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Resonance heterodyne optical Kerr effect spectroscopy of population wave packets with intense chirped pulses

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Abstract

We propose a new method for studying the time evolution of population wavepackets in the ground and excited states of a large dye molecule dissolved in polar liquids: resonance heterodyned optical Kerr effect (HOKE) technique with intense chirped pulses. We found a profound effect on both the ground and excited state transient populations using intense positively and negatively chirped pulses. The dump process is very effective when the sample is excited by negatively chirped intense pulses.

Keywords: Optical Kerr effect; Femtosecond; Coherent control

1. Introduction

Recent experiments on optical control involved the use of chirped pulses. The interaction of intense chirped ultrashort pulses with molecular systems in liquid solutions has shown that it is possible to control the ratio of the ground state population to the excited population. The interaction of an intense pulse with a probe molecule in solution can be thought of in terms of sequential interactions with the field. In the nonlinear regime, more than one photon interacts with the molecular probe and both absorption and stimulated emission can occur.

The effects of varying the chirp and intensity of an ultrashort pulse, exciting probe molecules in liquid solutions, have been investigated experimentally [1–3] and theoretically [4–6]. In these experiments the integrated fluorescence (which is directly proportional to the integral excited state population) was measured as a function of pulse chirp after the completion of the pulse action. In addition, the absorption spectrum of chirped pulses was measured [1,3]. For low-power excitation, it was found that the absorption and excited state population were independent of chirp while, for high-power excitation, the absorption exhibited a strong chirp dependence.

It has been shown in Ref. [7] that the absorption spectrum, $\alpha_{\mathrm{abs}}(\Omega)$, gives information about the population wave packet difference in the ground and excited electronic states, $\Delta'(\omega_{21-}\omega(t), t)$, at the time, t, when measured using strongly chirped pulses:

$$\alpha_{\mathrm{abs}}(\Omega) \sim \Delta'(\omega_{21} - \omega(t), t), \tag{1}$$

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where $\omega(t)$ is the instantaneous frequency, $\Omega = \omega(t)$ and ω_{21} is the frequency at the absorption band maximum. In this paper, we propose an alternative method which can be also used for studying the time evolution of population wave packets under intense chirped pulse excitation: resonance heterodyne optical Kerr effect (HOKE) spectroscopy with intense chirped pulses. In general, the last method enables us to obtain complimentary information about population wave packets versus the absorption spectrum of an intense chirped pulse. The point is that the absorption spectrum directly reflects the time evolution of population wave packets' difference only at the configuration coordinate corresponding to the instantaneous Franck–Condon transition at time t (see Eq. (1)). In contrast, the resonance HOKE spectroscopy enables us to obtain a similar information for any instantaneous Franck–Condon transition corresponding to time $t-\tau$ where τ is a variable delay between the pump and probe (or local oscillator-LO) pulses:

$$J_{\mathrm{HOKE}} \sim -\int_{-\infty}^{\infty} |\varepsilon_{\mathrm{LO}}(t-\tau)|^2 \times \Delta'^{\mathrm{NL}}(\omega_{21} - \omega(t-\tau), t)\,\mathrm{d}t. \tag{2}$$

Here, $\omega(t-\tau)$ is the instantaneous LO frequency (or probe frequency), ω_{21} the frequency of the peak of the absorption spectrum, $\Delta'^{\mathrm{NL}}(\omega_{21} - \omega(t-\tau), t)$ the deviation of $\Delta'^{\mathrm{NL}}(\omega_{21} - \omega(t-\tau), t)$ from its equilibrium value at the configuration coordinate corresponding to instantaneous Franck–Condon transition at time $t-\tau$ and $\varepsilon_{\mathrm{LO}}(t-\tau)$ the LO field amplitude. In other words, the HOKE spectroscopy enables us to obtain information about the population wave packet difference for *any* τ, i.e. for the values of the configuration coordinate corresponding to instantaneous Franck–Condon transitions for different frequencies $\omega(t-\tau)$ (not only for $\omega(t)$ as in the absorption spectrum measurements).

