Heterodyne detected transient grating spectroscopy in resonant and non-resonant systems using a simplified diffractive optics method

Qing-Hua Xu, Ying-Zhong Ma, Graham R. Fleming *

Department of Chemistry, University of California, Berkeley and Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
Received 2 February 2001

Abstract

We report a simplified optical heterodyne detected transient grating setup consisting of a single diffractive optical element based on modifications of the arrangement used by Miller and co-workers [J. Phys. Chem. A, 103 (1999) 10619]. Our arrangement features ease of alignment, suppression of scattering and is free of pump–probe contamination in the detected transient grating signals. The capability of our arrangement is demonstrated by measurements on a non-resonant system, CS₂, and a resonant system, malachite green in ethanol. © 2001 Published by Elsevier Science B.V.

1. Introduction

Transient grating (TG) spectroscopy has been widely applied to study gas and condensed phase dynamics due to its sensitivity to a variety of photophysical and photochemical processes [1–6]. In this technique, two temporally coincident laser pulses are crossed in a medium, and their interference produces spatially periodic material excitation, which results in a spatially modulated complex refractive index in the crossing region [5,6]. The time evolution is probed by a third, temporally delayed pulse, which is scattered off the grating into the Bragg angle. The intensity of the diffracted signal, usually homodyne detected, depends on the square of the third-order polarization $P^{(3)}$ [7]. The real and imaginary parts of the complex $P^{(3)}$ cannot be determined separately, which can compromise the information gained on the electronic relaxation and the corresponding nuclear response in the resonant system. Our recent study of the isomerization of 1,1′-diethyl-4,4′-cyanine [8] with different third-order non-linear techniques suggests that different decay profiles can be associated with the real and imaginary parts of $P^{(3)}$. Separate measurement and proper characterization of both contributions is important to understand the underlying reaction dynamics and mechanism. Homodyne detection also introduces additional cross terms and can mask some low-amplitude contributions, reducing the information content of the data. These difficulties, however, can be overcome with optical heterodyne detection (OHD).

OHD is performed by coherently mixing the weak signal field $E_s(t)$ with a relatively strong...
beam $E_{LO}(t)$, the so-called local oscillator (LO). The resulting signal can be expressed as [9],

$$I_T(t) = \frac{n(\omega)c}{4\pi} |E_{LO}(t) + E_s(t)|^2$$

$$= I_{LO}(t) + I_s(t) + 2\frac{n(\omega)c}{4\pi} \text{Re}[E_{LO}^* E_s(t) + E_{LO} E_s^*(t)]$$

where $n(\omega)$ is the refractive index of the solution and $c$ is the speed of light. The first term is the intensity of the LO, which can be easily removed by using lock-in amplifier detection, and the second term is the homodyne signal and can be ignored when $|E_s(t)| \ll |E_{LO}(t)|$. The OHD signal is given by the third term, and is thus amplified by a factor of $2|E_{LO}(t)|/|E_s(t)|$ in comparison to the homodyne signal. Depending on the relative amplitudes of the LO and signal fields, an enhancement of several orders of magnitude can be routinely achieved. Additional attractive features of OHD include the linearization of the detected signal with the signal field and the capability in separating the real and imaginary parts of $P^{(3)}$. To illustrate the last feature, we rearrange the last term in Eq. (1) as,

$$I_{Het} \propto \text{Re}[E_{LO}^* E_s(t)] = \text{Im}[E_{LO}^* P^{(3)}(t)]$$

$$= E_{LO} \cdot \text{Im}[e^{i\phi}P^{(3)}]$$

$$= E_{LO} \cdot [\cos(\phi) \text{Im} P^{(3)} + \sin(\phi) \text{Re} P^{(3)}],$$

where $\phi$ is the phase difference between the signal and the LO field. Thus the real and imaginary parts of the third-order signal can be selectively determined by controlling the LO in quadrature ($\phi = \pi/2, 3\pi/2, \ldots$) or in phase ($\phi = 0, \pi, \ldots$) with the signal field, respectively. According to Eqs. (1) and (2), the small homodyne contribution can be completely removed by subtracting two data sets with a $\pi$-phase shift from each other, since the OHD signal will change sign with a $\pi$-phase shift but the homodyne signal does not.

