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Liu, Jinjun; Schmutz, Hansjürg; Merkt, Frédéric

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Generation of widely tunable Fourier-transform-limited terahertz pulses using narrowband near-infrared laser radiation

Jinjun Liu, Hansjürg Schmutz, and Frédéric Merkt*

Laboratorium für Physikalische Chemie,

ETH-Zürich, 8093 Zürich, Switzerland

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Abstract

Widely tunable, Fourier-transform-limited pulses of terahertz (THz) radiation have been generated using (i) crystals of the highly nonlinear organic salt 4-*N,N*-dimethylamino-4'-*N'*-methylstilbazolium tosylate (DAST), (ii) zinc telluride (ZnTe) crystals, (iii) gallium phosphide (GaP) crystals, and (iv) low-temperature-grown gallium arsenide (LTG-GaAs) photomixers with THz spiral antennas. Outputs from two narrowband ($\Delta\nu < 1$ MHz, $\lambda \sim 800$ nm) cw titanium-doped sapphire (Ti:Sa) ring lasers with a well-controlled frequency difference were shaped into pulses using acousto-optic modulators (AOM), coupled into an optical fiber, pulse amplified in Nd:YAG-pumped Ti:Sa crystals and used as optical sources to pump the THz emitters. The THz radiation was detected over a broad frequency range and its bandwidth was determined to be ~ 10 MHz. The spectroscopic potential of the THz source is illustrated by the absorption spectrum of a pure rotational transition of OCS.

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*Electronic address: merkt@xuv.phys.chem.ethz.ch

I. INTRODUCTION

Terahertz (THz) radiation, which lies in the frequency gap between microwave and infrared radiation and is loosely defined by the frequency range $10^{11} - 10^{13}$ Hz, has recently found applications in imaging, spectroscopy, and material and biomedical analysis (see, for example, Refs. [1–5] and references therein). Although there have been significant advances in recent years, the use of THz radiation remains more limited than that of its neighboring bands in the electromagnetic spectrum, primarily because of difficulties associated with its generation and detection.

As a result of the limited availability of THz radiation sources, only little information is known to spectroscopists in this frequency range. Table-top sources of THz radiation are particularly attractive for use in experiments with supersonic beams and involving multiply resonant excitation schemes. Particularly desired would be narrowband tunable sources to study low-frequency vibrations of polyatomic molecules and molecular clusters, and the rotational motion of small molecules (see, for instance, Refs. [6–11] and references therein), and in the identification of possible molecular carriers of astrophysical spectra, for which there is considerable current interest in the context of the new observational facilities ALMA [12] and Herschel [13].

In recent years several techniques have been developed to obtain spectroscopic data in the THz range. Whereas Fourier-transform spectroscopy is well suited to study the upper part of the THz range [14], backward-wave oscillator (BWO) based sources are attractive in the region up to 2 THz [9, 15–18]. Quantum cascade lasers appear to be the most promising sources in the THz range but are still in the development stage [19–21]. The use

of synchrotron radiation in combination with Fourier-transformation interferometers [22] and of free electron lasers [23] appears very promising but requires large-scale facilities. Broadly tunable coherent THz radiation can also be generated from visible or near-infrared (NIR) laser sources by difference-frequency generation (DFG) in nonlinear crystals and by photomixing in photoconductive materials, which represent the methods used in the present work.

The organic crystalline salt 4-*N,N*-dimethylamino-4'-*N'*-methyl stilbazolium tosylate (DAST) possesses very high nonlinear susceptibilities and electro-optic coefficients, which makes it one of the best nonlinear materials for THz generation and detection up to date [24]. THz radiation has so far been generated in DAST by optical rectification (OR) of a single fs laser pulse [25, 26] and by DFG using two ns laser pulses [27–31]. By DFG of two ns laser pulses from a dual-wavelength optical parametric oscillator (OPO) with two potassium titanyl phosphate (KTP) crystals (1300-1800 nm, pulse energy 21 mJ, pulse duration ~ 10 ns, repetition rate 10 Hz), continuously tunable radiation over a wide frequency range (0.3-30 THz) with pulse energies up to 2.4 μ J (at 27 THz) has been demonstrated by Suizu *et al.* [29, 30]. The bandwidth of the THz pulses so generated, however, was limited by the bandwidth of the OPO lasers (~ 70 GHz). Recently we reported DFG of widely tunable, pulsed, Fourier-transform-limited THz radiation (bandwidth ~ 10 MHz, peak power on the order of 100 μ W, up to a frequency of 11 THz limited only by the detection method) from pulse-amplified NIR ($\lambda \sim 800$ nm) laser radiation using a DAST crystal that was cut to fulfill the phase-matching condition [31]. In the present paper, we report the experimental details of the THz source and, for comparison, the generation of THz radiation using an as-grown

