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2D-Raman-THz Spectroscopy with Single-Shot THz Detection

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We present a 2D-Raman-THz setup with multichannel (single-shot) THz detection, utilizing two crossed echelons, in order to reduce the acquisition time of typical 2D-Raman-THz experiments from days to a few hours. This speed-up is obtained in combination with a high repetition rate (100 kHz) Yb-based femtosecond laser system and a correspondingly fast array detector. The wavelength of the Yb-laser (1030 nm) is advantageous, since it assures almost perfect phase matching in GaP for THz generation and detection, and since dispersion in the transmissive echelons is minimal. 2D-Raman-THz test measurements on liquid bromoform (CHBr_3) are reported. An enhancement of ~ 5.8 times in signal-to-noise ratio is obtained for single-shot detection when comparing to conventional step scanning measurements in the THz time-domain, corresponding to speed up of acquisition time of ~ 34 .

I. INTRODUCTION

Liquids exhibit a manifold of low-energy excitations in the terahertz (THz) frequency range and the thermally excited modes ($\hbar\omega \lesssim k_B T = 200 \text{ cm}^{-1}$) of the molecular systems are directly observed in this spectral region. However, one-dimensional spectra in the THz region are very blurred due to the fast dynamics of the intermolecular modes and the structural complexity of liquids. To disentangle these one-dimensional spectra, multidimensional spectroscopies are desired. We refer to “2D spectroscopy” as a multi-pulse experiment with two experimentally controllable time delays between incident laser pulses, controlling two coherence times of the molecular system, according to which Fourier-transformation may be performed to reveal a 2D spectrum. 2D spectroscopy has first been reported for nuclear magnetic resonance (NMR)¹ and subsequently implemented in the infrared (IR) to study vibrational excitations and in the visible (VIS) spectral range for electronic and vibronic transitions.^{2–5}

Compared to the well-established 2D IR and 2D electronic spectroscopy, the methodology and applications of the 2D spectroscopy in the THz spectral range are still in the early days. However, the field has recently seen rapid development.^{6–9} Techniques that have been applied until now to study the low-frequency mode of liquids (water, aqueous solutions as well as CHBr_3 , CCl_4 and CBr_2Cl_2) are hybrid methods, i.e., 2D THz-Raman,^{10–12} THz-infrared-visible,¹³ and 2D-Raman-THz spectroscopy.^{9,14–16} 2D-THz spectroscopy, with all laser pulse in the THz range, has so far been restricted to solids as well as gases.^{17–25}

In any case, these THz multidimensional methods are time-domain techniques, and their implementation requires multiple mechanical delay stages to time the various laser pulses. Since very many time-points need to be collected to acquire a 2D data set, the total acquisition time can be very long, days up to weeks,^{7,14–16,18,26} which severely limits the applicability of the method. Multichannel detection of at least one spectroscopic dimension

is nowadays standard in 2D electronic and 2D IR spectroscopy, significantly speeding up the acquisition time. Most commonly, multichannel detection is achieved by spectrally dispersing the emitted field and detecting different frequency components in parallel, thereby performing one of the Fourier transformations optically. Due to the long wavelength, multichannel detection in the frequency domain will be very difficult, if not impossible, in the THz spectral range.

On the other hand, multichannel (single-shot) detection of THz pulses in the time-domain has realized with the help of echelons, generating many beamlets for the detection by electro-optic sampling that are delayed with respect to each other in time.^{26–28} In the present paper, we combine this technique with a 100 kHz laser system, further speeding up data acquisition. Finally, the laser system runs at 1030 nm, which is almost perfect for phase matching of THz generation and detection in GaP.²⁹ We will show that these measures together can reduce the acquisition time of high-quality 2D-Raman THz spectra from days to just a few hours.

II. EXPERIMENTAL SETUP

A. 2D-Raman-THz Implementation

The 2D-Raman-THz setup is shown in Figure 1, which is run by a Yb-doped fiber laser/amplifier system (short-pulse Tangerine, Amplitude) with repetition rate 100 kHz and pulse energy 220 μJ . Directly after the output of the main laser, the 1030 nm radiation is split. The majority ($\sim 200 \mu\text{J}$) diverges into an optical parametric amplifier (OPA, Twin STARZZ, Fastlite), delivering 900 nm non-resonant Raman pump pulses with pulse duration of 70 fs. A 50 kHz chopper (310CD, Scitec Instruments Ltd) is used for background subtraction and/or referencing. To pass the small slits of the chopper, the beam is focused and re-collimated with two 10 cm lenses (L5 and L6 in Figure 1). A fast-scanning, electromagnetically driven stage (DS1, V-408, Physik Instrumente), which