A signal in a pump–probe and resonance HOKE spectroscopy [8] can be found if one knows the population wave packets in both the ground and excited electronic states. These wave packets can be calculated by a non-perturbative analytic approach to the problem of the interaction of high-power chirped ultrashort pulses with molecular systems developed in Ref. [4] on the basis of 'moving potentials' pictures. This approach has been generalized in Ref. [6] by inclusion of high-frequency quantum intramolecular modes as follows:

$$\left(\frac{\partial}{\partial t} - L_n\right)\rho_n(\alpha, t) = \sum_{k=0}^{\infty}(-1)^n \frac{\pi}{2\hbar^2}|D\varepsilon(t)|^2 \times \big[F_1(\omega(t) - (\omega_{21} + k\omega_0) + \alpha)\rho_1(\alpha, t) - F_2(\omega(t) - (\omega_{21} - k\omega_0) + \alpha)\rho_2(\alpha, t)\big], \tag{3}$$

$$L_n = \tau_{ns}^{-1}\left[1 + (\alpha - \delta_{n2}\omega_{\mathrm{st}})\frac{\partial}{\partial(\alpha - \delta_{n2}\omega_{\mathrm{st}})} + \sigma_{2s}\frac{\partial^2}{\partial(\alpha - \delta_{n2}\omega_{\mathrm{st}})^2}\right], \tag{4}$$

where ρ_n is the population of state n, D the dipole moment, $F_{1,2}$ the spectra of the absorption and the emission respectively, ω_{st} the Stokes shift frequency, ω_0 the frequency of the optical active vibration mode, τ_{ns} the solvation correlation time in state $n, \sigma_{2\mathrm{s}}$ the contribution of the solvation to the width of the absorption spectrum of the dye molecule and α a variable, defined as the deviation of the transition energy from ω_{21} at the solvation coordinate q. This model concerned a Debye solvent. The relaxation in a Debye solvent provides an example of relaxation corresponding to a Markovian perturbation with an exponential correlation function. In this study we solved Eqs. (3) and (4) numerically. We calculated and measured the resonance HOKE signal of Rhodamine 800 in methanol excited by an intense chirped pulses.

2. Experimental setup

The optical experimental setup consists of a femtosecond laser source, an optical parametric amplifier (OPA), a pulse shaping devise and a setup for measurement of the resonance HOKE signal. The laser system consists of a Ti:Sapphire based oscillator (Mira Seed Coherent) and a multipass based Ti:Sapphire amplifier (Quantronix Odin) which produces laser pulses of 40 fs duration, centered near 800 nm, with a pulse energy of

~600 μJ and at a repetition rate of 1 kHz. These pulses are used to pump an OPA which generates tunable short intense and coherent pulses of 50 fs with ~25 nm bandwidth in the spectral range of 600–770 nm. The pulse shaping apparatus consists of a pair of 600 lines/mm gratings and two identical lenses with focal length of $f = 15$ cm. By moving one of the gratings collinearly with the optical axis, the pulse gains positive or negative linear chirp [9]. The chirp sign depends on the direction of the movements with respect to the lens focus. During the experiments, two chirp rates were chosen, −50,000 and 50,000 fs^2, hereafter negative and positive chirp rate respectively. The pulse temporal shape was diagnosed by a frequency resolved optical gating technique for determining the pulse chirp [10]. The sample was irradiated by 10 μJ pulses and focused by a 15 cm lens. The cell was placed about 2 cm from the focus (the spot size there is 360 μm) to avoid other nonlinear effects. Neutral density filters attenuated the pulse intensity. In the experiments, we used Rhodamine 800 dye which was purchased from Exciton, in 1 or 0.2 mm quartz cells. The dyes were dissolved in methanol. The optical density of the solution was about 0.7. In the time-resolved resonance HOKE experiment, the laser-induced anisotropy created by the resonant absorption of the pump pulse photons is probed by a variably delayed, weakly polarized probe pulse. The change in the polarization state of the probe beam was detected by transmission through a crossed polarizer pair of the probe beam as a function of the time delay between the pump and probe pulses. In order to amplify the optical Kerr signal, and avoid complexity due to the quadratic nature of the signal, we used heterodyne methods for signal detection. A local oscillator was derived by minor rotation of the analyzer polarizer by <1° from the maximum extinction position part of the probe pulse which is in phase with, and polarized perpendicularly to the probe polarization. The magnitude of the local oscillator intensity is about 30 times larger than that of the Kerr signal. The use of a local oscillator with field $\varepsilon_{\mathrm{LO}}$ and light intensity I_{LO} to detect a signal with a field ε_{s} and intensity I_{s} results in a detector response of:

$$I_{\mathrm{LO}} + I_{\mathrm{s}} + \frac{nc}{8\pi}(\varepsilon_{\mathrm{s}}^{*}\varepsilon_{\mathrm{LO}} + \varepsilon_{\mathrm{LO}}^{*}\varepsilon_{\mathrm{s}}). \tag{5}$$

The crossed term in parenthesis is the heterodyne term.

3. Results and discussion

We fit the experimental data of the resonance HOKE signal of Rhodamine 800 in methanol and DTTCI (3,3′-diethylthiacarbocyanien iodide) in methanol by solving the differential equations (Eqs. (3) and (4)) numerically. The calculation is based on the time propagator in a Chebyshev polynomial expansion given by Tal–Ezer–Kosloff method [11]. The computer routine calculates the populations as a function of the α coordinate and time and then calculates the HOKE signal by using Eq. (2). The resonance heterodyne HOKE signal provides similar information to that of traditional pump–probe experiment signals. An advantage of the HOKE signal is that it is a null technique, where prior to the pump excitation no light passes through the analyzer. The signal is directly related to the time-dependent deviation from the equilibrium value between the ground and excited state populations $\Delta'^{\mathrm{NL}}(\omega_{21} - \omega(t-\tau), t)$ which is defined in Eq. (2). Three processes influence the HOKE signal: the ‘doorway’, the ‘window’ and the ‘propagation’ processes (these terms were suggested in Ref. [12]).

1. In the ‘doorway’ process (referring to the region of the solvation coordinates where the pump transfers the populations), the pump pulse determines the population transfer from the ground state and vice versa, i.e. from the excited state back to the ground state (‘dump’ process). The net result of these two processes is the generation of a ‘particle’ population in the excited state (which we will denote as electron population) and ‘hole’ population in the ground state.
2. In the ‘window’ process (referring to the region of solvation coordinates where the probe ‘scans’ the populations), the probe pulse monitors the sum of both electron and

'hole' populations at a certain position of the generalized solvent coordinate, each of which has a specific frequency component. Since the chirp of the pulse is linear, the chirp of the probe determines the scan rate of the relevant solvation coordinates.

3. In the 'propagation' process, the dynamics of the populations of both 'hole' and electron is controlled by the diffusion back to the equilibrium. An efficient dump process takes place when spatially local population inversion is generated. The relatively large width of both the population distribution of 'holes' and electrons explains why the HOKE signal intensity does not decay to zero, even though the relaxation is over (long time signal).

Now we review the influence of the pulse characteristics and the solvent–solute system properties as studied from the numerical simulations.