(*c*-cut) DAST crystal.

Other nonlinear optical crystals than DAST can be used as THz emitters, and many such crystals have already been tested experimentally. One important category of THz crystals consists of semiconductors, such as zinc telluride (ZnTe) and gallium phosphide (GaP). Ref. [32] gives a comprehensive theoretical analysis of THz generation by DFG in semiconductor crystals.

Photoconductive antennas represent a further important class of THz emitters. First used by Brown *et al.* in 1995 to generate radiation up to 5 THz [33, 34], low-temperature-grown gallium arsenide (LTG-GaAs) has been so far the most frequently used of all photoconductive materials. Mouret *et al.* reported narrow-bandwidth radiation up to 3 THz generated by mixing two cw Ti:Sa laser beams using a LTG-GaAs photomixer vertically integrated in the middle of THz spiral antennas [35–37].

Following our previous paper [31], we describe here a technique to generate widely tunable Fourier-transform-limited nanosecond THz pulses using several THz emitters, including nonlinear crystals of DAST, ZnTe and GaP, and LTG-GaAs photomixers. The laser-based source relies on the use of Fourier-transform-limited NIR pulses of programmable shape and length [38–40]. Its narrow bandwidth, high absolute frequency accuracy, and tunability through the entire THz range make it a promising radiation source for THz spectroscopy. The emphasis of this article is placed on the characterization of these properties and on a comparison of the THz emitters listed above.

II. EXPERIMENTAL SETUP

The experimental setup used for the generation of THz radiation and its detection is displayed schematically in Fig. 1. THz radiation was produced by DFG of two amplified narrow-bandwidth laser pulses in nonlinear optical crystals and by photomixing of the laser pulses using photoconductive antennas. The laser system, consisting of two Fourier-transform-limited pulse-amplified NIR lasers, has been described in previous publications [38–40] and only slight modifications have been introduced for the present investigation. Two Ti:Sa ring lasers (Coherent, 899-29 and 899-21, output power 300~400 mW), both pumped by diode-pumped, frequency-doubled Nd:YVO₄ lasers (Coherent, Verdi, 532 nm, output power 5 W) and both operated near 800 nm, were used to provide single-mode narrow-bandwidth ($\Delta\nu < 1$ MHz) cw radiation. Through combinations of a Fresnel rhomb and a polarization beamsplitter, the outputs from both ring lasers were split into two components, one of which was used for frequency calibration and/or frequency stabilization, the other for THz generation. The frequency of the first laser (899-29) was tuned and calibrated, while that of the second laser (899-21) remained locked. The Doppler-free saturation absorption spectrum of molecular iodine in a 75-cm-long cell heated to 900 K [41, 42] was used for the calibration of the absolute frequency of the first laser (899-29), while a confocal Fabry-Pérot (FP) étalon (free spectral range, FSR=161.653(3) MHz and finesse=10) was used for the relative frequency calibration. The frequencies of the hyperfine components of the I₂ transitions were determined with an accuracy of better than 100 kHz by comparing with positions measured using a frequency comb [42] in a separate measurement. The FSR of the étalon was determined using two such I₂ lines. The frequency stabilization of the

