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Wavelength-dependent resonant homodyne and heterodyne transient grating spectroscopy with a diffractive optics method: Solvent effect on the third-order signal

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We carried out a wavelength-dependent homodyne and heterodyne transient grating (TG) studies on a resonant system, rhodamine 640 in dimethylsulfoxide, with a simplified diffractive optics method. The real and imaginary components of the third-order molecular polarization at different excitation wavelengths have a similar longtime decay (>200 fs), while the amplitude of the real component is strongly wavelength dependent. The nonresonant solvent and the resonant solute contributions to the third-order polarization are found to have a similar magnitude in a dilute solution. The interference of the wavelength-dependent resonant solute contributions with the nonresonant solvent contribution is found to be crucial to properly understand the wavelength dependence of the initial dynamics in homodyne TG and other four-wave mixing techniques. Such an interference effect is further confirmed by concentration-dependent homodyne TG measurements. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473653]

I. INTRODUCTION

Four-wave mixing spectroscopies, such as the transient grating (TG) method, have been widely used to study ultrafast chemical dynamics in the condensed phase. In a TG experiment, a spatial transmission grating is formed in the medium by the interference of two temporally coincident laser pulses, resulting in a spatially modulated complex refractive index in the crossing region. A third, temporally delayed pulse is scattered off the grating into the Bragg angle. Therefore the TG is sensitive to any process that causes the change of the complex refractive index, such as population relaxation, spectral diffusion, thermal grating, and laser-induced birefringence.1,11

The nature of the initial decay of the TG signals has been discussed by several groups. A large initial spike, usually observed to increase as the excitation wavelength was shifted to the blue side of the absorption band, was previously attributed, at least in part, to the ultrafast solvation process. It was recently shown, based on simulations that introduced all the modes observed in the resonance Raman spectrum, that a significant contribution could arise from vibrational modes. An alternative explanation was given by Gumy et al., who suggested that this initial spike arises from the interference between a population phase grating and a thermal phase grating, the latter being generated by the high repetition rate laser pulses used in their experiments. However, a similar wavelength dependence of the initial decay in the TG signal was also observed with a “crossed grating geometry,” which should be free of the thermal grating contribution. Accordingly, the authors interpreted this wavelength dependence as arising from selective probing of different sets of solvated chromophores within the absorption spectrum. Inconsistencies between the experimental and simulation results at short times have also been reported in other four-wave mixing techniques, such as the three-pulse photon echo peak shift and frequency resolved echo experiments. Clearly, this wavelength-dependent spike needs to be carefully characterized in order to understand the short time dynamics of the third-order nonlinear signals.

TG measurements are normally performed in a homodyne detection scheme, in which the signal intensity depends on the square of the third-order polarization $P^{(3)}$. Thus the real and imaginary components of $P^{(3)}$, which do not always show the same decay profile, cannot be determined separately. The imaginary component is mainly sensitive to population change and solvation dynamics, while the real component is also sensitive to the thermal phase-grating and the nonresonant solvent contribution (the optical Kerr response). Although the nonresonant Kerr response of the pure liquids has been widely used to study reorientational dynamics, its possible effect on the homodyne signals obtained in a resonant system has not been systematically considered. Previously, it was found that the photon echo signal detected in the UV region is buried under the nonresonant signal of the neat solvent. In contrast, this nonresonant contribution in the visible region was usually observed to be much smaller than the resonant contribution and therefore was generally ignored. In this paper we will show that an interference effect introduced by the small nonresonant solvent contribution can significantly alter the short time dynamics detected in homodyne TG measurements, especially when very dilute solutions are used. The solvent contribution to the overall TG signal can be directly monitored by separate measurements of the real and imaginary components of

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the third-order signal, which can be achieved with the optical heterodyne detection (OHD) technique.