FIG. 1. 2D-Raman-THz experimental setup. Brewster windows (BW), step scanning stage (DS2), fast scanning motor (DS1), polarizer (P), polarizing beam splitter cube (PBC), gallium phosphate crystal (GaP), echelons (Es), optical parametric amplifier (OPA). L1=0.6 cm, L2=10 cm, L3=25 cm, L4=30 cm, L5=10 cm, L6=10 cm, L7=50 cm, L8=30 cm, L9=-10 cm, L10=-10 cm. The dashed boxes show the two possible positions for the chopper, as described in the text.

constantly moves in a triangular manner at a repetition rate of 2 Hz, delays the Raman pump-pulses before focusing them into the sample with a 50 cm lens (L7). The pulse energy at the sample is $\sim 5 \mu\text{J}$.

The smaller fraction ($\sim 14 \mu\text{J}$) of the Yb-laser is split yet another time for THz generation by optical rectification ($\sim 6 \mu\text{J}$) and for detection by electro-optical sampling ($\sim 8 \mu\text{J}$). In both cases, we use a 200 μm GaP crystal (MolTech) instead of 100 μm in our previous works,^{14–16} which became possible since the 1030 nm from the Yb-laser is almost perfectly phase-matched in GaP, in contrast to 800 nm from a Ti:sapphire laser system.²⁹ GaP is the preferred crystal for 2D-Raman-THz spectroscopy, since it reveals the cleanest THz pulses ranging up to ~ 7 THz without any ringing. The thicker crystal enhances the THz signal size 2.5 times.

The generation pulses are focused into the GaP crystal with a 30 cm lens (L4). The generated THz pulses are imaged with two custom-made elliptical mirrors¹⁴ first into the sample in spatial overlap with the Raman pump pulse (both $\sim 250 \mu\text{m}$ in diameter), and then into the detection crystal for electro-optical sampling.

The detection pulses are delayed with respect to the THz generation pulses with a motorized step-scanning delay line DS2 (M-405.DG, Physik Instrumente). Their beam diameter at the output of the Yb-laser is ~ 3 mm. They are magnified 16 times with a telescope consisting of L1 (-0.6 cm) and L2 (10 cm) before encountering the two custom-made transmissive echelons with open aperture $15 \times 15 \text{ mm}^2$. The beam size after the expansion would be ~ 48 mm; however, the diameter of L2 is only 1". Therefore, only the center of the Gaussian beam passes through the echelons. The loss due to the expansion, collimation and transmission through the echelons is $\sim 90\%$ of the initial energy, resulting in $\sim 0.8 \mu\text{J}$ at the detection crystal with a fairly equally distributed energy

FIG. 2. a) Vertically and b) horizontally mounted echelons. The thickness of the thinnest glass piece and the increments are indicated. c) Crossed echelons mounted to generate a six by six mask of beamlets delayed by 44 fs. The detected pixels are shown in light-red.

across the area of the echelons.

Figure 2 shows the design of the echelons. They are constructed of six pieces of BK7 glass $20 \times 2.5 \text{ mm}^2$ each with properly adjusted thicknesses (custom made by EMATAG AG). To that end, a larger substrate has first been polished down to the required thickness, and only then cut into the size of each glass piece, guaranteeing that the two faces, across which the detection beam is transmitted, are plane-parallel with the same quality as the original substrate (20"). Relatively wide (2.5 mm) glass pieces were chosen for easy handling. The six glass pieces are pressed together with an Al-mount, leaving an open aperture of $15 \times 15 \text{ mm}^2$.

The two echelons are placed in sequence and rotated 90° with respect to each other. Figure 2a shows the vertical echelon with step sizes of $\Delta d_2 = 0.150 \pm 0.002 \text{ mm}$ (for the most part, see below), starting with $2.000 \pm 0.002 \text{ mm}$ for the thinnest glass piece. The horizontal echelon has step sizes of $\Delta d = 0.025 \pm 0.002 \text{ mm}$ (Figure 2b). Both echelons together generate a six-by-six mask of beamlets, as displayed in Figure 2c. We, however, found that preserving the quadratic shape downstream from the echelons can be challenging when circular optics such as lenses are used. To resemble the circular shape of the optics, we decided to discard the four beamlets in the corners of the square and to detect only thirty-two THz waveforms (those colored in light red in Figure 2c). To that end, the step size of the first and the last glass pieces in the vertical echelon was reduced to $\Delta d_1 = 0.125 \pm 0.002 \text{ mm}$ (Figure 2c). The totally covered time range is 1.4 ps in steps of 44 fs.