second, fixed-frequency laser (899-21) was achieved by dithering the laser frequency around, and locking it to, the transmission maximum of another FP étalon (FSR=149.966(3) MHz, also determined using the I_2 lines, and finesse=30) by adjusting the driving voltage controlling the position of a Brewster plate placed inside the laser cavity using a home-built proportional-integrator-derivative (PID) controller. The FP étalon itself was locked to a polarization-stabilized He-Ne laser (SIOS Messtechnik GmbH, SL-02/1). The output from the He-Ne laser was dithered by an acousto-optic modulator (AOM, Brimrose, GPF-1000-500-800), sent through the FP étalon and monitored by a photodiode. A correction signal was then sent to a piezoelectric transducer (PZT) mounted on one of the two mirrors of the FP étalon to lock the étalon to the transmission maximum of the He-Ne laser using another PID controller. The frequency stability of the 899-21 laser was estimated as the half width at half maximum (HWHM) of the FP étalon fringes (~ 2.5 MHz) over one day. The absolute frequency of the lock position was measured by a wavemeter (Burleigh, WA-1500) with an accuracy of 75 MHz.

The other component of the cw radiation from each of the two ring lasers was sent to an AOM where pulses of adjustable duration and programmable shape were generated at a repetition rate of 25 Hz using an arbitrary waveform generator (Agilent, AWG-33250A). For the present experiment, the pulse shape was chosen to be a square function of 150 ns duration. The first-order sidebands of both laser beams, coming out of the AOMs with a 1 GHz frequency shift, were combined using a 50% beamsplitter and coupled into a single-mode polarization-maintaining optical fiber, which improved the mode matching and spatial overlap between the two lasers required for optimal THz generation. The temporal overlap

of the two lasers was achieved using delay generators (Stanford Research DG535). The radiation pulses exiting the optical fiber had a peak power of ~ 20 mW. These pulses were guided into a nine-pass Ti:Sa amplifier consisting of a Ti:Sa crystal, pumped at a repetition rate of 25 Hz by the second harmonic output of a Nd:YAG laser (Quanta Ray, Pro270, 532 nm, pulse energy 200 mJ, pulse duration 10 ns). Each pass gave an amplification factor of about 3. Another six-pass amplifier, pumped by the same Nd:YAG laser (pulse energy 200 mJ), was used when higher pulse energies were needed. The maximum pulse energy of the final output was ~ 40 mJ, i.e., 20 mJ for each NIR frequency component. A Fresnel rhomb and an optical isolator were inserted between the optical fiber and the first amplifier as well as after the two amplifiers to prevent back reflections and to suppress amplified spontaneous emission (ASE). Similar techniques to generate narrow-band NIR laser pulses in Ti:Sa amplifiers have been described in Refs. [43, 44].

To determine the bandwidth of the amplified laser pulses, a small fraction of the amplified laser beam was reflected toward a fast photodiode (Alphas, UPD-200-SP) by a beamsplitter and the signal was sent to a digital oscilloscope (LeCroy, Waverunner 6050, bandwidth 500 MHz). The frequency difference between the two cw ring lasers was set within the bandwidth of the oscilloscope so that a beat-note signal between the two amplified NIR pulses could be monitored. Fourier transformation of the beat-note signal indicated that the bandwidth of each frequency component was ~ 10 MHz for pulses of 150 ns duration. The frequency of the THz radiation corresponds exactly to the frequency difference between the two cw ring lasers ($f_{THz} = |f_{cw1} - f_{cw2}|$) because the frequency chirps occurring in the amplification are negligible [38] and the frequency shifts are identical for the two frequency components and

hence cancel out in the THz generation. For the same reason the frequency shifts introduced by the pulse generation in the two AOMs (1 GHz) also cancel out. The THz radiation has therefore the same absolute and relative frequency accuracy as the frequency difference between the two ring lasers.

The narrow-bandwidth NIR pulses were then sent to the THz emitters. Nonlinear optical crystals of DAST, ZnTe and GaP and LTG-GaAs photoconductive antennas were used. When the crystals were used, a 0.5 mm black ultra-high molecular weight (UHMW) polyethylene plate was placed immediately after the crystals to filter out the NIR radiation. The THz radiation was then collected by two gold-coated off-axis parabolic mirrors and detected by a 4.2 K germanium bolometer (IRLabs). Because of the far infrared cut-on filter of the detector only radiation of frequencies lower than 11 THz could be detected. When the photoconductive antennas were used, a hyperhemispherical silicon lens was attached to the back side of the antenna chips to prevent the total internal reflection of the THz radiation and to collimate the emitted THz beam [35–37]. Only one parabolic mirror was used to focus the THz radiation onto the detector.