Optical heterodyne spectroscopy is performed by coherently mixing the weak signal field \( \mathbf{E}_s(t) \) with a relatively strong beam, \( \mathbf{E}_{\text{LO}}(t) \), the local oscillator (LO). With \( |\mathbf{E}_{\text{LO}}(t)| \gg |\mathbf{E}_s(t)| \), the amplified heterodyne signal can be expressed as

\[
I_{\text{Het}} \propto E_{\text{LO}}^2 \left[ \cos(\phi) \text{Im}(P^{(3)}) + \sin(\phi) \text{Re}(P^{(3)}) \right],
\]

where \( \phi \) is the phase difference between the signal and the LO fields. Thus the real and imaginary components of the third-order polarization can be selectively determined by controlling the LO field to be in quadrature (\( \phi = \pi/2, 3\pi/2, \ldots \)) or in phase (\( \phi = 0, \pi, \ldots \)) with the signal field, respectively.

Optical heterodyne detected transient grating (OHD-TG) can be achieved by either active or passive phase locking. Active phase-locked OHD-TG using a Mach–Zehnder interferometer has been reported by several groups,\(^{22,23}\) however its application was hampered by the limited phase stability and experimental complexity. Recently, the use of diffractive optics (DO) for passively phase-locked OHD-TG has been shown to be an elegant and straightforward method, as demonstrated by Miller and co-workers\(^{4,24–26}\) and Nelson and co-workers.\(^{27}\) Such a method allows one to take full advantage of the OHD technique. To completely remove the contamination of the pump–probe (PP) signal in the same phase-matching direction in these experiments, Tokmakoff and co-workers\(^{28}\) introduced a setup based on dual DO elements.

Recently, we reported a simplified single diffractive optic OHD-TG method\(^{21}\) based on modifications of the arrangement used by Miller and co-workers.\(^{4,24–26}\) It features ease in alignment, suppression of scattering, and is free of PP contamination in the detected TG signals. In this paper, we report wavelength-dependent homodyne and heterodyne TG studies on a resonant system, rhodamine 640 in dimethylsulfoxide (DMSO), with this simplified single DO arrangement. The real and imaginary components of the third-order signal are separately measured using this OHD-TG arrangement. Our results show that the wavelength dependence of the initial dynamics in homodyne TG can be strongly contaminated by the interference between the nonresonant solvent and resonant solute contributions at the concentrations typically used in the experiments.

**II. EXPERIMENT**

The experimental arrangement used for passively phase-locked OHD-TG with a single DO element has been described in detail previously.\(^{21}\) Briefly, the pulse generated from a regenerative Ti:sapphire amplifier pumped optical parametric amplifier was compressed to \( \sim 40 \) fs with a SF10 prism pair and split into two beams. A strong pump and a weak probe with an intensity ratio of \( \sim 10:1 \). The maximal pulse energy of the pump beam was \( \sim 1.3 \) nJ at the sample position. As shown in Fig. 1, both the pump and probe beams separately passed through a combination of zero-order half-waveplate and polarizer in order to control their relative polarizations and intensities. The two beams were then spatially overlapped on a DO (Rochester Photonics) with a 20 cm focal length quartz lens. Each of the two beams was split into two replicas (\( \pm 1 \) diffractive orders) with an efficiency of around 30%. The crossing angle between the two replicas being \( \sim 2^\circ \). The resulting four beams were achromatically imaged onto the sample by a combination of an Al-coated concave spherical mirror with a 50 cm radius and a fold mirror. The spherical mirror was placed one radius away from the DO and slightly tilted off-axis horizontally to separate the outgoing beams from the incoming beams. Following the phase-matching condition, the signal \( \mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 \) was radiated along the LO direction \( \mathbf{k}_4 \). The probe beam \( \mathbf{k}_3 \) was chopped at 1150 Hz directly in front of the sample and the signal was detected by a silicon photodiode connected to a lock-in amplifier. An iris between the sample and the detector blocked the unwanted beams and scattered light. A second polarizer was mounted after the iris to set the signal polarization. Furthermore, a 150 \( \mu \)m thickness microscope cover slip (CS) was inserted into both the probe and LO paths, and the CS in the LO path was mounted on a rotating stage to control of the phase difference between the LO and signal fields. Because phase stability plays a crucial role in the heterodyne experiment, we have made efforts to...
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Improvement within the 1 h test period, the standard deviation of the phase fluctuation was 0.7°, while over 1 1/2 h the standard deviation increased to 1.1°.

