Utilization of Chirped Laser Pulses to Measure Stimulated Raman Scattering of Organic Liquids in the THz Regime

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With the present paper, we demonstrate an experimental setup connecting two highly innovative fields of research: stimulated Raman scattering (SRS) spectroscopy and terahertz (THz) spectroscopy of liquids. For this purpose, we use the spectral focusing method allowing us to excite and measure molecular vibrations by chirped laser pulses. With our experimental setup, we apply this method to the THz regime in order to detect the frequency dependence of SRS processes in organic liquids. More specifically, we focus two chirped laser pulses onto the sample to drive molecular vibrations at THz frequencies. Thereby, the time delay between the laser pulses is directly related to the driving frequency. Due to SRS process an energy transfer between the two laser pulses is established. By detecting the corresponding energy change of only one of the two laser pulses, we are able to observe inverse Raman scattering and stimulated Raman gain scattering as well as the transition between both processes at zero delay time. The peak positions and the line shapes of the measured spectra agree well with literature data obtained by spontaneous Raman scattering spectroscopy and optical heterodyne detection optical Kerr effect spectroscopy. With the present setup, we are able to excite and detect molecular vibrations ranging over two orders of magnitude from 10 THz to ultra-low frequencies at 100 GHz.

Recently, there has been a growing interest in stimulated Raman scattering¹. This interest is motivated by the desire to develop a label-free imaging technique for in vivo investigations of biological samples with a high signal-to-noise ratio, while reducing the incident power of the potentially damaging radiation as much as possible^{2,3}. In this regard, it has been shown that coherent Raman spectroscopic techniques such as SRS spectroscopy or coherent anti-Stokes Raman scattering (CARS) spectroscopy can provide imaging systems with high sensitivity and high frame rates^{2,4}. Thereby, SRS spectroscopy has the advantage that artifacts originating from non-resonant background signals or phase matching problems are not present.

Most prior research of SRS spectroscopy has been concentrated on the detection of infrared (IR) bands. When applied to living cells, the detection of IR bands with SRS spectroscopy enables to differentiate intracellular structures. Thereby, the IR bands characterize intramolecular vibrations which are specific to different molecules. In this regard, little attention has been paid to coherent Raman spectroscopy of intermolecular vibrations. Compared to intramolecular vibrations, intermolecular vibrations are mediated by weaker interaction energies and involve larger groups of atoms or molecules. For liquids the corresponding motions occur typically at THz frequencies⁵. Hence, THz spectroscopy provides access to the investigation of various phenomena like hydrogenbond dynamics in ionic liquids⁶, rattling motions of aqueous ions in their solvation shell^{7,8} or hydration dynamics of aqueous ions⁹ and proteins¹⁰. When studying biological systems, the hydration dynamics of proteins are of special interest because the function of proteins is supposed to be provided by intermolecular interaction^{11,12}.

In the following, we provide a experimental connection between THz spectroscopy of liquids and SRS spectroscopy. While such a connection was previously implemented with narrow-bandwidth lasers¹³, we investigate a different approach: Using broad-bandwidth, frequency chirped pulses, we utilize the spectral focusing method^{14,15} which was first demonstrated in the context of CARS spectroscopy exciting intramolecular vibrations in the mid-infrared (mid-IR) region. Recently, the spectral focusing technique has been shown to work also well

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FIG. 1. Displayed is a scheme of the experimental setup. The central diagram illustrates the time-frequency correlation of the incident laser beams at the sample position.

for SRS spectroscopy in the mid-IR region⁴ and CARS spectroscopy at THz frequencies¹⁶. Furthermore, chirped pulses were already used for broadband spectrum generation by coherent excitation of low frequency Ramanactive modes in crystals¹⁷.

Here, as a proof of principle, we measured the inverse Raman scattering (IRS) spectrum and the stimulated Raman gain scattering (SRGS) spectrum of iodobenzene and bromobenzene in the THz region. There, both liquids have well known intramolecular Raman bands^{18,19}. Here, we will demonstrate that the present setup can not only detect these Raman bands but also signatures of the intermolecular motions of these liquids. For iodobenzene the measured line shape agrees well with formerly reported data given by optical heterodyne detection optical Kerr effect spectroscopy (OHD-OKE) experiments²⁰.

At this point, we will give an description of our experiment setup for measuring the low-frequency stimulated Raman scattering of organic liquids by adapting the spectral focusing technique of Hellerer et al.¹⁴ to the THz regime (see Figure 1). A Ti:Sapphire regenerative amplifier provided 200 fs pulses with a repetition rate of 1 kHz $(\lambda \sim 800 \text{ nm}, \text{ bandwidth} \sim 34 \text{ nm})$. Using an Öffner stretcher $^{21-23}$, a linear chirp was imprinted to the fspulses expanding the pulse width to about 44 ps. Then, the pulse train passed an interferometer, where the beams were split by a 50/50 beam splitter (fused silica, thickness ~ 2.3 mm) into a pump and a probe beam. As a result of the linear chirp, a constant difference between the instantaneous frequencies of both ps-pulses could be adjusted by fine-tuning the delay stage of the probe beam. When overlapping both linear p-polarized pulses at the sample position, stimulated Raman scattering occured involving the excitation of the sample at the difference frequency of the pump and probe beam. Using a synchronized chopper at the half of the repetition rate of the fs-laser (i.e. 500 Hz), we suppressed every second pulse of the pump beam. After passing the sample, the pump beam was blocked. Finally, using a silicon photodiode and a lockin amplifier, we observed the energy change of the probe beam according to the stimulated Raman scattering.