III. MEASUREMENT OF THE THZ PEAK POWERS

A. DAST crystals

In the present work, an as-grown (*c*-cut) DAST crystal (Rainbow Photonics) of dimensions $a \times b \times c = 3.6 \text{ mm} \times 2.4 \text{ mm} \times 340 \text{ }\mu\text{m}$ was used. The crystal was pumped by the amplified NIR pulses in a collinear, normal-incident configuration and without focusing (beam size ~ 3

mm). Polarization vector of the NIR radiation was aligned along the a -axis of the crystal. The damage threshold at a wavelength of 800 nm was determined to be ~ 3 MW/cm² using a test crystal and 150 ns long laser pulses. A dark deposit appeared inside the crystal above this threshold, indicative of bulk damage.

Fig. 2 illustrates the quadratic dependence of the THz peak power ($\nu \sim 0.3$ THz) on the NIR input peak power expected for a second-order nonlinear process, which also implies that the DFG is not saturated. The THz peak power detected between 0.1 and 5.5 THz is displayed as a function of frequency in Fig. 3a. The peak power of the NIR pump beams was ~ 16 kW, which corresponds to a power density of ~ 0.23 MW/cm², i.e., about one order of magnitude lower than the damage threshold. The uncertainty in the THz peak power measurement was estimated to be 10% of the absolute value. It was determined from the output voltage of the bolometer using its specified responsivity (30 kV/W) without taking into account the absorption of the 0.5 mm black polyethylene filter, which increases from zero to about 90% from 0 to 11 THz, the absorption of the THz cut-on filter of the detector ($\sim 30\%$) and the absorption of the vacuum window of the dewar ($\sim 30\%$). Dividing the measured output powers by the transmission curves of these materials given in the manual of the bolometer and in Ref. [45] leads to the normalized THz peak power displayed in Fig. 3b. The normalized THz peak power is about 10 times smaller than indicated by our simulations [46] based on the reported optical and THz properties of the DAST crystal [24, 26, 47–50] and the well-known formula for the output power of difference-frequency generation [51, 52]. The same observation was made for the normalized THz peak powers generated in the crystals of ZnTe and GaP (see Section IIIB). This suggests that the peak

power of the generated THz radiation is actually 10 times larger than the detected THz radiation normalized by the transmission of the filters. We attribute this factor to the absorption efficiency of the diamond substrate of the bolometer and the acceptance of the detector [53]. The numerous sharp dips in Figs. 3a and 3b are absorption lines of water vapor in the air. The broader dips at 1.1 THz and 3.2 THz are attributed to absorptions by the crystal itself [26, 48].

Fig. 3b illustrates the relatively low conversion efficiency (10^{-8} - 10^{-7} taking into account the detection efficiency) compared with that of the dual-frequency OPO experiments (10^5 - 10^{-4}) [27–30]. Beyond 4 THz, the peak power stays at $\sim 40 \mu\text{W}$. Both features can be explained by the fact that the phase-matching condition cannot be achieved under the present experimental conditions (as-grown crystal, collinear pump beams with $\sim 800 \text{ nm}$ wavelength). Recently, we used a DAST crystal that was especially cut to fulfill the phase-matching condition [31] and the generated THz radiation was detected up to 11 THz. The experimentally measured THz peak power using the cut DAST and the peak power normalized by the transmission of the filters are compared in Figs. 3c and 3d. In the higher-frequency part of the THz range ($> 7 \text{ THz}$), the peak power can be further increased by a factor of ~ 10 by adjusting the angle of incidence and thus the phase matching (full squares in Fig. 3d). This adjustment is necessary because the phase-matching angle between the NIR beams and the optical axis varies with THz frequency. In most of the scanned range, the maximum peak power that can be obtained using the cut DAST crystal is more than 10 times larger than using the as-grown DAST crystal. Because the phase-matching condition can be fulfilled using the cut DAST crystal, longer crystals may be used to generate larger THz radiation

intensity as long as the crystal absorption is small, an assumption that requires future investigations. In the region above 11 THz, our simulations suggest a continuous increase of the THz peak power [46]. The cut DAST crystal is therefore superior to the as-grown crystal in generating THz radiation.