Homodyne TG and PP measurements were carried out with the same setup. Homodyne TG was performed with the fourth beam (K4, LO) blocked, whereas the PP signal was collected with chopped pump and blocked K1 and K2 beams.

The measurements on R640/DMSO were performed using a 1 mm path length glass flow sample cell. In order to avoid any possible thermal heating effect, the solution was circulated with a gear pump at a speed that corresponds to less than 150 shots per fresh sample volume. The concentration of R640 was adjusted to give an OD of 0.55 per mm at the corresponding excitation wavelength in most measurements unless otherwise noted, to avoid the concentration effect discussed in later sections. To measure the birefringent signals of various solvents, a glass sample cell with 2 mm path length was carefully positioned to minimize possible contribution from the cell walls. The polarizations of all four beams were kept parallel and the pulse duration was ~33 fs.

Rhodamine 640 (R640) was obtained from Exciton Co. Carbon disulfide (CS2), carbon tetrachloride, toluene, benzonitrile, N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA), and dimethylsulfoxide (DMSO) were purchased from Aldrich, methanol and acetonitrile were from Merck, benzene and chloroform were from Fisher. The solute and solvents were used as received.

III. RESULTS AND DISCUSSION

A. Wavelength-dependent homodyne TG

Homodyne TG measurements on R640/DMSO were carried out at different excitation wavelengths, ranging from the blue to the red side of the absorption spectrum. The locations of excitation wavelengths are indicated by the arrows in the absorption spectrum as shown in Fig. 2 and the corresponding homodyne TG data are shown in Fig. 3. The pulse duration was fixed at ~40 fs at each of the different wavelengths for the measurements shown here, to avoid any possible pulse duration effects. It can be seen from Fig. 3 that as the excitation wavelength shifts toward the red, the amplitude of initial spike decreases. A similar decrease in the amplitude of the initial spike as the wavelength is shifted to the red has previously been reported in several systems. In the current experiment, the contribution of the accumulated thermal phase grating is expected to be small, due to the relatively low repetition rate and the rapid flowing of the sample. Measurements with different flow rates, furthermore, showed no detectable change of the decay profile, except that the signal to noise ratio became worse at very high flow rates. In addition, the oscillation period of the acoustic grating is normally around several nanoseconds and decays on an even longer time scale. Given the fact that the strong dependence on wavelength is usually observed only in the first 200 fs, it is unlikely that the contribution from the thermal phase grating plays a significant role. To obtain a clear picture of the underlying dynamics in the homodyne signal, we turn to a discussion of the real and imaginary components of $P^{(3)}$ measured in the OHD-TG signal, in other words, the amplitude and phase gratings.

B. Wavelength-dependent OHD-TG

The wavelength dependent OHD-TG profiles in R640/DMSO are shown in Fig. 4. The measurements were performed first by setting the desired phase difference between the signal and the LO fields using the nonresonant response of CS2, and then replacing the CS2 sample cell with an identical cell containing the sample. The phase settings were carefully checked before and after each measurement to ensure that no detectable phase shift had occurred. The measurements for each desired phase difference were repeated several times and the data were averaged to improve the accuracy of the phase settings. In order to remove a small homodyne contribution from the heterodyne signal, the real and imaginary components were obtained from the difference between two experimental data sets with a $\pi$-phase shift in the LO. The accuracy of the phase settings was also
double-checked by a two-step comparison as follows.\(^{21}\) The imaginary component was compared with the PP signal. The consistency of the two curves indicated that the phase for the measurement of the imaginary component was correctly set. (b) The homodyne signal reconstructed from the sum of squared experimentally measured real and imaginary components of \(P(3)\) was compared with the measured homodyne signal. The consistency of these two curves further guaranteed the accuracy of the phase settings for both the real and imaginary components.