For the liquid samples, a fused silica cuvette with 10

mm path length was used as a sample holder. An excitation power of roughly 600 μ W for both the pump beam and the probe beam was used. Finally, an averaging of 5 measurements (each took about 4 min) for every sample provided us with a sufficient signal-to-noise ratio.

To demonstrate the potential of our setup, we observed the spectrum of organic liquids at room temperature. Figure 2(a) shows the result of an overview measurement of iodobenzene. The spectrum shows an anti-symmetric line shape which can be explained by considering stimulated Raman scattering at the sample position: According to the linearity of the chirp, a temporal constant energy difference between the probe and the pump beam can be adjusted by changing the time delay between them with the delay stage of the interferometer (an illustration of the time-frequency correlation for both laser beams is shown in Figure 1). This energy difference causes an excitation of the sample by a stimulated Raman scattering process with respect to the corresponding third-order nonlinear susceptibility²³. Thereby, during the overlap of the pulses, the intensity of the beam with higher energy photons is decreased (IRS) while the intensity of the beam with the lower energy photons is increased $(SRGS)^{24}$. Due to the positive chirp of the laser pulses, we expect an energy transfer from the pulse which arrives earlier at the sample position to the pulse which arrives later. Hence, the direction of the transfer is inverted when the pump and the probe beam exhibit the same path length. This consideration is in agreement with the anti-symmetric line shape of the spectrum shown in Figure 2(a).

It is important to note that the measured datasets can contain an arbitrary offset of the time-axis, i.e. the point of equal path length between pump and probe beam does not necessarily coincide with the assignment of the zero point of the time axis. By assuming that the measured signatures for the IRS and SRGS signal should show up at the same absolute difference of the path length, we removed this offset from our datasets.

In order to assign a frequency axis to the measured SRS signal, we can relate the difference frequency f_d between the pump and the probe beam to the time delay τ using $f_d = b \times \tau^{14,16,23}$, where b denotes the chirp parameter. In doing so, the knowledge of the chirp parameter b is crucial for the evaluation of the measured spectra. To determine the chirp parameter, we have chosen an intrinsic method, which is independent from any data given by other experiments. In the following, we illustrate how the chirp parameter can be calculated by measuring the spectrum of the laser source and the intensity autocorrelation of the chirped pulses.

We start by assuming a linear chirp, i.e. the time dependent instantaneous frequency of a single pulse is given by $f(t) = f_0 + b \times t^{-14}$. Here, f_0 denotes the initial frequency. The time dependent pulse intensity I(t,b), after the stretcher, can be related to the spectral intensity I_f by $I(t,b) = I_f(f_0 + b \times t)$. We measured the spectral intensity I_f at the output of the laser source with a



FIG. 2. Shown is (a) the SRS time domain signal of iodobenzene and (b) an exemplary fit of the autocorrelation of the laser spectrum (dashed) to an intensity autocorrelation measurement of the chirped pulses (solid).

fiber-coupled spectrometer (Ocean Optics HR4000 CG-UV-VIS) covering a spectral range from 200 nm up to 1100 nm. Using this dataset, we can calculate the delay time τ dependent intensity autocorrelation $S(\tau, b)$ with the following equation:

$$S(\tau, b) = \beta \int_{-\infty}^{\infty} I(t, b) I(t - \tau, b) dt$$
$$= \beta \int_{-\infty}^{\infty} I_f(t \times b) I_f(b \times (t - \tau)) dt \qquad (1)$$

assuming an arbitrary chirp b and a proportionality factor β . In the next step, we determined $S(\tau, b)$ independently by measuring the sum frequency signal between the pump and the probe beam with a GaP diode. The sum frequency signal was generated by a BBO crystal placed at the sample position. Finally, we obtained a chirp parameter of $b = 0.511 \pm 0.019$ THz/ps by fitting $S(\tau, b)$ from equation 1 to the sum frequency signal (see Figure 2 (b)). Here, the denoted confidence interval with a confidence level of 95 % was calculated by taking into account four independent measurement for each required dataset.