B. ZnTe and GaP crystals

ZnTe (Ingcrys, $\langle 110 \rangle$ orientation, 10 mm $\times$ 10 mm $\times$ 1 mm) and GaP (Ingcrys, $\langle 110 \rangle$ orientation, 10 mm $\times$ 10 mm $\times$ 0.4 mm) have also been tested as nonlinear media for the generation of THz radiation by DFG using a collinear, normal-incident pump configuration and without focusing the NIR radiation. The damage threshold of ZnTe and GaP (surface damage for both) was measured to be ~ 1 MW/cm 2 and ~ 5 MW/cm 2 , respectively. In the present experiments, they were pumped by 0.23 MW/cm 2 and 0.85 MW/cm 2 NIR peak powers, respectively. The measured THz peak powers and those corrected by the transmission losses of the filters are shown in Figs. 3e-h. The normalized peak powers are again about ten times smaller than predicted by our simulations [46], in which the optical and THz properties of the crystals from Refs. [54–57] for ZnTe and Refs. [58–61] for GaP were used. No radiation was detected beyond ~ 3 THz using ZnTe and ~ 8 THz using GaP, respectively, which is consistent with our predictions. As an example, the measured and the calculated THz peak powers generated using ZnTe, the properties of which were best determined in the literature [54–57], are compared in Fig. 4. The THz frequency ranges that can be generated by DFG using ZnTe and GaP are narrower than using the cut DAST crystal and the peak powers of the THz radiation are lower. The broad dips in the GaP traces at 3.4 THz and

5.6 THz are attributed to a phase mismatch [46].

C. LTG-GaAs photomixers

Similar LTG-GaAs photomixers as used in Refs. [35–37] (Institut d’Electronique, de Microélectronique et de Nanotechnologie, Université des Sciences et Technologies de Lille) were employed to generate THz radiation using pulsed NIR radiation. The amplified narrow-bandwidth NIR laser pulses with their wavelength both near ~ 800 nm were focused onto the photomixer by a lens (focal length $f=200$ mm). The polarization of the NIR laser beams was set perpendicular to the fingers of the photomixer to optimize the generation of THz radiation. Fig. 5 displays the peak power of the THz radiation generated at a frequency of 0.3 THz as a function of the bias voltage applied to the antenna when pumped with NIR pulses of ~ 0.4 MW/cm² peak power and the current-voltage relationship measured under the same experimental conditions. The measured peak power (~ 70 μ W) is two orders of magnitude higher than the average power obtained in the previous experiment using two cw Ti:Sa lasers as pump sources [37]. The breakdown voltage has been determined to be ~ 30 V, corresponding, for an LTG-GaAs layer of 1 μ m, to a breakdown field of $\sim 3 \times 10^5$ V/cm. Increasing the pump power above ~ 0.4 MW/cm² did not lead to a significant increase of the power of the THz radiation, probably because of saturation. Burns on the antennas were observed when pulses of >1 MW/cm² NIR peak power were used, presumably caused by optical heating. Since the maximum THz radiation is limited by the damage threshold, increasing the active area of the photomixer and/or cooling the photomixer would therefore undoubtedly enable the generation of more intense THz radiation. However, the generation of

THz radiation by photomixing remains limited to the range below ~ 3 THz by the properties of the charge carriers in the photoconductive materials as shown in Refs. [35–37].