We decided for transmissive^{26,30} instead of the more commonly used reflective echelons.^{28,31–33} The latter are typically CNC (computerized numerical control) machined single pieces of metal. However, we found that it was impossible to produce optically flat steps of the required size in that way. Furthermore, the requirement on the accuracy of the step heights is reduced by a factor ~ 4 , as the time step is $(n-1)\Delta d/c$ (where $n \sim 1.5$ is the index of reflection of the glass) for a transmissive echelon versus $2\Delta d/c$ for a reflective echelon. One argument against transmissive echelons, a dispersion that changes with each step, is negligible here since we aim only for

a relatively small time-range (1.4 ps) and since the dispersion at 1030 nm is small (another advantage of the Yb-laser). It appears feasible to scale up this concept to around twice the number of glass pieces, each of which would have been narrower, resulting in ~ 120 time points, which should be sufficient for most applications.

Electro-optic (EO) sampling in GaP is implemented to detect the broadband THz waveforms in the time domain.³⁴ The detection beam with its 32 beamlets is focused into the crystal with a 25 cm lens (L3), and its polarisation is cleaned just before the detection crystal with a polariser, depicted as P in Figure 1. The beam is subsequently re-collimated with a 30 cm lens (L8) before entering a set of three ZnSe Brewster windows (BW, 70 mm dia, 2.0 ± 0.1 mm thick from Crystal Ltd) for signal enhancement, and a 2" quarter-wave plate and 2" polarising beam cube for balanced detection.³⁵ The Brewster windows transmit the s-component without loss but reflect a large portion of the p-component, thereby increasing the ellipticity of the polarization of the detection beam and thus the detected THz signal, albeit at the expense of reducing pulse energy.³⁶ The beam after L8 (18×18 mm²) is small enough to pass these optics without clipping. Finally, to adjust the detection beams to the size of the array-detector (30×30 mm²), they are further expanded with two negative lenses (L9, L10, -10 cm).

The home-built photo-detector consists of two 32 pixel arrays of Si-photodiodes, which are arranged spatially to match the shape of the beamlets in the detection beam. The Si-photodiodes (VEMD5080X01, Vishay) have been selected based on their electronic response time, the fact that they are enhanced towards the near IR (1030 nm is at the edge of the spectral range of Si-photodiodes), and the ratio between active area versus footprint on the PCB to maximize the amount of detected light. The photodiode signals are amplified and AD-converted in parallel with an electronics that is similar to that described in Ref. 37. The electronics read the 64 signals at a 100 kHz repetition rate and transfers the data to a computer via an USB 2.0 interface. It also transfers the chopper state as well as a position signal of the fast scanning delay stage DS1 needed to properly sort the data.

In electro-optical sampling with balance detection, the signal is typically calculated as differences:

$$Signal = (I_{2,ON} - I_{1,ON}) - (I_{2,OFF} - I_{1,OFF}), \quad (1)$$

where I_1 and I_2 are the intensities detected by the two photodiodes (whose difference is typically determined in an analog fashion in a balanced detector), and *ON* and *OFF* the two states of the chopper. With this approach, however, the signal size would scale linearly with pulse energy on each pixel (which is not perfectly uniform) and also with the quality of the spatial overlap of each beamlet with the THz beam in the detection signal (see below). Instead, we calculate the signal as follows:³⁸

$$Signal = \frac{I_{1,OFF} \cdot I_{2,ON}}{I_{1,ON} \cdot I_{2,OFF}} - 1 \quad (2)$$

FIG. 3. a) Thirty-two THz waveforms used to generate the single-shot THz signal. b) Picture of the detection beam taken just before the focus in the detection crystal. c) Peak of the THz waveforms as a function of pixel. d) Four subsequent multichannel THz waveforms are shown in blue, which have been measured with two single laser shots for the two states of the chopper, and which are compared to a waveform measured with a single-pixel and by scanning DS2 (in red). The boxes enlarge the single-shot waveforms around the peaks.

which normalizes out these effects, as discussed in the following. The linearized version Eq. 2 holds if the ellipticity of the polarization is small; in Ref. 26 a generalized equation is given for larger ellipticities.

