jet under a small angle and recollimated using all reflective optics. Dye solutions of DTTCl (Lambda Physik) in EG (Merck p.A.) were made with a peak optical density of about 0.2 over a jet thickness of 100 μm . After traversing the jet both beams are focused in a 100 μm LBO crystal to generate the second harmonic signal. This enables measurement of the phase-locked interferometric collinear autocorrelation, providing an accurate position of zero delay within each pulse pair. The autocorrelation was recorded simultaneously with the HSPE experiments for continuous inspection of the phase-locking process. It yielded a pulse duration of 14 fs, independent of whether the jet was off or on. The zero delay point between the two pulse pairs was set by recording pump–probe as well as non-collinear autocorrelation signals.

The HSPE was detected by a silicon photodiode positioned in the beam carrying pulses 3 and 4, and processed by a lock-in amplifier. It was referenced to the sum-frequency of a dual-frequency mechanical chopper positioned in the first interferometer, and chopping both beams 1 and 2. Excitation pulse energies were kept as low as 250 pJ per pulse to avoid interference with higher-order (for instance, $\chi^{(5)}$)

optical nonlinearities. The experiments were performed at a repetition rate of 4 MHz; lowering this rate had no effect on the signal shape.

3. Results and discussion

The pulse sequence for HSPE and the four double-sided Feynman diagrams that describe the stimulated photon echo in a two-level system are depicted in Fig. 1. The heterodyne detected photon echo signal can be expressed in the form [15]

$$S_{\text{HSPE}}(\tau', T, \tau, \phi_{12}, \phi_{34}) = -2 \operatorname{Im} \int_0^\infty dt E_{\text{loc}}^*(t - \tau') \times P_{\text{SPE}}^{(3)}(k_4, T, \tau, \phi_{12}, \phi_{34}, t). \quad (1)$$

Here $P_{\text{SPE}}^{(3)}$ is the third-order polarization at time t and $E_{\text{loc}}^*(t - \tau')$ the complex conjugate of the local oscillator field (E_3 and/or E_4). The HSPE signal was calculated on basis of 16 Feynman diagrams, being the number of relevant permutations of the four basic ones. It was assumed that the delay time T is long enough not to mix the pulse pairs 1 and 2, and 3 and 4. In this situation the HSPE signal for impulsive excitation and τ and $\tau' \geq 0$ is calculated to be

$$S_{\text{HSPE}}(\tau', T, \tau, \phi_{12}, \phi_{34}) \sim \operatorname{Re} \{ [R_1(0, T, \tau) + R_2(0, T, \tau)] \exp(-i\phi_{12}) + [R_3(0, T, \tau) + R_4(0, T, \tau)] \exp(+i\phi_{12}) \} \times A_1 A_2 (A_3^2 + A_4^2) + 2 \operatorname{Re} \{ [R_1(\tau', T, \tau) + R_2(\tau', T, \tau)] \times \exp(-i\phi_{12}) + [R_3(\tau', T, \tau) + R_4(\tau', T, \tau)] \times \exp(+i\phi_{12}) \} \exp(+i\phi_{34}) A_1 A_2 A_3 A_4. \quad (2)$$

Here $R_{1-4}(\tau', T, \tau)$ are the nonlinear response functions that correspond to the four different Feynman diagrams (Liouville pathways) displayed in Fig. 1b. Their general form has been published [15], in particular: $R_1(0, T, \tau) = R_2(0, T, \tau) = R_3^*(0, T, \tau) = R_4^*(0, T, \tau) = \exp[-g(\tau)]$. A_i is the real part of the electric field amplitude of pulse i . Note that contributions due to pulse events like 1134 and 2234 have

been omitted from Eq. (2), because these are not measured in our detection scheme. The generalization of Eq. (2) for negative times τ and τ' is straightforward.

In MBO theory the line broadening function $g(t)$ is [15]

$$g(t) = i\lambda \int_0^t d\tau M(\tau) + \Delta^2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 M(\tau_2). \quad (3)$$

Here λ is the reorganization energy, Δ the amplitude of the stochastically fluctuating force, and $M(\tau)$ the so-called oscillator–bath correlation function.