IV. MEASUREMENT OF THE BANDWIDTH OF THE THZ SOURCE

The bandwidth of the THz pulses has been determined in two different experiments. In both experiments, radiation at a frequency of 0.3 THz was generated by an as-grown DAST crystal. The reason for choosing such a low frequency was that the measurement of the frequency spectrum of the pulse can be made using heterodyne techniques at 0.3 THz. Although these experiments were carried out at the lower frequency end of the THz range, the measured bandwidth is expected not to increase at higher THz frequencies because it is determined by the characteristics of the NIR pump pulses. The THz pulses were measured using a Schottky diode harmonic mixer [62] that extends the measurement frequency range into the submillimeter-wave region. Local oscillation was generated by a spectrum analyzer (Rohde & Schwarz, FSEK30) and sent to the harmonic mixer. The output of the mixer itself was calibrated using an absolute power meter (Thomas Keating) via a millimeter-wave synthesizer (Analytik & Messtechnik, AM-MSY3) used as a transfer standard. In the first experiment, the THz peak power was monitored while sweeping the center frequency of the spectrum analyzer around a preset frequency difference of the two ring lasers, with bandwidth and step size both set at 1 MHz. The intermediate frequency from the harmonic mixer resulting from the local oscillation and the THz radiation was sent back to, and monitored by, the spectrum analyzer. This measurement, illustrated in Fig. 6, gave a full width half maximum (FWHM) of ~ 10 MHz. In the second experiment, the THz radiation

was downconverted with the harmonic mixer to an intermediate frequency (f_{IF}) of 159 MHz. Local oscillation (f_{LO}) with negligible bandwidth was provided by the spectrum analyzer, and the intermediate frequency was recorded on an 500 MHz bandwidth digital oscilloscope. Fig. 7a shows the downconverted signal with center frequency $f_{IF} = f_{THz} - f_{LO} = 159$ MHz. The FWHM was determined to be ~ 10 MHz by Fourier transformation (Fig. 7b), in good agreement with the result of the first experiment (see Fig. 6).

V. ABSORPTION SPECTRUM OF A PURE ROTATIONAL TRANSITION OF OCS

In order to illustrate the potential of the new source of THz radiation for spectroscopic investigations, the absorption spectrum of a pure rotational transition ($J' = 35 \leftarrow J'' = 34$) of OCS at $\nu = 425481.2135(200)$ MHz [63] was recorded. A 1-m-long sample cell with white UHMW polyethylene windows was filled with OCS at a pressure of 0.5 mbar and placed between the two parabolic mirrors. To reduce the noise originating from the pulse-to-pulse fluctuations of the pump source, a small fraction of the pulse-amplified NIR radiation was reflected by a beamsplitter before the DAST crystal and its intensity was monitored with a photodiode. The THz radiation was then normalized to the square of the NIR power at each laser shot. An example of the measured spectra as a function of the frequency of the tunable ring laser is displayed in Fig. 8, along with the calibration traces. Fig. 8a shows the measured THz peak power. The spectrum is noisy because of the large fluctuations of the NIR radiation from the Ti:Sa amplifier. Fig. 8b shows the normalized THz peak power. Comparison between Fig. 8a and Fig. 8b clearly demonstrates the quadratic dependence

of the DFG process on the input NIR power and the effectiveness of the normalization to reduce the noise level of the spectrum. No measures were taken to eliminate the étalon effect that is noticeable in Fig. 8b. This effect usually disappears in the higher-frequency region.

The spectra were linearized using the transmission signal through the FP étalon by cubic spline interpolation and then calibrated using the a_1 hyperfine component of the P84, $\tilde{B} - \tilde{X}(0-15)$ rovibronic transition of I_2 , the frequency of which was previously determined with an accuracy of 20 kHz [64]. The frequency of the THz radiation corresponds to the difference between the frequencies of the tunable ring laser (899-29) and the frequency-locked ring laser (899-21). The frequency of the latter was measured by the wavemeter to an accuracy of 75 MHz. Several measured spectra with different lock positions of the 899-21 ring laser were calibrated independently. Compared with the reference value $\nu = 425481.2135(200)$ MHz [63], the frequency errors were found to always be smaller than 75 MHz, limited by the accuracy of the NIR wavemeter. Currently, we are building another Doppler-free saturation absorption spectrograph, which will be used to lock the frequency of the 899-21 ring laser to a selected line of the hyperfine-resolved Doppler-free I_2 spectrum. Given the accurately known frequencies of the iodine transitions and the FSRs of the étalons, this new setup is expected to enable a frequency accuracy of better than 10 MHz.