B. Optimization of Single Shot THz Detection

Figure 3a shows the 32 THz waveforms measured with all pixels and scanning delay stage DS2 at the same time. To achieve this quality of data, we found that it is helpful to monitor the shape of the beam just before the detection crystal and to align the optics for a regular shape as shown in Figure 3b. While the various THz waveforms are very much the same, the amplitudes vary by a significant factor of 3, as shown in Figure 3c. We assume this modulation to be due to the fact that the beamlets are overlapped in the detection crystal with the THz pulse in slightly different ways. It is interesting to note that

FIG. 4. Signal-to-noise ratio of multichannel THz waveform measured with two laser shots for the two states of the chopper as function of the detector counts.

the modulation of the peak intensities has a periodicity of 6, reflecting the periodicity of the 2D array (Figure 2). When initially planning the setup, we decided on two crossed echelons with a square-shape of each beamlet, anticipating that this would make imaging easier and more uniform. That didn't come entirely true. A recent work by Blake and coworkers used a 1D echelon,²⁸ in which case each beamlet deviates very strongly from a square-shape. It might still be that imaging issues lead to a non-uniform signal size also in this case, but the effect is less obvious since the modulation is not periodic.

The blue lines in Figure 3d show a sequence of multichannel THz waveforms taken as a cut through the data set of Figure 3a for delay stage DS2 set to 0 ps. Each waveform is acquired with two laser shots only for the two states of the chopper, i.e., within 20 μ s, demonstrating the excellent stability of the signal. The signal-to-noise ratio (SNR) of such a multi-channel, single-shot THz waveform is ~ 60 . Furthermore, the single-shot waveforms are compared with the one shown in red, which has been obtained with a single pixel and by scanning DS2, revealing an excellent agreement.

The waveforms in Figure 3a have been calculated with Eq. 2, and the chopper moved into the THz generation branch (lower dashed box in Figure 1) In this case, the different detection pulse energies of the pixels are normalized out, and the chopper takes care of the misbalance between related pixels in the two arrays. However, the different overlaps of the THz beam and the beamlets in the detection crystal are not normalized out, leading to the observed variation of peak intensities (Figure 3c). For the 2D-Raman-THz experiment discussed below, the chopper has been moved into the Raman-pump branch (upper dashed box in Figure 1), in which case Eq. 2 normalizes twice, and the double-difference signal will not be affected by the modulation of the intensity of the THz signal.

Since the detection pulse energy is split among 32 beamlets, and due to the intentionally lossy transmission through the echelons, the pulse energy on every single Si-diode is low (10's of pJ), and it has been adjusted such that the intrinsic noise of the photo-detector is not lim-

FIG. 5. 2D-Raman-THz signal of CHBr_3 in time domain acquired with a) single-shot technique and b) step-scanning delay line DS2. Delay time t_1 refers to the Raman time, delay time t_2 to the THz time. The color scale is defined on the right side with the signal given in ppm (parts-per-million) relative to the peak THz signal.

iting for the overall noise. To that end, Figure 4 shows the SNR calculated for the multichannel THz waveform acquired at different detector counts, where the pulse energy was adjusted with a neutral density filter positioned just before DS2 (Figure 1). We calculated the SNR as the ratio between the peak-to-peak signal of the THz waveform vs its standard deviation (the noise is also indicated by the four waveforms shown in Fig. 3d as blue lines). Based on these results, we typically work with ~ 10000 - 30000 detector counts, where the SNR reaches a plateau since the detector noise is no longer limiting. To reach this amount of detector counts, we had to reduce the number of Brewster windows from four in Ref. 36 to three here. The THz signal enhancement then is ~ 9 times compared to measurement without ZnSe Brewster windows, while the corresponding factor has been ~ 18 with the four Brewster windows in Ref. 36.

III. PERFORMANCE DEMONSTRATION: 2D-RAMAN-THz SPECTROSCOPY

To demonstrate the performance of the setup, we consider the 2D-Raman-THz spectroscopy of liquid bromoform (CHBr_3), which we have investigated before.^{15,16} In order to quantify the enhancement in SNR, data acquisition is carried out in two operational configurations for the same amount of total measurement time of 2 h. In the first operational mode, the data are acquired through single-shot THz detection and in the second operational mode, the THz detection is delayed with respect to the generation beam by step-scanning delay line DS2 from -700 to 700 fs in steps of 44 fs and considering only the central pixel of the array detector. In either case, the Raman pump is delayed by fast-scanning delay line DS1.

