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IMPLEMENTATION OF ULTRA-LOW FREQUENCY NON-LINEAR RAMAN SPECTROSCOPY WITH THE GUN LASER AT FLUTE

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Abstract

At the Karlsruhe Institute of Technology (KIT) the new compact versatile linear accelerator FLUTE is currently under commissioning. This accelerator will provide intense broadband terahertz (THz) pulses for spectroscopic experiments. Here, we demonstrate the implementation of a coherent Raman spectrometer using the RF gun laser of FLUTE. With our experiment, we can measure the Raman spectrum at ultra-low frequencies. The measurement principle is based on the excitation of the observed sample with non-linear Raman scattering. The spectrometer consists of a stretcher and an interferometer, which can be simply built from standard optics. We will show that the accessible spectral range overlaps well with that from the THz pulses of the planned FLUTE experiment. Thus, the coherent Raman experiment can provide spectral information complementary to absorption measurements using the THz radiation of FLUTE.

INTRODUCTION

Weak interactions such as hydrogen bonding or van-der Waals forces are fundamental for the structuring and functioning of biological systems [1]. As these forces act between macromolecules like proteins or nucleic acids, the corresponding dynamics takes place at picosecond (ps) time scales. Hence, THz spectroscopy is a natural choice when the investigation of such dynamics is desired as one THz cycle corresponds to a time scale of one ps.

At the KIT, the new linear accelerator FLUTE (Ferninfrarot Linac- Und Test-Experiment, (engl.) far infrared linac- and test-experiment) will provide intense THz pulses, which can be utilized for non-linear THz spectroscopy or THz time-domain spectroscopy (TDS) of biomolecules. In this regard, Raman scattering spectroscopy is a complementary method, which can provide additional information.

Here, we set up an experiment measuring the imaginary part of the third-order susceptibility of aqueous samples in the THz range with non-linear Raman scattering. In 2014, this experiment was carried out, for the first time, at the Research Center for Development of Far-Infrared Region at the University of Fukui [2].

The implementation at the FLUTE accelerator has several advantages: It will be shown below that the frequency range of vibrations, that can be addressed with our experiment, overlaps well with the emission spectrum of FLUTE. Due to the utilized method, the experiment does not require any notch filter (as in standard Raman experiments), although spectral information in the frequency range below 1 THz can be recorded. Moreover, when a pulsed gun laser is already in place, the experiment, which combines an stretcher with an interferometer, can be set up with standard optics.

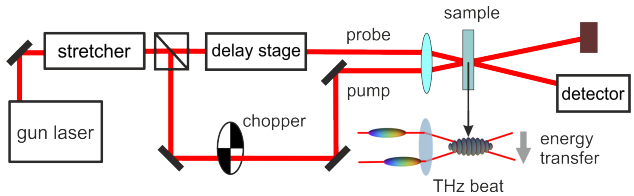

Figure 1: Schematic drawing of the stimulated Raman scattering setup with the FLUTE gun laser.

EXPERIMENT

Figure 1 displays a schematic drawing of our experiment. The setup enables to measure the imaginary part of the sample's third-order susceptibility by inverse Raman scattering (IRS) or stimulated Raman gain scattering (SRG). The used FLUTE gun laser, a Coherent Astrella USP-1K-HP, consists mainly of an oscillator, a stretcher/compressor, and a regenerative amplifier emitting around 800 nm wavelength [3]. The amplifier delivers a train of laser pulses with a repetition rate of 1 kHz at an energy of 6 mJ per pulse. Initially, the Fourier-transform limited pulses exhibit a time duration of about 35 fs.

For the experiment, we stretched every pulse to a few ps by adjusting the internal compressor of the gun laser. In other similar experiments the pulse stretching was simply achieved by sending the laser pulses through dispersive glass elements [4–6]. The stretching process causes a chirp of the laser pulse, so that the photon frequency shows a linear time dependence. After the stretching, the beam passes an interferometer, where the beam is initially split by a thin beam splitter into a pump and a probe beam. The pump beam is modulated with a chopper synchronized to the regenerative amplifier, so that every second pulse passes. A delay stage

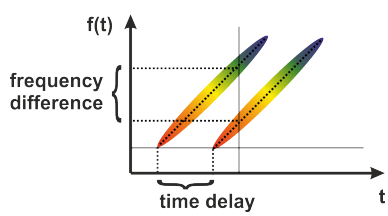

Figure 2: Visualization of the dependence of the frequency difference with respect to the chirp and the time delay.