The normalized THz peak power was converted to absorbance using Beer's law ($\alpha = \ln(I_0/I_T)$), where I_0 is the empty cell transmission intensity and I_T the transmitted intensity, as displayed in Fig. 9. The spectral linewidth (FWHM) of the rotational line is about 10 MHz. The pressure broadening coefficient of this transition (given in HWHM) was previously reported to be $b=4.33(15)$ MHz/mbar [65], which leads to a pressure broadening (FWHM) of

4.33(15) MHz for the present measurement, a minor contribution to the measured linewidth. The Doppler broadening of this transition of OCS at room temperature is negligible. The upper limit of the bandwidth of the THz source is therefore about 9 MHz. This is consistent with the heterodyne bandwidth measurement presented in Section IV.

VI. CONCLUSIONS

Widely tunable Fourier-transform-limited THz radiation pulses have been generated using pulse-amplified NIR laser beams from two narrowband Ti:Sa ring lasers using both nonlinear optical crystals (DAST, ZnTe, GaP) and LTG-GaAs photomixers as THz emitters. The advantages of the present laser system for the generation of THz radiation lie in the optimal combination of (i) the narrow spectral bandwidth (~ 10 MHz) that results from the Fourier-transform-limited nature of the NIR laser pulses, (ii) the high intensity of the pulse-amplified NIR radiation which is a prerequisite for the efficient driving of nonlinear optical processes, (iii) the facile tunability over a wide frequency range made possible by the fact that the THz radiation frequency is scanned by tuning the frequency of one of the NIR lasers, (iv) the high frequency accuracy based on the frequency calibration of the NIR lasers, and (v) the effective suppression of the noise introduced by the fluctuation of the NIR radiation by normalizing the THz radiation to the square of the NIR radiation. These advantages make this technique suitable for future applications in gas-phase spectroscopy, as demonstrated in a proof-of-principle experiment on OCS and also in a similar measurement on HF at 4.9 THz [31]. The main limitation of the present method is the damage threshold of the THz emitters.

Given its large nonlinear susceptibilities and its applicability over a wide frequency range when it is cut to fulfill the phase-matching condition [31], DAST appears to be the most promising material for the generation of THz radiation by DFG using NIR lasers. Limited by the scarcity of experimental data on the THz properties of the DAST crystal, especially along the b - and c -axes, the optimal length for the cut DAST crystal cannot be predicted in the present work. Future experimental investigations are therefore greatly desired.

More economical and more versatile versions of the present experimental setup can be realized by replacing one (or both) of the ring lasers by fixed-frequency (and tunable) diode lasers. The two AOMs can be removed if controlling of the pulse shape is not required. (The ring lasers and AOMs were used in the present work because they were available in our lab and are required for other experiments using the same apparatus.) NIR sources with broader bandwidth can be used, for instant, for THz spectroscopy of the liquid or solid phase, in which only moderate resolution is required. If only the frequency range below 8 THz need to be covered, GaP crystals, which are cheaper than DAST crystals, are also good candidates for THz generation.

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Figure Captions

1. Experimental setup for the generation and detection of THz radiation. FR = Fresnel rhomb, PBS = polarization beamsplitter, AOM = acousto-optic modulator, M = mirror, BS = beamsplitter, OF = optical fiber, OI = optical isolator, PE = polyethylene, PD = photodiode. Only one Ti:Sa amplifier is shown in the graph although two were used whenever pulse energies of more than 1 mJ were needed.
2. Peak power of the THz radiation generated by DFG in a DAST crystal as a function of NIR peak power. The dotted line represents a least-squares fit assuming a quadratic relationship.
3. (Color on line) Measured THz peak powers generated using as nonlinear media (a) an as-grown DAST crystal, (c) a DAST crystal cut to fulfill the phase-matching condition, (e) a ZnTe crystal, and (g) a GaP crystal. The corresponding peak powers, normalized by the transmission of the filters (see text), are shown in panels (b), (d), (f) and (h), respectively. In (c) and (d), the peak powers obtained for three different configurations are displayed: normal-incident NIR pump beam with polarization perpendicular to the b -axis (narrow solid line), normal-incident NIR pump beam with polarization parallel to the b -axis (bold solid line), and NIR pump beam with optimal angle of incidence and polarization parallel to the b -axis (full squares) [31]. The actual peak powers are estimated to be 10 times larger (see text).
4. (a) Measured THz peak power generated using a ZnTe crystal and normalized by the transmission of the filters, (b) calculated THz peak power (see text). The vertical