OHD can be achieved by either active or passive phase-locking. The simplest OHD setup is probably the pump–probe (PP) technique, in which the signal is passively locked in phase with the probe beam (which also acts as the LO) and thus only the imaginary part of $P^{(3)}$ can be detected. A separation of the real and imaginary parts of $P^{(3)}$ can be achieved in the OHD–optical Kerr effect (OHD–OKE) and OHD–Raman-induced Kerr effect spectroscopies (OHD–RIKES), in which a perpendicularly arranged polarizer pair and a quarter waveplate are used to introduce an LO either in-phase or in-quadrature with the signal field [10–14]. A limitation of the OHD–OKE or OHD–RIKES techniques is the lack of polarization control between the pump and probe pulses.

OHD–TG is an ideal choice to separate the real and imaginary parts of $P^{(3)}$ because of the capability of arbitrary phase setting and full control of the polarization of pump and probe beams. The initial OHD–TG measurements were performed using an active phase-locking technique [15–17]. In this case, phase-locking was realized by directing the signal and LO beams into each arm of a Mach–Zehnder interferometer and adjusting the optical path of one arm with sub-wavelength accuracy. However, the application of this technique was hampered by the poor phase stability and experimental complexity.

Recently, the use of diffractive optics (DO) for OHD–TG has been shown to be an elegant and straightforward method, as demonstrated by Miller and co-workers [18–21], and Nelson and co-workers [22]. Such a method provides access to the full advantage of the OHD technique. In this technique, two beams (one pump and one probe) are focused and spatially overlapped at the DO and the resulting four beams with ±1 diffracted orders are in the boxcar geometry. As a result of the phase-matching geometry, the TG signal is radiated along the same direction as the fourth beam, which acts as the LO, and is spatially and temporally overlapped with the LO and heterodyne detected. The phase between the signal and LO fields can be adjusted simply by rotating a microscope cover slip (CS) inserted into the LO path. Recently, Tokmakoff and co-workers [23] introduced a new setup based on dual DO elements, aiming to completely remove the contamination of the PP signal in the same phase-matching direction. In their setup, only three beams (two pump beams and one probe beam) were incident on the sample and the signal field was combined with the residual probe beam (which acts as the LO) at the second DO and heterodyne detected.
The control of the phase was accomplished by rotation of a CS in the LO arm. However, the success in the complete removal of PP contribution comes at the cost of a more complex alignment and a loss of signal as it passes through the second DO element.

In this Letter, we report a simplified OHD–TG setup based on a single DO element. This new arrangement allows use of the full capability of the OHD–TG method with arbitrary polarization selectivity and is free of contamination from the PP contribution.

2. Experimental

The femtosecond excitation source was a regenerative Ti:sapphire amplifier pumped optical parametric amplifier (OPA) system as described in detail previously [7,24]. Briefly, a mode-locked femtosecond Ti:sapphire oscillator (Coherent Mira) was used to seed a Ti:sapphire regenerative amplifier (Coherent RegA), which typically generates 50 fs full width at half maximum (FWHM) pulses at 800 nm with a repetition rate of 250 kHz. The output of the amplifier was then used to pump an OPA (Coherent 9450) to produce pulses at the desired wavelength. A SF10 prism pair was employed to compensate for the group velocity dispersion induced by the optics in the OPA and in the experimental setup, and nearly transform limited pulses of 40 fs FWHM were obtained. The compressed pulse was split into two beams, a strong pump and a weak probe, and the probe pulse was delayed with respect to the pump pulse by a stepping-motor driven optical delay stage (MM3000, Newport) with 0.6 fs resolution. The intensity ratio between the pump and the probe beams was typically set to 10:1, and the maximum pulse energy of the pump beam was ∼1.3 nJ at the sample position.

The experimental setup of the OHD–TG with passive phase-locking is similar to the one described by Miller et al. [18–21], however, some simple but key modifications were introduced to enhance the performance. As shown in Fig. 1, both the pump and probe first passed through a polarizer and zero-order half-waveplate separately in order to control their intensities and relative polarizations. The two beams were then spatially overlapped on a DO (Rochester Photonics) with a quartz lens of 20 cm focal length. Each of the two beams was split into two replicas (±1 diffraction orders) with an efficiency of around 30%. The crossing angle between the two replicas is ∼2°. The two replicas from the strong beam act as the pump (k_1 and k_2), one of the two replicas from the weak beam was used as the probe (k_3) and the other as the LO (k_4). All other diffractive orders were blocked with a metal mask. The resulting four beams were imaged achromatically onto the sample by a combination of an Al-coated concave spherical mirror with a 50 cm radius and a fold