The first term between braces in Eq. (2) contains contributions to the HSPE signal from pulse events 1233 and 1244, these are PLPP effects to be discussed first. The second term between braces in Eq. (2) holds the true stimulated echo-like contributions to the HSPE signal. In the HSPE experiments to be discussed later, we scan τ' while τ and T remain fixed. In this situation the PLPP contributions to the total HSPE signal provide only a constant background, which can be subtracted by making an additional scan for very large τ' , where the genuine HSPE signal is negligible.

We first discuss the special case for zero time delay between the third and fourth pulses but with a phase difference of either 0 or $\pi/2$. In this, effectively three-pulse phase-locked experiment, we measure the PLPP signal. The reason of employing this exotic pulse configuration is for demonstrating the kind of phase control we have (vide infra). From Eq. (2) we can then easily deduce how the PLPP signal depends on the phase differences between the four pulses. The results are given in Table 1, assuming all pulse amplitudes to be equal. In PLPP the in-phase and in-quadrature signals can be directly related to the real and imaginary part of $g(t)$. Note that $g(0)$

Fig. 2. Results (a, b) and analysis (c, d) of phase-locked pump-probe measurements. The rhombi ($\diamond$) and triangles ($\blacktriangle$) in (a, b) represent the measurements with $\phi = 0$ and $\pi/2$ respectively. The dots ($\bullet$) in (c, d) represent the data derived by point-by-point processing of the data in (a, b) according to Eq. (4). The solid lines are fits to the data with parameters shown in insets of (c, d). Separation between pulse pairs $T = 5$ ps.

= 0. The important relations from which $g(t)$ can be calculated are

$$\begin{aligned} \text{Im}[g(t)] &= \arctan[S(\phi_{12} = \pi/2)/S(\phi_{12} = 0)], \\ \text{Re}[g(t)] &= -\frac{1}{2} \ln[S^2(\phi_{12} = \pi/2) + S^2(\phi_{12} = 0)]. \end{aligned} \quad (4)$$

Figs. 2a and 2b display the measured PLPP signals for four different phase combinations. The first thing to note is that the PLPP signals measured for $\phi_{34} = 0$ are twice as intense as for $\phi_{34} = \pi/2$, as expected from Table 1. Of course, this is basically a trivial effect caused by interference between waves

Table 1
Phase-locked pump-probe signal for different phase settings ϕ_{12} and ϕ_{34}

ϕ_{12}	ϕ_{34}	$\tau > 0$: $S_{\text{HSPE}} = \exp(-\text{Re}[g(\tau)]) \times$	$\tau < 0$: $S_{\text{HSPE}} = \exp(-\text{Re}[g(-\tau)]) \times$
0	0	$2 \cos(\text{Im}[g(\tau)])$	$2 \cos(\text{Im}[g(-\tau)])$
$\pi/2$	0	$2 \sin(\text{Im}[g(\tau)])$	$-2 \sin(\text{Im}[g(-\tau)])$
0	$\pi/2$	$\cos(\text{Im}[g(\tau)])$	$\cos(\text{Im}[g(-\tau)])$
$\pi/2$	$\pi/2$	$\sin(\text{Im}[g(\tau)])$	$-\sin(\text{Im}[g(-\tau)])$

E_3 and E_4 , but it demonstrates that we have excellent control over the optical phase differences in the excitation pulse pairs. Figs. 2c and 2d contain plots of the imaginary and real parts of $g(t)$, obtained by processing the data displayed in Figs. 2a and 2b by employing Eq. (4).

It is clear from Fig. 2c that $\text{Im}[g(t)]$ can be well approximated by a linear function of time over the first 60 fs. For $\text{Im}[g(t)]$ to behave in this manner, $M(\tau)$ must be constant over this time range. Eq. (3) then predicts $\text{Re}[g(t)]$ to be a quadratic function of time, in excellent agreement with the results displayed in Fig. 2d. From a linear and quadratic fit, respectively, to the data displayed Figs. 2c and 2d we obtain: $\lambda = 32$ THz, and $\Delta = 45$ THz. With these constants the solid lines in Figs. 2a and 2b are calculated, with the amplitude being the only fit parameter for all four curves. It is interesting to note that for $\lambda = 32$ THz the dissipation–fluctuation theorem predicts in the high-temperature limit of the MBO model [15] $\Delta = 50$ THz. This close correspondence between experiment and theoretical prediction shows that the relevant Brownian oscillators must have low frequencies compared to kT .