Figure 5 shows the results in the time domain. The signal size is about the same as in our previous

FIG. 6. 2D-Raman-THz signal of CHBr_3 in frequency domain acquired with a) single-shot technique and b) step-scanning delay line DS2. Frequency f_1 refers to the Raman time, frequency f_2 to the THz time. Both non-rephasing ($f_1 > 0$) and rephasing ($f_1 < 0$) quadrants are shown.

experiments,^{15,16} with a spike around time zero and oscillatory contribution towards positive Raman times. The latter is only visible in the single-shot data (Figure 5a). The SNR was retrieved as the peak-to-peak intensity of the data around time zero, divided by the standard deviation of the data at negative Raman delay times, from -1.5 ps to -100 fs. This analysis reveals that the SNR improves by a factor of 5.8 upon single-shot detection. As the measurement time is expected to scale quadratically with the SNR, this enhancement factor ($5.8^2 = 34$) almost perfectly reflects the fact that 32 pixels are measured simultaneously in single-shot detection.

Finally, Figure 6a shows the the 2D magnitude spectrum obtained by Fourier-transformation of the data in Figure 5a from 700 fs onwards (to suppress the spike around time-zero), revealing a cross peak in the non-rephasing quadrant between an intra-molecular mode of CHBr_3 at $f_1=6.7$ THz and intermolecular degrees of freedom of the liquid.^{15,16} The corresponding data measured with a single pixel (Figure 6b) are too noisy to show any sign of that cross peak. It is worth noting that we have observed another cross peak with $f_1=4.7$ THz in Ref. 16, which doesn't show up with the current laser system, regardless with one performs the experiment with the single shot technique, or, by step-scanning.¹⁵ We assume that this difference is due to the different pulse characteristics of the THz pulses (single-cycle pulse here vs half-cycle pulse in Ref. 16), an effect that will have to be explored in future work.

IV. DISCUSSION AND CONCLUSION

We present a novel 2D-Raman-Terahertz spectrometer that combines a high repetition rate (100 kHz) Yb-laser system with single-shot THz detection and a 100 kHz array detector. The wavelength of that laser, 1030 nm, is advantageous for the phase-matching in the GaP generation and detection crystal, as well as due to the lower dispersion in the echelon. Measurements on CHBr_3 demonstrate that good quality 2D-Raman THz data can be acquired within only a few hours of measurement time. We have investigated the same sample with about equal quality in previous publications.^{15,16} In Ref. 16, that was done with a 5 kHz Ti:sapphire laser system, and in Ref. 15 with the same Yb-laser system as here, albeit running at 10 kHz. In either case, the THz time delay was scanned, and the response was measured with a single balanced photodiode. As compared to these previous works, one might naively expect a speed-up of 20×32 or 10×32 , respectively, where the first factor accounts for a higher repetition rate of the present setup and the second factor for the multichannel detection. We don't quite achieve that factor; when comparing with this previous experiment, the speed-up is "only" a factor of 10-20.

First, there are always trade-offs that one has to accept for multichannel detection. For example, since the pulse energy per pixel is much lower due to the splitting of the detection beam into 32 beamlets, we had to reduce the number of Brewster windows by one. More importantly, such estimates are based on the assumption that noise is uncorrelated, both in time as well as across the multichannel detector. That is not necessarily the case. For example, the speed-up of measurement time does not necessarily parallel the repetition rate since the noise of femtosecond lasers often has long (1 s) correlation times. On the other hand, the comparison in Figure 5, which has been performed with precisely the same optical layout by just switching the mode of operation, in fact, reveals the theoretical speed-up factor of 32, indicating that we do not gain from the correlation between pixels. Finally, from experience, we know that the performance of such complex instruments improves over time due to many small optimization steps during daily usage. Significantly longer optimisation time went into the experimental setups of Refs. 15 and 16 than into the present one. We can currently not disentangle these effects but stress that a speed-up by a factor of 10-20 is still very significant. It reduces the measurement time of good-quality 2D-Raman-THz spectra from days to hours. We are confident that this speed-up will greatly facilitate the wider applicability of THz multidimensional spectroscopies.

Data Availability Statement: The data used in this article have been deposited on Zenodo (the link will be added at the proof stage). Upon a reasonable request, the array detector and the measurement electronics will be made available to academic institutions in the form

of a kit at cost price.

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