![Fig. 1. (a) Simplified diffractive optics arrangement for an optical heterodyne-transient grating (OHD–TG) experiment: λ/2, half-waveplate; P, polarizer; L, 20 cm lens; DO: diffractive optic; CS: cover slip; Ch: chopper; SM: concave spherical mirror; FM: fold mirror; PD: photodiode. (b) Phase stability test over a 1 h period.](image-url)
mirror. The spherical mirror was placed at one radius from the DO and was tilted slightly off-axis horizontally by around 3° to direct the beams to the folding mirror. This allows us to separate the outgoing beams from the incoming beams. Following the phase-matching geometry, the signal (\(k_s = k_1 - k_2 + k_3\)) was radiated along the LO direction (\(k_4\)). The probe beam was chopped at 1150 Hz right in front of the sample and the OHD-TG signal was detected using a silicon photodiode and a lock-in amplifier. An iris between the sample and the detector blocked all the unwanted beams and scattered light, which otherwise could interfere with the signal and the LO and produce a randomization of the phase. It is therefore crucial to ensure that only the signal and the LO beam are incident on the photodiode. A third polarizer was mounted after the iris to set the signal polarization. Furthermore, a 150 μm thickness CS was separately inserted into the probe and LO paths. The CS in the LO path was mounted on a rotating stage whose fine adjustment allowed control of the phase difference between LO and signal fields. The rotation angle needed for a \(\pi\)-phase change is around 2°, which could be set with an accuracy of 0.01°, corresponding to a phase change of \(\sim 1°\). Except for the thin CSs, no other transmissive optics was inserted in the beam paths between the DO and the sample.

Malachite green (MG) was obtained from Exciton and carbon disulfide (CS₂) and ethanol were purchased from Aldrich. The solute and solvents were used as received. A glass sample cell with 1 mm pathlength was used for the measurement of CS₂ and the sample cell was not flowed. An identical sample cell was used for the measurement of MG/ethanol and the solution was circulated using a gear pump, to avoid any possible thermal heating effect. The concentration of MG was adjusted to give an optical density of 0.8 per mm at the absorption maximum, to avoid aggregation of the dye molecules.

3. Results and discussion

As shown in Fig. 1, although the present setup is similar to the one described by Miller and co-workers [18–21], the modifications introduced lead to several advantages. First, removal of the high reflector in the LO beam and the corresponding compensation glass in the probe beam avoids the time-consuming step of finding the temporal overlap between these beams. This is particularly helpful for the case when very low pulse energy is employed, as in this work. Since no transmissive optics, except the thin CS pair, was introduced between the DO and sample cell, excellent spatial and temporal overlap of the beams at the sample position is readily obtained. Second, we selectively chopped the probe beam (\(k_4\)) right in front of the sample, instead of chopping the pump beam in front of the DO. With this simple change, we can, on the one hand, avoid the scattering from the strong pump beams and, on the other hand and most importantly, completely remove the PP contamination in the TG signal. This has previously been achieved by employing a dual DO setup, as described by Tokmakov and co-workers [23]. To illustrate the latter capability, we need to classify the signals along the \(k_4\) direction. With the boxcar geometry, there are four different third-order signal fields that are generated along the \(k_4\) direction: TG (\(k_s = k_1 - k_2 + k_3\), \(PP_1(k_s = k_1 - k_1 + k_4)\), \(PP_2(k_s = k_2 - k_2 + k_4)\) and \(PP_3(k_s = k_3 - k_3 + k_4)\), but only the TG signal is of interest. If the pump or the probe beam is chopped in front of the DO, all the four signals would be detected and the TG signal is contaminated by the PP signals. Although such a contamination could be ignored in case of non-resonant system, in which the dichroic contribution (i.e., the imaginary part) detected by PP is much smaller than the corresponding birefringent contribution (the real part), such contamination will definitely cause problems for a resonant system. Our recent experiments on 1,1'-diethyl-4,4'-cyanine showed that the homodyne TG kinetics could not be simply understood as the square of the PP signal and the two signals exhibited very different wavelength-dependent decay profiles [8]. Given the fact that PP signal is not negligible for a resonant system, the contamination of the TG by it would lead to a distortion of the observed kinetics. By chopping the \(k_3\) beam in our setup, only the TG and PP signals can be detected. The PP signal has no time
dependence and thus contributes only a small constant background, since the intensity of \( k_1 \) is much lower than that of \( k_2 \) and \( k_3 \). This small constant PP signal can be easily subtracted from the detected signal. Therefore, we can easily obtain PP free OHD–TG signal in a straightforward way using our simplified one DO setup.