The linear short-time behaviour of $\text{Im}[g(t)]$ implies that *there is no noticeable solvation dynamics in ethylene glycol at a time scale of 60 fs*. This conclusion would not change if the finite excitation pulse duration would be taken into account. It can be shown that if an appreciable fast component exists in the solvation dynamics there would be a distinct bend in the $\text{Im}[g(t)]$ versus τ plot. The absence of ultrafast solvation dynamics in EG accords with the analysis of earlier pump–probe [11] and optical Kerr effect [23] studies but contradicts the conclusions of third-order [8–10,12,13] and fifth-order [24] photon echo measurements. In particular Joo et al. [24] concluded that 75% of the solvation dynamics in EG takes place within the first 70 fs. We return to a discussion of this point later.

In order to probe solvation dynamics on a time scale longer than 60 fs we performed conventional stimulated photon echo experiments. In these experiments we focused on the *shift of the echo maximum* as a function of T , on scanning the separation between the first two excitation pulses (Fig. 3). It has been shown [10,24,25] that this shift is very sensitive to spectral diffusion, caused by, for instance, solva-

Fig. 3. Shift of the position of echo maximum (●) measured in time-integrated stimulated photon echo experiment as a function of T , while scanning the delay τ . The solid lines represents a four-exponential-fit to the overall decay of the echo-maximum shift versus T , with times of 330 fs, 5 ps, 50 ps, 500 ps and weights of 0.5, 0.16, 0.17, 0.17, respectively. The dashed line is meant as a guide to the eye.

tion. The shift for delays up to 30 fs is caused by the finite duration of the excitation pulses [26], while the oscillations in it are assigned to wavepacket dynamics [27]¹. We note that this is the first time that it is demonstrated that the echo-peak shift exhibits ‘quantum beats’. The fastest overall decay time in the echo-peak shift is ≈ 330 fs. This time scale was also obtained in pump–probe experiments by Cong et al. [11]. Decay of the echo-peak shift on a 5 ps and longer time scales (50 and 500 ps) is also observed. In closing of this section we draw attention to the fact that Fig. 3 provides no evidence either for solvation dynamics in EG on a 60 fs time scale.

We now present results of HSPE experiments for different delays between the excitation pulses, and for all combinations of 0 and $\pi/2$ phase differences (Fig. 4). Equation (2) shows that the HSPE signal generally depends on the sum and difference of ϕ_{12} and ϕ_{34} . Only in the large inhomogeneous broadening limit and in case the echo is a δ -function in time,

¹ For DTTCI a mode with a frequency of ≈ 160 cm^{-1} and some others at higher frequencies can be observed in the (non-resonant) Raman spectrum. These modes are also very prominent in frequency-resolved pump–probe and stimulated photon echo experiments. For a similar dye molecule, HITCI, we also observed strong quantum beats in the pump–probe and stimulated photon echo signals. The low-frequency ≈ 150 cm^{-1} mode in this case is more strongly damped than for DTTCI.

the Liouville pathways R_3 and R_4 can be neglected, and the HSPE signal depends solely on $(\phi_{12} - \phi_{34})$. The fact that for different phase combinations the signals are substantially different corroborates the importance of taking all four Liouville pathways into account. From Eq. (2) we derive that for the chosen phase combinations the real or imaginary part of $(R_1 + R_2) \pm (R_3 + R_4)$ is probed.

Several things can be noted in Fig. 4. Firstly, the particular shape of the signals (absorption- or dispersion-like) is not determined by the fact whether the imaginary or real part of the response function is probed, but rather on the combination of phases ϕ_{12} and ϕ_{34} . For instance, Eq. (2) yields that in Figs. 4a, 4d the real and in Figs. 4b, 4c the imaginary part is measured. Secondly, in Fig. 4a the signal broadens with increasing delay between the first two excitation pulses. This is caused by the fact that the photon echo maximum shifts to later times [13,24] (consult, for instance, Fig. 5) with increasing delay between the first two pulses. Thirdly, for certain phase differences (lower two panels) the signals grow in with

Fig. 4. Heterodyne detected stimulated photon echo signals for different phase combinations as indicated in the insets. Separation between pulse pairs $T = 5$ ps.