3.1. The effects of the pulse characteristics

Two parameters characterize the pump pulse the first is the chirp rate and central frequency of the pulses (ω_c) and the second is the intensity of the pump, which is characterized by the pulse maximal power density (J_{max}) (the probe pulse intensity is weak and hence does not influence the population):

3.1.1. The chirp rate and central frequency of the pulses

The calculated HOKE signals, as a function of the chirp rate for negatively and positively chirped pulse, are depicted in Figs. 1a and b. The amount of population transferred from the excited state back to the ground state depends on the synchronization of the chirp rate and the solvent relaxation, since a momentary population inversion is achieved. When the chirp rate is too fast (small $\phi''(\nu)$), the population of the excited state will not reach the 'doorway' (on the upper potential surface) where population inversion takes place at the time of arrival of the relevant frequency component of the laser pulse that can stimulate the population transfer. In the opposite case, the chirp rate is slow (large $\phi''(\nu)$) and the population relaxation occurs prior to the arrival of the relevant frequency component that is capable of dumping the population to the ground state. Maximum population transfer will occur at a certain chirp rate that corresponds to the best match with the generalized solvent relaxation time. In the case that results in negligible dump or the case of positively chirped pulses, the chirp affects the buildup of both 'hole' and electron population

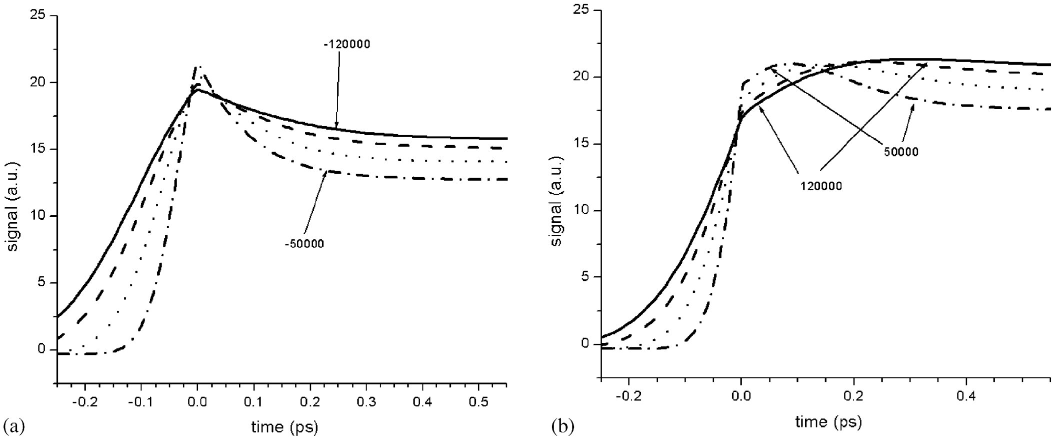

Fig. 1. Simulations of HOKE signals for DTTCI in methanol solution as function of the pulse chirp. (a) Negative chirp (−50,000, −75,000, −100,000, −120,000 fs^2), (b) positive chirp (50,000, 75,000, 100,000, 120,000 fs^2). The model parameters are: $t_p = 30$ fs, $\tau_s = 50$ fs, $\omega_{st} = 800$ cm^{-1}, $\omega_c = 13000$ cm^{-1}, $J_{max} = 3 \times 10^{10}$ J/cm^2 s.

profiles only. Again, the synchronization between solvent relaxation time (τ_s) and chirp rate has a profound effect on the effectiveness of the dump process. For a relatively long relaxation time, compared with chirp rate ($\tau_s > t_p$, t_p is the chirped pulse temporal width) or when the spectral width of the pulse is narrow (large temporal width in transform-limited case), the population profile will be almost independent of the chirp or its sign, since the solvent dynamics are slow with respect to the rate of population excitation. Therefore, the pump for typical solvation energies and relaxation dynamics should be below 35 fs at the transform-limited.

In contrast to positively chirped pulses, where the population buildup takes place in the opposite direction with respect to the molecular nuclear dynamics, for a negatively chirped pulse, the population reaches the equilibrium position (bottom of the potential well of the excited state) faster. For this reason, the buildup of the HOKE signal for negatively chirped pulses is faster than that of positively chirped pulses (as seen in Figs. 1a and b).

We should also consider the chirp rate and the central frequency of the probe, which is identical to the pump in our study. The central frequency determines the 'window' region and the chirp rate determines the 'scan rate' of the 'window' region. As seen in Figs. 1a and b, the chirp determines the pulse width and reflects the 'scan rate' of the 'window' region, therefore the HOKE signal rise time and fall time increase with the increase in the chirp.

