Polarization Dependence of Chirp-induced Nonlinear Raman Scattering Spectroscopy of Aqueous Ions and Organic Liquids in the THz Regime

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Abstract— **We present polarization dependent measurements of coherent Raman spectra of liquids with chirped ps-pulses in the THz regime. In order to detect the coherent Raman spectrum we made use of a, previously introduced [1, 2], nonlinear pump and probe scheme involving an experimental technique called "spectral focusing". As a result, we are able to resolve spectrally stimulated Raman gain and inverse Raman scattering. Our experiment covers the entire THz range from 10 THz down to 100 GHz. Thereby, we show that different spectral features of aqueous ions and organic liquids can be distinguished using different polarization states of the pump beam.**

I. INTRODUCTION

WHILE THz spectroscopy of liquids has been extensively used for the investigation of low-frequency modes of molecules mediated by weak intermolecular interactions [3], a main disadvantage of spectral measurements in the THz regime is the broadening of spectral line shapes due to large scale intermolecular disorder in the liquid state. Hence, a valuable tool to increase the spectral specificity and receive further information about the nature of the measured signals might be polarization dependent measurements [4].

II. EXPERIMENTAL SETUP

Here, we present polarization dependent measurements of liquids using nonlinear stimulated Raman spectroscopy at THz frequencies. A simplified scheme of our experiment is shown in Figure 1. We use a regenerative amplifier to produce broadband p-polarized fs-pulses at repetition rate of 1 kHz. In the next stage, we employ a stretcher to change the pulse width to about 4.4 ps. After the stretcher, the laser pulses exhibit a constant linear chirp. Hence, a linear relationship between time t and carrier frequency f is established, which can be describe by:

$$f(t) = b * t + f_0,$$

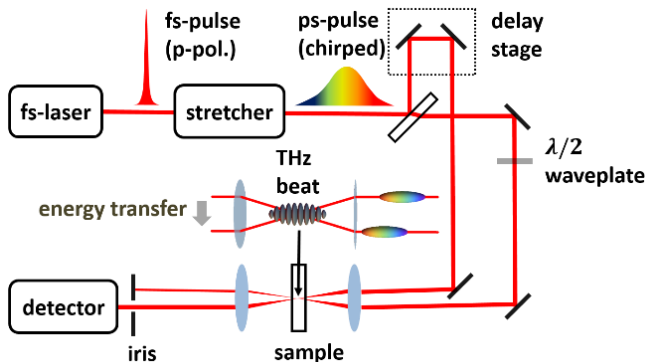where b is the chirp parameter and f_0 is the frequency at $t = 0$.
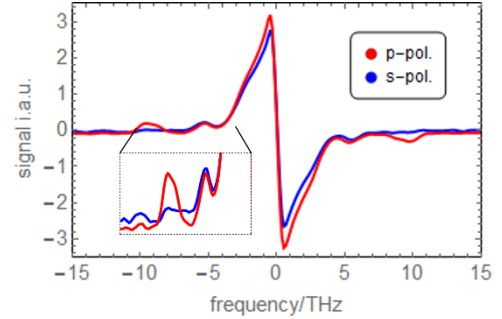

Fig. 1 Experimental setup.

Fig. 2 Spectrum of bromobenzene measured with p- and s-polarized light of the pump beam. The inset displays a zoom into the gain side of the coherent Raman spectrum.

Using a beam splitter, we separate the beam in a pump and a probe beam part in an interferometer, where we adjust the time delay τ between both arms with a delay stage. Furthermore, we control the polarization of the pump beam with a $\lambda/2$ waveplate. After the interferometer, both beams are focused and overlapped at the sample position. Depending on the time delay, the pulses excite the sample at the difference frequency Δf (THz beat) between the pump and the probe beam resulting in a nonlinear Raman scattering process inducing an energy transfer between both beams. Due to the linearity of the chirp the difference Δf of the carrier frequencies can be simply described by:

$$\Delta f = f_{probe} - f_{pump} = b * \tau.$$

Thus, the amount and the direction of the energy transfer depend on the chirp, the time delay, the polarization of the beam and the imaginary part of the third-order susceptibility χ at Δf. After the sample position we separate probe beam and pump beam with an iris and observe the energy change of the probe beam with a Si-photodiode. By scanning the signal with the delay stage, we directly measure the frequency dependence of the coherent Raman spectrum. At $\tau = 0$ the energy transfer direction between both beams is changed due to the transition between stimulated Raman gain scattering and stimulated Raman loss scattering. Therefore, the sign of the measured signal is also changed.