The success of a phase-locked experimental setup, no matter whether it is based on an active or a passive mechanism, depends critically on how well the phase can be stabilized. For the DO-based OHD–TG experimental setup, reduction of the air currents between the DO and sample was found to be crucial for maintaining high phase stability [4]. Placing the optical chopper between the DO and sample in the present setup unavoidably produces air currents, which decrease the phase stability. However, within 1 h we obtained a phase fluctuation that was within \( \pm 3^\circ \) and no detectable slow-phase drift was observed during the test period (Fig. 1b). The influence of phase fluctuations can be further minimized by averaging the experimental data over multiple scans, which generally could be completed within 10 min. Tokmakoff and co-workers [23] reported a phase fluctuation within \( \pm 10^\circ \) for a 2 h period when they placed the chopper between the sample and the second DO element in their dual DO setup.

To demonstrate the success of our OHD–TG experimental setup, we performed measurements on a non-resonant system, \( \text{CS}_2 \), and a resonant system, \( \text{MG/ethanol} \), respectively. Fig. 2 shows the data obtained using \( \text{CS}_2 \) at 620 nm with four different phases. As expected for a transparent liquid at the given wavelength, the real part of the \( P^{(3)} \) or the birefringence, determined with phases of odd multiples of \( \pi/2 \), is much larger than the corresponding imaginary contribution, the dichroic signal. The latter was measured under phases of even multiples of \( \pi/2 \). The data are in an excellent agreement with the results reported by Tokmakoff and co-workers [23], measured using a dual DO setup and a comparable pulse duration. We can clearly see the structure in the small dichroic signal and even the sign flip with the \( \pi \)-phase shift of the LO. The structure in the dichroic signal is also consistent with the results recently reported by Constantine et al. [25], using a novel technique to obtain an amplified dichroic signal, illustrating the high-phase stability in our experiments. In addition, the reconstructed homodyne data from the sum of squared real and imaginary OHD–TG signals can reproduce the corresponding experimental homodyne detected TG signal very well (see Fig. 2b). The homodyne signal was measured by blocking the LO beam (\( k_A \)) in front of the sample.

Polarization-dependent OHD–TG measurements can also be performed using this setup by rotating the half-waveplate in the pump or probe beams. Fig. 3 shows the data obtained for \( \text{CS}_2 \) by rotating the half-waveplate in the probe beam to set its polarization to parallel, perpendicular, and the magic angle (54.7°) with respect to the polarization of the pump beam, while keeping the phase difference between the signal and the LO at \( \pi/2 \).
As shown in Fig. 3, the data obtained using our simplified setup are again in excellent agreement with the previously reported results, measured using an OHD–TG setup with either an active or a passive phase-locked mechanism [17, 23]. The isotropic and anisotropic dynamics are strikingly different. The anisotropic dynamics is dominated by the inertial intermolecular response followed by bi-exponential decay with time constants of 480 ± 20 fs and 1.6 ± 0.1 ps, which are close to those previously reported [23, 25, 26]. The origin of the first component has not been clearly established while the latter corresponds to the reorientational dynamics. However, the isotropic dynamics is dominated by a rapid exponential decay with a time constant of 120 ± 10 fs followed by a 480 ± 20 fs exponential decay. A similar difference in the isotropic and anisotropic dynamics was also observed by Tokmakoff et al. [23] and the isotropic dynamics was found to be non-exponential. The ~500 fs exponential component was also reported by Constantine et al. [25] for the isotropic and anisotropic dynamics of the dichroic signal of CS₂. The appearance of the identical ~500 fs component in the isotropic and anisotropic responses of both birefringent and dichroic signals may help to identify the mechanism of relaxation and the intermolecular interactions in CS₂ [25].

The OHD–TG measurements were also performed on a resonant system, MG in ethanol. This molecule is well known to undergo large amplitude motion in the excited state, which leads to population relaxation to the ground state within several picoseconds in low-viscosity solvents [27]. The wavelength for this experiment was chosen to be at 622 nm, the peak of the absorption spectrum. The polarization of the four beams was set parallel to each other. The measurements were performed by first setting the desired phase difference between the signal and the LO using CS₂, and then replacing the sample cell containing CS₂ with an identical cell containing the sample. The phase settings were carefully checked before and after each measurement to ensure that no detectable phase drift had occurred. The measurement for each desired phase difference was repeated four times and the data were averaged to improve the accuracy of the phase settings. In order to remove the small contribution of homodyne signal, the real and imaginary parts were obtained from the difference between the two experimental data sets with a π-phase shift of the LO. As shown in Fig. 4,
the real and imaginary parts are quite different in their amplitudes and the decay profiles.