scales of (a) and (b) differ by a factor of 10 because of the limited absorption efficiency of the diamond substrate of the bolometer and the acceptance of the detector (see text). The sharp lines in panel (a) are water absorption lines whereas those in panel (b) result from phase mismatch.

5. (a) THz peak power generated with LTG-GaAs antennas as a function of bias voltage when pumped with 150 ns long NIR radiation pulses of 0.4 MW/cm² peak power. The dotted line represents a least-squares fit assuming a quadratic relationship. (b) Current-voltage relationship of LTG-GaAs antenna under same conditions. The dotted line represents a linear fit.
6. Measured THz peak power as a function of the center frequency of the spectrum analyzer relative to the reference frequency (0.3 THz). The bandpass of the spectrum analyzer was set to 1 MHz.
7. (a) THz signal measured after frequency downconversion using a harmonic mixer. The down-converted signal was recorded on a digital oscilloscope with center frequency at $f_{IF} = f_{THz} - f_{LO} = 159$ MHz. (b) Frequency spectrum of the down-converted THz signal determined by Fourier transformation.
8. Spectrum showing the pure rotational transition ($J' = 35 \leftarrow J'' = 34$) of OCS as a function of the tunable ring laser wave number along with the étalon and I₂ calibration traces. The position of the a_1 hyperfine component of the P84, $\tilde{B} - \tilde{X}(0-15)$ rovibronic transition of I₂ was determined to be at 377914083.12(2) MHz using a frequency comb [64].

9. Absorbance as a function of the relative frequency for the pure rotational transition ($J' = 35 \leftarrow J'' = 34$) of OCS shown in Fig. 8. The center frequency is 425481.2135(200) MHz [63]. The linewidth (FWHM) is ~ 10 MHz.

FIG. 1: Experimental setup for the generation and detection of THz radiation. FR = Fresnel rhomb, PBS = polarization beamsplitter, AOM = acousto-optic modulator, M = mirror, BS = beamsplitter, OF = optical fiber, OI = optical isolator, PE = polyethylene, PD = photodiode. Only one Ti:Sa amplifier is shown in the graph although two were used whenever pulse energies of more than 1 mJ were needed.

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FIG. 4: (a) Measured THz peak power generated using a ZnTe crystal and normalized by the transmission of the filters, (b) calculated THz peak power (see text). The vertical scales of (a) and (b) differ by a factor of 10 because of the limited absorption efficiency of the diamond substrate of the bolometer and the acceptance of the detector (see text). The sharp lines in panel (a) are water absorption lines whereas those in panel (b) result from phase mismatch.

FIG. 5: (a) THz peak power generated with LTG-GaAs antennas as a function of bias voltage when pumped with 150 ns long NIR radiation pulses of $0.4 \text{ MW}/\text{cm}^2$ peak power. The dotted line represents a least-squares fit assuming a quadratic relationship. (b) Current-voltage relationship of LTG-GaAs antenna under same conditions. The dotted line represents a linear fit.

FIG. 6: Measured THz peak power as a function of the center frequency of the spectrum analyzer relative to the reference frequency (0.3 THz). The bandpass of the spectrum analyzer was set to 1 MHz.

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FIG. 9: Absorbance as a function of the relative frequency for the pure rotational transition ($J' = 35 \leftarrow J'' = 34$) of OCS shown in Fig. 8. The center frequency is 425481.2135(200) MHz [63]. The linewidth (FWHM) is ~ 10 MHz.