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inserted into the beam path of the probe beam allows the fine tuning of the timing between both interferometer arms.

To induce the non-linear Raman scattering process the pump and probe pulses are spatially overlapped at the sample position via a focusing lens. Due to the linear chirp, the difference of the photon frequencies between both pulses is constant during the time when both pulses are present (see Fig. 2). As a consequence, energy is transferred between the pump and the probe beam, according to the magnitude of the imaginary part of the third order susceptibility at the difference frequency [2, 7]. This energy transfer can be interpreted as stimulated Raman gain scattering and inverse Raman scattering depending on which laser pulse is considered. At zero time delay the direction of this energy transfer is inverted [2]. Due to the chopper at the pump arm, which blocks every second pulse, the energy transfer is repeatedly turned on and off. The corresponding signal modulation of the probe pulses is measured with a Si photodiode detector connected to a lock-in amplifier (we use the 500 Hz signal from the chopper as a reference).

RESULTS

Figure 3 displays in red the average of five Raman scattering measurements of dimethyl sulfoxide (DMSO). DMSO is a non-toxic solvent with strong Raman bands in the THz range [8]. For our measurements we used a cuvette with 10 mm path length. The long path length leads to a strong interaction between the pump and probe beam and thus to an increase in the signal strength.

In the experiment, the dependence of the Raman scattering intensity with the time delay between the two interferometer arms is recorded. At zero time delay, which corresponds to 0 THz, the transfer of the energy is inverted so that the inverse Raman scattering and Raman gain scattering spectrum can be measured within a single scan.
To convert the time delay into a frequency axis, either a substance with well-known Raman bands or measurements of the laser pulse autocorrelation together with their spectrum can be used [2]. Here, we omitted this step by fitting the data to a spectrum of DMSO adapted from reference [9], which is also shown in Fig. 3. We used negative frequencies to display the inverse Raman scattering spectrum. After the fit, the results of both experiments coincide well over the measured range proofing that the spectral features of DMSO could be detected with our experiment.

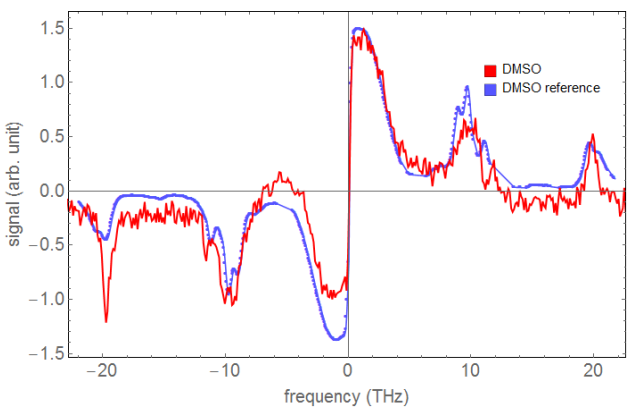

Figure 3: Non-linear Raman scattering measurements of DMSO with the experiment implemented at FLUTE (red) compared to data adapted from reference [9] (blue).

Furthermore, the results show that the experiment is sensitive at least in a spectral range between 1 THz up to 20 THz (the FWHM of the inverse Raman scattering peak at -20 THz can be estimated to be around 0.82 THz by fitting a normal distribution to the peak). This covers in particular frequencies around 3 THz, where the FLUTE emission spectrum is initially expected to deliver the highest spectral intensity [10].

After these initial experiments with the laser of the FLUTE facility, there are further possibilities to improve the signal-to-noise to reach similar values as shown in reference [9]. First, a better alignment of pump and probe beam can be achieved, which will remove the slight asymmetry of the spectrum with respect to the inversion point at 0 THz (see [2] for discussion about the symmetry). Second, slight deviations between the weighting of the peaks in both measurements, probably due to unequal changes of the polarization in both interferometer arms, can be observed. Nevertheless, we could reproduce the main results from [9].

SUMMARY AND OUTLOOK

We measured the inverse Raman scattering and stimulated Raman gain scattering with DMSO using the FLUTE gun laser. By comparing our measurements to [9], we validated our experiment. In future, the high spectral intensity of FLUTE provides us with the opportunity to combine THz excitation experiments with Raman measurements (for example THz-pump, Raman probe). Implementing single-shot detection systems, which are available at KIT, this technique might be also useful in wideband THz spectroscopy of plasma in plasma accelerators.

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