It is worth noting that the sign of the signal in this paper is defined so that the nonresonant signal from the solvent is positive at phase \(\phi = \pi/2\). The signal is presented in terms of transmission change, rather than absorption change. Thus for a simple two-level resonant system, the PP signal (imaginary component) is positive instead of the conventionally defined, negative photobleaching and stimulated emission signal in terms of transient absorption.

As shown in Fig. 4, the real and imaginary components show very different wavelength dependence. In comparison to the imaginary component, the real response is much more sensitive to the excitation wavelength. The imaginary component of the response is positive at all excitation wavelengths, while the amplitude of the real component changes sign from positive to negative as the wavelength is shifted from the blue to the very red edge of the absorption spectrum. When the blue part of the absorption band (570 and 580 nm) is excited, both the real and imaginary components are positive. However, the signs of the real and imaginary components are opposite upon excitation at the red edge of the absorption band (615 nm). At intermediate wavelengths such as 607 nm, the real component is positive at very short times and then rapidly changes to negative prior to decaying to zero. Except for the differences in the sign of the amplitude and initial decay behavior, the two components show the same decay features and share the same oscillatory behavior within the experimental uncertainty for all four detection wavelengths. This similarity is expected since the decays of both real and imaginary components result from the same dynamic processes, including solvation, electronic and vibrational relaxation. It has been demonstrated previously that PP and homodyne TG measure the same dynamics in the absence of a thermal acoustic grating,\(^{5,31}\) implying that the real and imaginary components of \(P(3)\) carry the same dynamic information.

The wavelength dependence of the real component can be easily understood by considering the Kramers–Kronig relation.\(^{11,32}\) The dispersion spectrum \((n_p)\) of R640/DMSO was obtained from the Kramers–Kronig transformation of its absorption spectrum as shown in Fig. 2. The amplitude of dispersion \((n_p)\) has opposite signs for wavelengths on the two sides of absorption maximum and is zero at a wavelength near the absorption maximum. A similar relation also holds between the transient absorption and transient dispersion in the third-order signals.\(^{3,7,12,33}\) As discussed by Gumy et al.,\(^{3}\) the real component of \(P(3)\) or the population phase grating \(\Delta n_p\) is proportional to \(-n_p\), thus it would be negative on the red side of the absorption spectrum and positive on the blue side.\(^{3,30}\) The wavelength corresponding to zero dispersion is usually observed to be located slightly to the red of the absorption maximum.\(^{30}\) In R640/DMSO, this turning point was found to be at around 600 nm instead of at the absorption maximum of 585 nm.

At short times, the nonresonant contribution from the solvent alters the relative amplitudes associated with the real and imaginary components of \(P(3)\). To estimate the magnitude of this nonresonant contribution, one needs to take into account the attenuation of the incident beams by solute mol-
The correction factor is 0.16. The pure DMSO signal, scaled by an OD of 0.55 at each excitation wavelength. In this case, the used to obtain the data shown in Fig. 4 were adjusted to have the solution phase, the real component is equal to the sum of contributions in homodyne TG signals.

C. Interference effect between the solvent and solute

The amplitudes are scaled relative to DMSO signal at $t=0$, which is set to 1.0.