Fig. 5. Plot of the position of the time-resolved two-pulse photon echo maximum in respect to the second excitation pulse (●) versus delay between excitation pulses. The solid line is a fit using two overdamped Brownian oscillators with parameters given in the text. The dashed line gives the position of the echo maximum for infinite inhomogeneous broadening.

increasing delay, before decaying. This can be understood from Eq. (2), where for $\phi_{12} = \pi/2$ and $\tau = 0$ one obtains exact cancellation of the amplitudes for the different Liouville pathways (R_1 and R_2 , and R_3 and R_4 in Fig. 1b) for any delay τ' . Finally, in Fig. 4c the HSPE signal decays rapidly with increasing delay τ . This effect is also a manifestation of interference between different Liouville pathways, which will be addressed in a separate paper [28]. While the overall behaviour of the HSPE signal accords with our expectations based on Eq. (2), the details depend, of course, on the specifics of the optical dynamics.

It was recently demonstrated [13] that time-resolved fs photon echo provides considerable more information than time-integrated fs echo experiments. In time-resolved echo experiments the temporal shape of the echo intensity is measured as a function of delay between the excitation pulses². Fig. 5 shows a plot of the shift of the time-resolved echo maximum for DTTCI in EG, including a fit

² Recently we have been able to determine the echo position with respect to the excitation pulses with an accuracy of ± 2 fs (Fig. 5 and also Ref. [13]). It was measured by up-conversion of both the echo and the light, scattered from the excitation pulses by the sample jet irregularities towards the echo direction.

based on the MBO model. In the analysis the finite excitation pulse widths were taken into account. The data were fit using two overdamped Brownian oscillators: one fast ($\Delta = 65$ THz, $\Lambda = 90$ THz), the other slow ($\Delta = 50$ THz, $\Lambda \leq 1$ THz). With these oscillators we have calculated HSPE signals for the different phase combinations. While the simulated signals match those depicted in Fig. 4 rather well, some of the details differ. Work is in progress to refine our dynamical model to obtain a better fit of the data.

We now turn to the riddle of the time scale of solvation in ethylene glycol. While time-resolved [13] and fifth-order [24] photon echo experiments seem to provide strong evidence for an ultrafast (inertial) component in solvation, pump-probe [11], PLPP and stimulated photon echo-maximum-shift experiments (Figs. 2 and 3) provide no evidence for this effect. We suggest that the noted discrepancies relate to wavepacket dynamics, which affects the signals in the various four-wave mixing spectroscopies quite differently. The importance of wavepacket dynamics to optical dephasing measurements has been pointed out before [11,29–31]. Fig. 3 shows that the *shift* of the echo maximum in stimulated photon echo also exhibits wavepacket dynamics with an oscillation period typical for a low-frequency vibrational mode [27]. It would be a mistake to interpret the initial decay of the echo-peak shift, which is due to wavepacket dynamics, to a solvation effect. Solvation dynamics manifests itself, of course, in the overall decay of the echo-peak shift, as shown by the solid lines in Fig. 3. A simulation of the temporal shape or intensity of the photon echo, without taking into account wavepacket dynamics, may thus lead to erroneous conclusions. In other words the fast oscillator, ubiquitous present in the MBO description of third-order and fifth-order echo effects, may not be directly related to solvent dynamics. It could effectively represent the combined effect of vibrational coherence and solvation processes, occurring at different time scales longer than 60 fs. We end by noting that in HSPE experiments wavepacket dynamics plays a role also, but, by taking the ratio of the imaginary and real part of the signal, its effect on the nonlinear solute–solvent response function seems to be nullified.

Recapitulating: we have performed phase-locked

four-wave mixing experiments for the first time and showed that HSPE is a unique tool for the exploration of solute–solvent interactions. In the specific case of DTTCl in EG we conclude from PLPP measurements that the bath–oscillator correlation function is constant over the first 60 fs. This implies that no fast solvation dynamics exist in this solvent. This is confirmed by stimulated photon echo-peak shift measurements. The HSPE experiments demonstrate also that we can exercise control over the interference between different Liouville pathways, and that for a correct description of solvation dynamics both the so-called rephasing and non-rephasing Feynman diagrams are essential. Finally, we suggest that the temporal shape and decay of fs photon echoes in solution can be substantially affected by wavepacket dynamics. Future work will be aimed at further exploration of phase-locked four-wave mixing towards studies of optical dynamics.

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