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Infrared Photon-Echo Spectroscopy of Water: The Thermalization Effects

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Abstract. The larger part of the nonlinear response in IR photon-echo and transient-grating spectroscopy on HDO-D₂O mixtures at >1-ps delays is found to originate from the D₂O refractive index modulation due to local volume thermalization.

1. Introduction

The complex and even peculiar properties of liquid water are largely determined by the presence of a network of hydrogen bonds. The hydrogen bonds undergo continuous transformations that occur on sub-ps timescales [1-6]. The molecular vibrations are especially sensitive to the presence of the hydrogen-bond network. The microscopic structure and the dynamics of water manifest themselves in the IR vibrational spectrum, and, therefore, can be studied by methods of ultrafast IR spectroscopy. The technique of IR photon echo [3-7] allows obtaining the most direct information about the systems dynamics.

It is well known that the hydrogen bonding in water is extremely sensitive to temperature. Excitation of a vibrational mode, followed by ultrafast population relaxation and energy thermalization, ultimately leads to a local increase of the temperature. Therefore, the delayed probe pulse interrogates a system whose spectral properties have been modified by the absorbed energy of the first pulse(s), causing impediments in the analysis and interpretation of the experimental results. In this contribution a comprehensive study of thermal effects in IR spectroscopy of liquid water, employing heterodyne-detected photon echo and transient grating (TG) techniques, is presented. We directly demonstrate that the main part of the thermal contribution to the TG signal originates from a refractive index modulation of the solvent (D₂O). The model that includes energy absorption by the OH stretching mode, local temperature increase after population relaxation, and subsequent heat diffusion, perfectly describes the experimental data.

2. Results and discussion

The TG signal of the OH-stretch vibrational mode of HDO molecules dissolved in D₂O is shown in Fig.1a by a solid line. The initial part of the signal decays with a time constant of ~700 fs that is consistent with the population lifetime [8].

However, after reaching a minimum around 2 ps the TG signal begins to *grow* again and finally levels-off at ~ 10 ps. Heterodyne-detected transients are shown in Fig.1b. At short delays ($t_{23}=500$ fs), the response is mainly determined by the HDO molecules. This conclusion is made on the basis of signal position, shape, and decay constant: the contour is shifted from zero delay to positive values and its decay rate equals the OH-stretching vibration population relaxation. Also, the spectrum of the response coincides well with the pulse spectrum convoluted with the absorption spectrum (Fig.1c). In contrast, at long delays ($t_{23}=10$ ps) the characteristics of the response change drastically: it narrows in time, its phase shifts by $\sim \pi$ (Fig.1a, inset), and its spectrum becomes identical to the spectrum of the probe pulse (Fig.1c) which points at the instantaneous origin of the system response. This makes us conclude that the TG signal at long delays results from the grating imprinted in the solvent, that is, D_2O .

A schematic representation of the energy equilibration is depicted in Fig.2a. The population (absorption) spatial grating originally imprinted in HDO by the excitation pulses, relaxes with a lifetime of ~ 700 fs (Fig.1b, open circles). The energy, stored in the grating, is released by the chromophore to the surrounding D_2O molecules, giving rise to an increase in local temperature. This temperature raise leads to modifications of the shape and amplitude of the D_2O stretching mode absorption band at $4.5 \mu\text{m}$ and, hence, both absorption and refractive index spatial gratings are imprinted in the solvent. The former is of a little importance for the TG signal at $3 \mu\text{m}$ because its amplitude scales with the inverse squared of the detuning ($\sim 1000 \text{ cm}^{-1}$). However, the spatial modulations of the D_2O refractive index decrease much slower, as the inverse detuning from the resonant frequency. Therefore, the probe pulse is scattered of the off-resonance grating written in the solvent refractive index (Fig.1a, solid squares). This is reflected in the phase of the

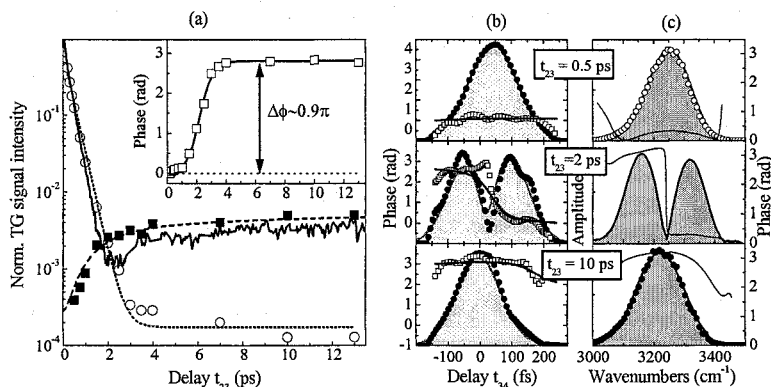


Fig.1. (a): Experimental TG signal (solid line) and amplitudes of its additive components: chromophore response (open circles) and solvent response (solid squares) as found from the analysis of heterodyne-detected TG data. Inset: the phase of the TG signal at $t_{34}=0$. (b): Amplitudes (solid dots) and phases (open squares) of heterodyne-detected TG signals. Results of simulations are depicted as shaded contours (amplitudes) and solid lines (phases). (c): Spectra (shaded contours) and phases (lines) of the corresponding signals as calculated by Fourier transformation of the experimental data. Closed and open circles show the pulse spectrum and its convolution with the system response, respectively.

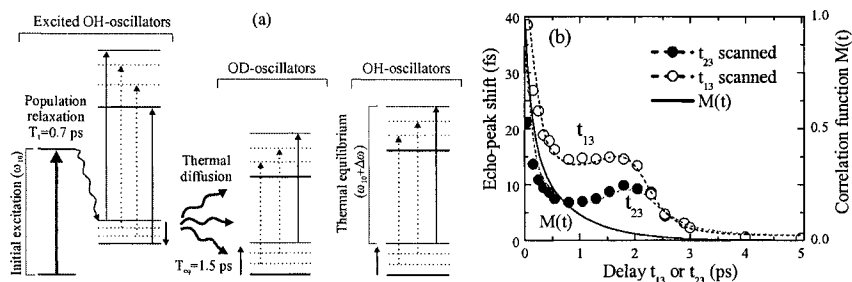


Fig.2. (a): The energy equilibration scheme for photon echo experiments on HDO molecules dissolved in D₂O. (b): Experimental echo-peak shift data for the fixed delays t_{13} (solid circles) and t_{23} (empty circles), and theoretical simulations (dashed lines). Note that the EPS functions acquired while keeping the delays t_{13} and t_{23} fixed, are shifted along the vertical axis as a consequence of the relatively short excited-state lifetime (700 fs).

heterodyned signal that is almost π -shifted compared to the signal phase at short delays (Fig.1a, inset). The temporal build-up of the refractive index grating is well described by the macroscopic heat diffusion equation (Fig.1a, dashed line) with a time constant of ~ 1.5 ps.

We applied the developed model to the analysis of the echo-peak shift experiments (Fig.2b) in order to extract information about the water dynamics. The peak in the EPS function around ~ 2 ps is explained as arising from interference between the chromophore and solvent responses. The delicate balance between the phases of genuinely nonlinear and thermal contributions as the delay t_{12} between the two excitation pulses is increased, leads to the enhancement of the integrated signal that is measured in the EPS experiment.

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