<table>
<thead>
<tr>
<th>Time (fs)</th>
<th>DMSO</th>
<th>Methanol</th>
<th>Acetonitrile</th>
<th>Benzene</th>
<th>CS$_2$</th>
<th>Chloroform</th>
<th>CCl$_4$</th>
<th>DMA</th>
<th>DEA</th>
<th>Toluene</th>
<th>Benzonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>0.39</td>
<td>0.42</td>
<td>1.35</td>
<td>3.42</td>
<td>0.78</td>
<td>0.71</td>
<td>2.20</td>
<td>1.56</td>
<td>1.13</td>
<td>1.55</td>
</tr>
<tr>
<td>150</td>
<td>0.056</td>
<td>0.054</td>
<td>0.094</td>
<td>0.42</td>
<td>1.75</td>
<td>0.12</td>
<td>0.054</td>
<td>0.45</td>
<td>0.30</td>
<td>0.31</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*A The amplitudes are scaled relative to DMSO signal at $t=0$, which is set to 1.0.

TABLE I. Relative amplitude of the birefringent contribution of different solvents.

The solvent response is roughly independent of the wavelength and remains positive within the entire spectral region of our detection, whereas the real component of the resonant solute contribution changes its sign from positive in the blue to negative in the red sides of absorption spectrum. Correspondingly, at 570 and 580 nm, the blue side of the spectrum, both the real components of the resonant and nonresonant contributions have positive signs, and their superposition leads to enhancement of the initial spike in the positive real component measured using R640/DMSO. At 615 nm, the red side of the spectrum, these two contributions have opposite signs and their superposition results in a suppressed spike in the negative signal [Fig. 4(d)]. At an intermediate wavelength such as 607 nm, the real signal is dominated by a positive solvent contribution at the very short times, and following the rapid decay of the solvent response, by the negative response of the solute. In Sec. III C, we provide a qualitative discussion of the influence of the solvent contribution on homodyne TG data. In Sec. III D, we attempt a quantitative model of the concentration dependence of homodyne TG signals.

The homodyne detected TG signal is proportional to a sum of squared real and imaginary components of $P^{(3)}$. In the solution phase, the real component is equal to the sum of the wavelength-dependent solute and the wavelength-independent solvent contributions. An interference cross term, resulting from the squared sum of the real components of the solute and the solvent, can have a profound effect on the homodyne TG signal. We should note here that the imaginary component of the nonresonant solvent contribution is considerably weaker than its real component and thus is neglected in the following discussion. As described in Sec. III B, the real components associated with the solute change sign from positive to negative with the shift of wavelength from blue to red, in contrast to the wavelength-independent, positive solvent response. This wavelength-dependent solute contribution will lead to wavelength-dependent interference with the solvent contribution in the homodyne TG signals. In the blue part of the absorption spectrum, the real components of the solvent and solute contributions are of the same sign, and will interfere constructively at short times and give rise to a large initial spike in the homodyne TG signal. This interference can persist for several hundred femtoseconds, depending on the time scale of the relaxation of solvent response. In contrast, when the excitation wavelength is on the red edge of the absorption band, the real component of the solute contribution will change sign while the solvent contribution does not. The resulting destructive interference at short times will produce a less pronounced initial spike. A simple estimate can be made to demonstrate this interference effect. In round numbers, the real contribution of the solvent, and the real and imaginary components of the solute have relative maximum amplitudes of 1:15:9 [Fig. 4(a)]. Typically, in a heterodyne measurement one checks for a solvent contribution by comparing the signal amplitude from the solution and the pure solvent. However, this can be a falsely reassuring procedure: In the present case the ratio of the homodyne signal maxima from the solvent alone, to that from the solute alone is $1/(9^2+15^2) = 0.3\%$. However, the difference between the homodyne signal maxima when the solvent adds either constructively or destructively is 22% since $(16^2+9^2)/(14^2+9^2) = 1.22$.