3.1.2. The intensity of the pump

For negatively chirped pulses, the intensity of the pump pulse determines the effectiveness of the dump process. In general, the larger the pulse intensity, the larger the HOKE signal, since the sum of 'holes' and electrons in the relevant coordinates is larger (excluding saturation effects). For positively chirped pulses, the normalized HOKE signal shape (i.e. the normalized signal) is independent of the pump pulse intensity. This finding arises from the fact that the amount of population raised to the excited state is proportional to the pulse intensity.

The equations of motion of the electrons both in the ground and excited states are determined by the Debye–Smoluchowski equation (DSE) under harmonic potential (see Eqs. (3) and (4)). The DSE is a linear partial differential equation and, therefore, the population profile is independent when the amount of population is increased by a certain factor. The time dependent profile depends on the potentials' surface shape and the relaxation times.

Unlike the positively chirped pulse excitation, for a negatively chirped pulse under effective dump 'conditions', the shape of the normalized HOKE signals depends strongly on the pump pulse intensity. This is explained by the fact that the amount of the transferred population (from the excited state to the ground state) depends not only on the laser intensity but also on the total population of the state, which was previously transferred from the ground state. In the case of a 'dump' process, the 'blue part' of the pulse transfers population to the excited state which is proportional to the total population in the ground electronic state. The 'red part' of the pulse transfers population from the excited state back to the ground state in proportion to the excited state population. Thus, the overall process of population transfer is not linear. The intensity dependence of the HOKE signals of a negatively chirped pulse indicates the effectiveness of the dump process. If the shape of the normalized HOKE signal is independent of the pulse intensity then a dump process is not taking place. If the shape depends on the pulse intensity, then the dump process affects the dynamics of the population.

3.2. The effects of the solvent–solute system properties

In addition to the dependence of the HOKE on both the pump and probe pulse parameters, the HOKE signal also depends on the probe molecule and the solvent bath properties. The molecular parameters are the solvation relaxation time, τ_s, the Stokes shift, ω_{st}, the probe molecule oscillator strength, the high-frequency optical active vibration mode and S_0 (Huang–Rhys parameter). We determined the last four parameters from the fit of the absorption or emission spectra of the probe molecule in a particular solvent using Eq. (39) of Ref. [6]. For a negatively chirped pulse, the HOKE signal exhibits a steep rise, limited by the chirped pulse temporal width followed by a partial fast decay of the signal amplitude. The relative amplitude of the fast decay component depends on both τ_s and the pump pulse intensity (see Fig. 2a). The shorter the solvation relaxation time, the smaller the amplitude of the fast decay component. The latter behavior can be explained by an efficient dump process, since the population inversion condition period of time, is dependent on the solvation relaxation time. The longer τ_s, the longer the population inversion condition and hence an efficient dump can take place. Unlike the fast decay observed for the HOKE signal of a negatively chirped pulse, for a positively chirped pulse, when τ_s is short, we see an additional rise in the HOKE signal with a time constant of about ~100 fs and, subsequently, the HOKE signal intensity decreases with a relatively long time constant (Fig. 2b).

Another parameter that influences the HOKE signal is the Stokes shift, ω_{st}. If the solvation relaxation is non-exponential then the measured