Finally, for a comprehensive description the polarization has to be taken into the account. In this context, Munhoz et. al. showed that the dependence of the measured signal on the pump beam polarization angle α_p (defined relative to the probe beam polarization angle) is given by [5]:

$$S(\alpha_p) \propto Im(\chi(\Delta f)) \left[\frac{\rho_r}{1 - \rho_r} + cos^2\alpha_p \right] .$$

Here, we introduced the depolarization ratio ρ_r. With our

experiment, we measured the signals for pump beam polarization of 0° ($S(\alpha_p = 0°)$) and 90° ($S(\alpha_p = 90°)$). In doing so, we can estimate ρ_r by $\rho_r = S(\alpha_p = 90°)/ S(\alpha_p = 0°)$ (see [5]). This depolarization ratio ρ_r coincides with the depolarization ratio measured by spontaneous Raman scattering spectroscopy. In general, values of $0.75 > \rho_r \geq 0$ arise from totally symmetric modes, while non-totally symmetric vibrations are characterized by $\rho_r = 0.75$ [6]. Thus, measuring the depolarization ratio can help to assign unknown Raman bands.

III. RESULTS

In Figure 2, the coherent Raman spectrum of bromobenzene is shown for p- and s-polarization directions of the pump beam (compare also [7]). While the peak at 9.4 THz is strongly suppressed for the s-pol. direction, there is nearly no dependence for the peak at 5.3 THz on the polarization of the pump beam indicating that both features have different depolarization ratios. Thereby, the suppression of the 9.4 THz peak might arise from a totally symmetric vibration.

With same experiment, we can separate different overlapping spectral features for aqueous $ZnBr_2$ [8]: Figure 3 depicts a measurement of the coherent Raman spectrum for an aqueous solution of $ZnBr_2$ at a concentration of 4M for p- and s-polarized light. In order to compare these measurements, we removed a constant offset from the p-polarized measurement, which might result from an insufficient block of the pump beam during the measurement. Furthermore, we scaled the p-polarized spectrum by another constant factor (≈ 0.78). From the comparison of both spectra, we find that the prominent peak at around 5.3 THz is suppressed for the s-pol measurements. Hence, the narrow-band peak can be separated from the broad-band contribution, which is present in both spectra, by calculating the difference. The peak can be assigned to vibrational modes of $ZnBr_2$, $ZnBr_3^-$ and $ZnBr_4^{2-}$ complexes [9], which were not resolved by our experiment. In our experiment, an increase of the temporal width of the stretched pulse leads to a higher spectral resolution but reduces the signal-to-noise ratio (see [10]).
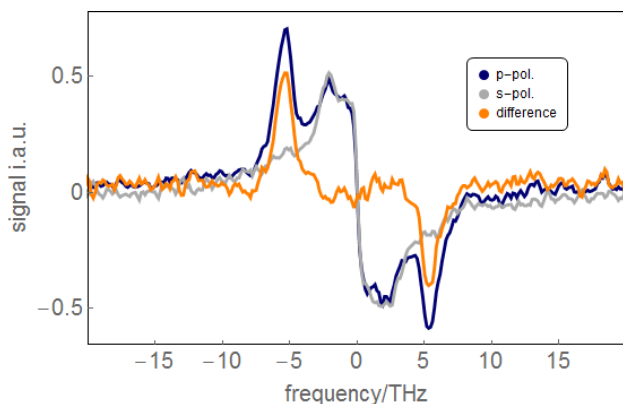

Fig. 3 Spectrum of aqueous $ZnBr_2$ at a concentration of 4M for s-polarized (dark blue, scaled with 0.78) and p-polarized light (gray) and the difference between them (orange).

IV. SUMMARY

We presented an experimental setup, which is capable to measure the coherent Raman spectrum of aqueous solution in the THz regime. Using the spectral focusing technique, we only need to combine an interferometer with a stretcher to generate the stimulated Raman spectrum. Unlike techniques investigating spontaneous Raman scattering [11], our experiment does not require filter to cut out the light of the laser source. Consequently, we can investigate the third-order susceptibly in the ultra-low frequency range such as 100 GHz (see [1,2]). Furthermore, with polarization dependent measurements we are able to specify the spectral line shape, which might lead to new insights in the origin of intra- and intermolecular dynamics of liquids.

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