By multiplying the chirp parameter b with the delay time τ , we can determine the frequency dependence of the observed SRS signal. Figure 3(a) depicts the resulting IRS spectra of iodobenzene and bromobenzene. For comparison the arrows indicate peak positions of Raman bands given by polarization sensitive spontaneous Raman measurements from reference 18. It is proposed that the observed resonances are originated from in-plane (higher frequency) and out-of-plane motions (lower frequency) of the benzene ring, which include motions of the halogen atom^{18,19}. This assignment is in agreement with the halogen mass dependent frequency shift of the corresponding Raman bands, which can be seen in Figure 3(a).

When critically examining in Figure 3(a) the measured peaks in comparison to the positions given by the literature data, one can recognize probable systematic shifts. Therefore, we would like to discuss shortly an alternative calculation of the chirp parameter \tilde{b} . First, we estimated all four peak positions by fitting the sum of two normal distributions to each spectrum. Subsequently, we correlated these peak positions with a linear fit to the peak positions given by the literature data. As result we obtained $\tilde{b} = 0.490 \pm 0.016$ THz/ps being the slope of the linear fit. For the calculation a confidence level of 95 % was chosen.

While both approaches lead to similar estimates of the chirp parameter, the weak overlap between the corresponding confidence intervals of b and \tilde{b} indicates that, beside pure statistical errors, systematic effects might influence the accuracy of these estimates. In the case of b, systematic effects could originate from the wavelength dependence of the grating efficiency or the wavelength dependence of the sum frequency conversion efficiency of the BBO crystal²⁵. The estimate of \tilde{b} , in contrast, could be systematically influenced by the choice of the line-shape functions used for fit of the time dependent peak positions.

Next, we will consider the low frequency side of the measured spectra. Here, an increase of the scattering signal and an additional shoulder is detected for both samples. A similar increase in the spectra of previous OHD-OKE measurements of iodobenzene at this frequency range was interpreted as a signature of collective molecular motions resulting from a combination of rotational and translational displacements²⁰. Such motions are of special interest, because they reflect the intermolecular interactions between the molecules.

In Figure 3(b), we compare the (scaled) Raman spectral density of iodobenzene calculated from these OHD-OKE measurements²⁰ with the IRS spectrum obtained with our setup. Thereby, it is important to note that the sample temperature for the OHD-OKE measurements was at 273 K, while our measurements where performed at roughly 295 K. For higher temperatures, a broadening of the intermolecular vibrational bands and a slight shift of the rotational diffusion band to higher frequencies is expected²⁰. Nonetheless, both measurements agree well in the observed spectral range. Hence, we estimate from the increase of the signal at lower frequencies that the THz SRS setup can detect Raman active modes at frequencies lower than 100 GHz at minimum. For an estimation of the lowest detectable frequency, it is also possible to consider the width of the frequency chirped pulses given by the intensity autocorrelation (see Figure 2(b)). From this measurement we estimate 44 ps for the full width at half maximum, which implies a limit of about 23 GHz for the lowest detectable frequency.



FIG. 3. (a) shows the IRS spectrum of iodobenzene and bromobenzene. The arrows indicate the frequencies of signatures given by reference 18 for spontaneous Raman scattering. (b) displays a comparison of the low frequency IRS spectrum of iodobenzene with the Raman spectral density (given by reference 20) calculated from OHD-OKE measurements.

In conclusion, we introduced an experimental setup for SRS spectroscopy of liquids at THz frequencies. In order to validate our setup, we measured the SRS spectrum of iodobenzene and bromobenzene. Thereby, we detected for both liquids the SRS signatures of intra- and intermolecular motions in the range between 100 GHz and 10 THz showing that a broad spectral range of about two orders of magnitude is accessible by THz SRS spectroscopy.

To realize the experiment with the spectral focusing method, our setup requires the implementation of a stretcher. Furthermore, after the scattering process the pump and probe beams have to be separated. Here, a separation with an optical filter (as for example in references 3, 4, and 27) is not possible because both beams overlap completely in frequency space. Therefore, we used a spatial separation by inserting an iris after the sample position. However, such an approach can be challenging when the laser beams exhibit a diffraction pattern and detection of small signals is required. Another approach using a time gating method by implementing an additional compressor was introduced before²³. While these examples show that some effort is necessary to separate the pump and probe signals, it is possible to avoid the implementation of two laser sources or additional laser systems like an optical parametric oscillator. This simplification can be regarded as a major advantage of the spectral focusing technique.

Finally, an additional, unique feature of the presented method is the possibility to observe IRS, SRGS and the transition between these processes in one single measurement. As a result, an anti-symmetric line shape is observed which helps to evaluate the reliability of the measured datasets. While our results are in good agreement with literature data, we expect that the assignment of the peak positions can be enhanced by using more sophisticated techniques to determine the chirp parameter b. For example, by using the frequency resolved optical gating (FROG) technique²⁸ it might be possible to directly monitor the time-frequency correlation of the ps-pulses at the sample position and eliminate the influence of prior optical systems (such as lenses or gratings) on the estimation of the chirp parameter. Due to the sharper spectral bands of crystals, one can expect to further increase the accuracy of the chirp parameter estimation by evaluating their spectral signatures²³.

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