In order to compare the described interference effect in different systems, we performed the OHD-TG measurements on 11 commonly used solvents (Table I). The nonresonant response of a pure solvent consists of an instantaneous electronic component and a slower (~200–2000 fs) nuclear contribution. At short times, the signal is dominated by the electronic response as long as the laser pulsewidth is short enough. The maximum signal occurs slightly after time zero, due to the asymmetric nuclear response. Table I summarizes the relative values of the amplitudes at their maxima, which are mostly determined by the electronic responses. The relative magnitudes of the nuclear responses are taken at 150 fs from the time corresponding to the maxima. Among these solvents, the so-called inner filter effect. We applied the same procedure described by Rector et al., who derived the inner filter for vibrational echo signals. For a heterodyne detected TG signal, the correction factor is given by

$$f_{\text{heter}}(A) = \exp(-A) \left[ 1 - \exp(-A) \right] A.$$
vents, methanol gives the weakest signal whereas CS₂ gives the strongest. In addition, the relative amplitudes of CS₂ and acetonitrile differ by a factor of ~8 at their maxima, which is considerably smaller than the value reported in Ref. 35, where a ratio of over 50 was obtained using the optical Kerr effect (OKE) technique. The acetonitrile response measured in this work is essentially identical to that obtained by Cho et al. using the OKE method with very similar pulse duration at 570 nm. However, these two temporal profiles appear substantially different from the one reported in Ref. 35, obtained with relatively long pulses. Since the instantaneous electronic response is strongly dependent on the pulse width, longer pulses will lead to a substantial nuclear contribution even at T = 0. Comparison of the signal amplitudes at a delay time of 150 fs from the time corresponding to the maxima, where the nuclear contributions dominate the solvent responses, indeed gives a larger ratio of ~20 (see Table I). Nevertheless, the similarity in the amplitudes of the various solvent responses found in the current work indicates that their interference effect with the contribution from the solute clearly cannot be simply assumed negligible in a homodyne TG signal at short times. For those solvents whose nuclear responses contribute substantially to the overall signal, such as acetonitrile, toluene, benzene, benzonitrile, DMA, DEA, and CS₂, this interference may persist for longer times, determined by the relaxation of the corresponding nuclear responses.

The above-described interference effect also applies to experiments in which higher vibronic bands are excited (see, for example, Ref. 13). Excitation on the red edge of the second vibronic band will give rise to negative signed real component for the solute according to the Kramers–Kronig relation. In this case, its destructive interference with the positive solvent response leads to a smaller amplitude of the initial spike than that observed upon excitation of the blue edge of the main absorption band. This is consistent with what we have previously observed.13

D. Concentration-dependent homodyne TG

To further confirm the interference effect on the homodyne detected signal as discussed in Sec. III C, concentration-dependent homodyne TG measurements were performed. In these measurements, the OD of the R640/DMSO solution was varied from 0.57 to 0.08, corresponding to a concentration change from 1.1×10⁻⁴ to 1.3×10⁻⁵ M. Within this range of concentration, no detectable change in the shape of the absorption spectrum was observed, which excludes the possibility of a solute aggregation effect. This change of concentration will lead to a corresponding change in the relative contributions of solvent and solute, and in turn alter the initial behavior of the homodyne detected TG signals. As shown in Fig. 5, a decrease of the solute concentration results in an increase of the amplitude of the initial spikes in the homodyne TG signals. This change can be easily understood from the argument in Sec. III C. For a lower concentration sample, the amplitude of the solute signal decreases, whereas the amplitude of the solvent response increases as a result of the reduced attenuation by the inner filter effect. Thus for a homodyne detected TG, a smaller solute concentration will result in a larger relative solvent contribution with respect to the solute contribution, and therefore a larger initial spike in the detected TG signal.

Convincing support for the interference effect on the homodyne TG signal would be provided by reproducing the homodyne profiles measured at different concentrations (Fig. 5) with the heterodyne data measured at the same wavelength, presented in Fig. 4(a). It should be noted that changing the solute concentration affects the heterodyne signals associated with both the solute and the solvent. For the solvent, the signal measured with pure DMSO will be attenuated by the concentration-dependent inner filter effect to a different extent from the one shown in Fig. 4(a). The real and imaginary components measured for R640/DMSO at a given concentration (C₀ = 110 µM) need to be scaled according to the sample concentration (C) to obtain the correct profiles of the real and imaginary components at other concentrations. After this scaling correction, the homodyne detected TG signals are calculated from the following:

\[
I_{\text{homo}} = f_{\text{homo}}(A) \left[ \frac{C}{C_0 f_{\text{heter}}(A_0)} \text{Im}^0(\text{R640+DMSO}) \right]^2 + f_{\text{homo}}(A) \left[ \frac{C}{C_0 f_{\text{heter}}(A_0)} [\text{Re}^0(\text{R640+DMSO}) - f_{\text{heter}}(A_0)\text{Re}(\text{DMSO})] + \text{Re}(\text{DMSO}) \right]^2, \tag{3}
\]

where \(\text{Im}^0(\text{R640+DMSO})\) and \(\text{Re}^0(\text{R640+DMSO})\) are the imaginary and real components measured for the R640/DMSO solution at the concentration \(C_0\), \(\text{Re}(\text{DMSO})\) is the real part of pure DMSO, and \(f_{\text{heter}}(A_0)\) and \(f_{\text{homo}}(A)\) are the attenuation factors for the heterodyne and homodyne TG signals, which are given by Eq. (2) and in Ref. 34, respectively. The curves calculated using Eq. (3) are shown in Fig. 6(a), and exhibit the same trend as the experimental data in response to the concentration change, i.e., the magnitude of the initial spike is enhanced as the concentration decreases. The calculated profiles show a smaller deviation from the experimental data at higher concentrations. To show more clearly
the effect of the interference on the homodyne detected TG signals, we also performed calculations in the absence of the interference effect differ significantly from the experimental data. All the curves are normalized at their maxima.

The agreement between calculated and experimental curves in Fig. 6(a) is not perfect. Two possibilities may account for the deviation between the calculated and experimental curves [Fig. 6(a)]. First, the attenuation factor given by Eq. (2) is derived for plane waves. Focusing of the beams may alter the attenuation factor from that calculated using Eq. (2). The deviation between the experimental data and the calculated profiles [Fig. 6(a)] indicates that the relative solvent contribution may have been underestimated. Second, the intensity of the homodyne signals is very low, particularly at the low concentration, with respect to the intensity of the heterodyne signals. The homodyne signal may be contaminated by a contribution from the OHD-TG signal, which arises from some small scattering from the probe pulse, serving as a local oscillator, and will be worst at the lowest optical density.

An obvious corollary to the above-presented discussion is that the relative contributions of the solute and solvent will vary as the laser wavelength is tuned through the absorption band. Clearly, particular care is required when working in the wings of the absorption spectrum.

IV. CONCLUSIONS

In this paper, we report wavelength-dependent homodyne and heterodyne TG studies on a resonant system, R640 dissolved in DMSO, using a diffractive optics method. The amplitude of the real component changes sign from positive to negative as the excitation wavelength is shifted from blue to red, while the corresponding imaginary component remains positive for all wavelengths within the absorption band, in accordance with the Kramers-Kronig relation. At longer delay times (>200 fs), the real and imaginary components of \( P^{(3)} \) measured in heterodyne TG show generally similar decay features at different wavelengths, consistent with previous suggestions that they reflect the same dynamical process. However, at short times, the real component is contaminated with the nonresonant solvent contribution, which has similar amplitude to the resonant solute contribution. This interference effect is further confirmed by concentration-dependent homodyne TG measurements.

Several other four-wave mixing techniques, such as the three-pulse photon echo peak shift and two-pulse photon echo, are usually carried out in a similar homodyne manner. One would expect that this interference effect between the resonant solute and the nonresonant solvent contributions would also affect the signal profiles in the initial time scale measured in these techniques and the corresponding frequency-resolved experiments in a dilute solution, especially for those solvents with a large electronic hyperpolarizability such as \( \text{CS}_2 \), benzene, toluene, DMSO, etc. We believe that proper characterization and subtraction of the solvent contribution may be necessary for the analysis of short time dynamical behavior in these techniques.

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