To confirm that the experimental results for the real and imaginary components shown in Fig. 4 are correctly measured, we carried out a two-step comparison. First, we compared the imaginary part of the OHD–TG signal with the PP profile, which was measured under identical experimental conditions when pump beam was chopped in front of the DO, and beam \( k_1 \) and \( k_3 \) were blocked in front of the sample. Since both measurements record the imaginary part of the third-order signal, they should be identical. As shown in Fig. 5a, the two kinetic traces are in excellent agreement, indicating that the phase setting for the measurement of the imaginary part of the OHD–TG was correctly made. Second, we compared the experimentally determined homodyne TG signal with the sum of the squared real and imaginary profiles, the so-called reconstructed homodyne data. As shown in Fig. 5b, the agreement between the two curves is quite good. The minor difference in the region from 2 to 5 ps could be due to contamination of the experimental homodyne signal by a contribution from the OHD–TG signal, which arises from some small scattering from the probe pulse, serving as an LO [17]. This possibility cannot be excluded since the homodyne signal is very small in the current experiment. Typically, its amplitude is 50 times smaller than the amplitude of the corresponding OHD–TG signals. Nevertheless, the comparison given above indicates that the real and imaginary contributions were determined with reasonable accuracy.

After confirmation of the experimental determination of the real and imaginary parts shown in Fig. 4, we can now compare the difference between the kinetics. As shown in Fig. 4, the initial amplitude associated with the real part is smaller than the corresponding imaginary counterpart by \( \sim 40\% \). The flat region between 0.3 and 1.2 ps observed in the imaginary part, which represents the induction period for the radiationless decay [28], is absent in the real part. Deconvolution of the curves with the pulse duration shows that the imaginary part decays initially with a time constant of \( 120 \pm 20 \) fs, and the subsequent and dominant decay following the induction period is characterized by a time constant of \( 1.4 \pm 0.1 \) ps. An additional slow decay component with a time constant \( 5 \pm 1 \) ps and a relative amplitude <4% improves the overall fit. In contrast, the real part starts with a pulse limited rise followed by a decay of \( 80 \pm 20 \) fs. The initial dynamics in the real part is strongly mixed with the solvent contribution. The subsequent and dominant decay component is characterized by a time constant of \( 1.7 \pm 0.1 \) ps. This decay leads to a slightly negative signal, which further recovers back to zero with a time constant of \( 4 \pm 1 \) ps. Although the decay profiles appear very different, the time constants of the dominant decay components associated with the real and imaginary parts are quite similar. This dominant decay can be ascribed to the ground-

Fig. 5. (a) The imaginary part of OHD–TG (solid line) and pump–probe trace (symbol) measured in MG/ethanol at 622 nm; (b) Comparison of homodyne TG profiles obtained directly from experiment (symbols) and from reconstruction from the sum of the squared real and imaginary parts (solid line).
state recovery process. It is also interesting to note the time constants of the small slow contribution in the real and imaginary parts were quite similar but their amplitudes have opposite signs. Such different decay behaviors in the real and imaginary parts and its possible effect in the homodyne signal have not been considered in previous work, but are critical for an understanding of the dynamical information contained in the homodyne TG signal. Careful measurement and characterization of the subtle differences and connection between the kinetics of the real and imaginary components should be very helpful in characterizing the underlying dynamics, which might otherwise be obscured in homodyne detected signals. A detailed analysis of the data and the physical origins of the different time courses of the two contributions will be presented elsewhere.

4. Conclusion

In this Letter, we describe a simple OHD–TG arrangement based on a single DO element and based on simple but useful modifications of the setup described by Miller et al. [18–21]. The removal of transmissive optics between the DO element and the sample cell and the selective chopping of the probe beam directly in front of the sample result in a number of attractive advantages. These include ease in obtaining an excellent spatial and temporal overlap of the four beams, the attainment of OHD–TG signals free of PP contamination and the suppression of scattering from the strong pump beams. The success of this simplified setup with a passive phase-locking scheme was demonstrated by performing measurements on a non-resonant system, CS2, and a resonant system, MG/ethanol. The consistency of the experimentally determined real and imaginary parts of the third-order signals was confirmed by comparing the experimental homodyne profiles with the reconstructed homodyne traces, and by comparing the imaginary component with the PP data. Moreover, the feasibility in setting arbitrary polarization was shown by polarization dependent OHD–TG measurements on CS2, and the data obtained are in an excellent agreement with previously reported results [23]. We believe an accurate characterization of the real and imaginary parts of the third-order signals for a reactive system, such as MG, will be helpful in understanding the underlying dynamics.

Acknowledgements

This work was supported by National Science Foundation (NSF). We thank Prof. Larry D. Ziegler for a critical reading of the manuscript and helpful discussions.

References