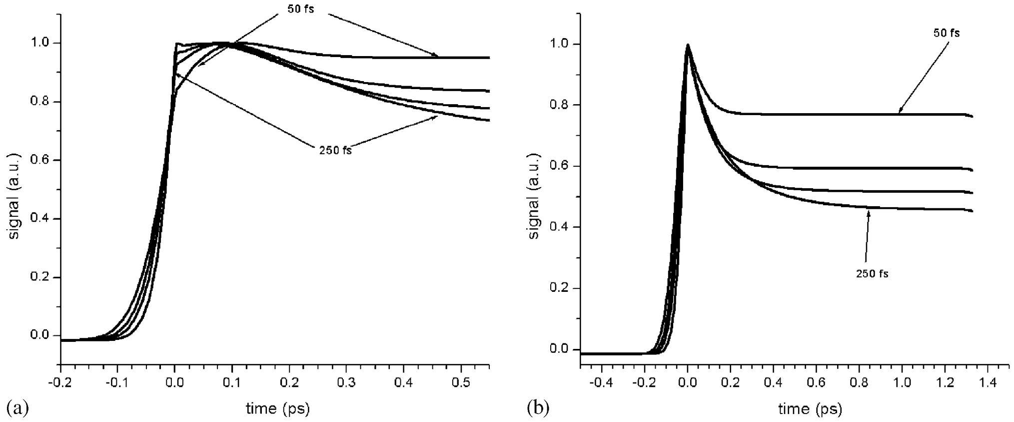

Fig. 2. Simulations of HOKE signals for DTTCI in methanol solution as a function of the system relaxation time (50, 100, 150, 250 fs). (a) Positive chirp (50,000 fs^2), (b) negative chirp (−50,000 fs^2). The model parameters are the same as in Fig. 1.

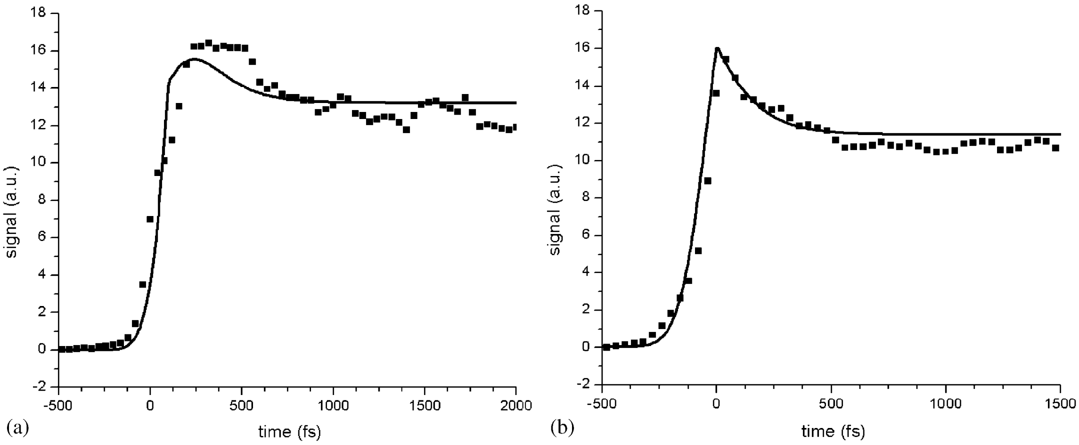

Fig. 3. Experimental results (squares) for OKE signals for Rh800 in methanol solution for (a) positive chirped pulse (50,000 fs^2) and (b) for negative chirped pulse (−50,000 fs^2). Theoretical fits are in solid lines.

value of the Stokes shift (either by absorption or emission measurements) is not the effective value for the population of the excited state during the pump pulse interaction with the solution. In this case, one needs to take into account only the solvation energy associated with the ultrafast component of the solvation dynamics. For methanol this component is only about 50% of the total spectral shift.

Finally we compared the experimental results with the computer simulations, which are shown in Figs. 3a and b for Rhodamine 800. As seen from the experimental OKE signal of Rhodamine 800, the computed fit is rather good.

5. Conclusion

In this work we have proposed and developed a new method for studying the time evolution of population wave packets under intense chirped pulse excitation: the resonance HOKE spectroscopy with intense chirped pulses. In general this method enables us to obtain complimentary information about population wave packets versus the absorption spectrum of an intense chirped pulse.

We have analyzed the effects of the parameters of the solvent–solute system and the electric field on the signal on the HOKE experiment. We got a good fit to the experimental HOKE signals for both positively and negatively chirped intense pulses.

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