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An intense tunable femtosecond gas-plasma THz source: Application in spectroscopic studies of polycyclic aromatic hydrocarbons

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ABSTRACT

We present a review on the emission of intense THz pulses from 2-color femtosecond laser filaments in gases. Through the tailoring of the filamentation process tuning of the emitted THz pulses is possible and is described in details. Using these THz pulses as a spectroscopic tool, the absorption spectra of small polycyclic aromatic hydrocarbons and their halogenated compounds are studied. Distinct resonance features for all the examined compounds have been observed, demonstrating the potential of the approach for rapidly discriminating the molecular structure of large organic molecules, in their crystalline form.

1. Introduction

The far-infrared region of the electromagnetic spectrum ranging from 0.1 to 10 THz, known as terahertz (THz) radiation, has become the last years an extremely attractive research field for scientists from various disciplines, including chemistry [1], metamaterials science [2], biology [3] and medicine [4]. The THz spectrum provides rich information of low frequency vibrational modes such as crystalline lattice or inter-molecular vibrational modes, hydrogen bonding stretches, and large-scale motions of an entire macromolecule or motions of particular subunits which occur on a sub-picosecond to tens of picosecond time scales. All these low lying frequencies are essential for several physical and chemical processes and their position and strength are highly sensitive to small conformational changes of a molecule and its environment.

The continuously increasing interest of studying physical/chemical phenomena, not accessible before, in this low frequency spectral regime, has been stimulated in the recent years thanks to tremendous technological development in photonics and materials science, which enabled the development of coherent sources and detectors operating in the THz region. Nowadays, numerous techniques such as photoconductive antennas [5] and optical rectification [6] have become standards and are now widely employed in various laboratories around the world, making the so-called "THz gap" routinely accessible. In addition, using techniques like the electro-optic sampling [7,8] or the photoconductive sampling [5], it is possible to coherently detect in the time domain the generated THz pulses, giving a direct access to the amplitude and more importantly the phase of the electric field.

In our days, one important line of research within the THz community is the increase of the intensity of the source that opens the way to the nonlinear THz science. Most techniques, even though popular, suffer from a lack of peak power. The energy per pulse is relatively small, usually barely reaching the nano-joule regime. In the last decade, three new techniques have successfully been introduced to scale up the strength of the THz pulse energy, the 2-color produced gas-plasmas, the tilt-pulse-front rectification, and the difference-frequency mixing [9–11]. All of them are based on the use of amplified lasers and can be easily implemented as table-top sources. The aim of this review paper is to introduce in details the attributes of the 2-color femtosecond filament plasma based THz source and its versatility through the tailoring of the plasma string. In addition, in the last part, in order to illustrate the capacity of our technique and its sensitivity to study small changes of the molecular structure, we will present various spectroscopy data of the halogenations of polycyclic aromatic hydrocarbon (PAHs) and some of their halogenated compounds.

2. Experimental approach

The formation of femtosecond plasma strings can be described as a self-action process, in which an intense ultrashort laser pulse undergoes strong spatial and temporal reshaping as it propagates in a transparent medium. It results in the propagation of the beam with a very narrow waist that remains almost constant over many Rayleigh lengths, leaving ionized channels in its wake. This phe-

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nomenon, known as filamentation, appears for input powers above a critical value, P_{cr}, and is the result of a competition involving linear and highly nonlinear effects, such as the optical Kerr effect, defocusing due to plasma created by optical field ionization, nonlinear losses, dispersion, and others [12]. In the last decade, filaments have been widely used for various applications spanning from single-cycle pulse generation for attosecond drivers [13,14], electric discharge triggering and guiding [15], as well as Light Detection and Ranging Techniques (LIDAR) for remote sensing of pollutants [16] and remote Laser Induced Breakdown Spectroscopy (LIBS) [17].

The use of filamentation for the emission of intense THz pulses started a decade ago with the approach presented by Cook and Hochstrasser [9], which consists of introducing a frequency doubling crystal (BBO, β-barium borate) prior to the formation of the plasma string. After long debates on the theoretical explanation of the generation of THz emission under this scheme it is now well accepted in the community that the emission of THz pulses from a 2-color filament is the result of a transversal photocurrent. In a simplified view one can describe the process like this: after the electrons get liberated at a certain velocity via the ionization process, they experience a drift from the remaining part of the laser electric field, which leads to a separation of charge in the transverse plane and the creation of a photocurrent. The presence of a slight ellipticity in the laser beam combined with the presence of the second harmonic field allows the projection of the photocurrent in any direction within the transverse plane. A direct consequence is that the technique offers a control on the polarization of the emitted THz pulse via the phase between the fundamental and its second harmonic. Different possibilities have been demonstrated in order to control the phase between ω and 2ω, either via the positioning of the frequency doubling crystal [18], or through the use of an attosecond phase controller [19] or via the accurate control of the surrounding gas pressure [20]. In the latter study, the plasma length has also been shown to play an important role on the control of the polarization, as we will discuss later. It is important to note that another approach has also been proposed to induce a net current in the plasma string using an external static DC bias field, of a few tens of kilovolts, at the vicinity of the plasma string [21]. Also in a recent publication was shown that both techniques, 2-color and DC bias, can be combined and that the total emission can be interpreted as the sum of both contributions [22].

Our THz-TDS system is based on a pump–probe, coherent detection approach and is shown in Fig. 1. A powerful amplified kHz Ti:Sa laser system delivering 35 fs pulses at 800 nm central wavelength and energy of 1.45 mJ per pulse is used. The initial beam is split in two arms (10% and 90% respectively). The most intense one, with energy equal to 1.3 mJ and a Gaussian beam profile with a diameter of 6.6 mm, is focused in ambient air with a positive lens of 200 mm focal length and partially doubled in frequency in a BBO crystal (50 μm thick) to produce a 2-color filament and subsequently, THz radiation. We have identified an optimum ratio of 1/9 between the fundamental and the second harmonic laser fields, above and below which the strength of the emitted THz field is considerably lower. The second arm, after being further attenuated is used for probing the THz-induced birefringence in an electro-optic crystal and monitoring the time profile of the THz electric field. This coherent detection technique, known as electro-optic sampling, is based on the well-known Pockel effect and is well documented [7,8]. A balanced detection is used to measure the induced phase delay on the probe beam. For the collection, collimation and refocusing the generated THz beam to the detection crystal, a set of four parabolic mirrors is used, as depicted in Fig. 1. Finally, a high resistivity silicon wafer (1 mm thick) placed at Brewster's angle just after the first parabolic mirror, insures that the residual laser beam is blocked from the THz beam path. The whole setup is enclosed in a purged gas (e.g. N_2) chamber for eliminating THz absorption from water vapor [23].

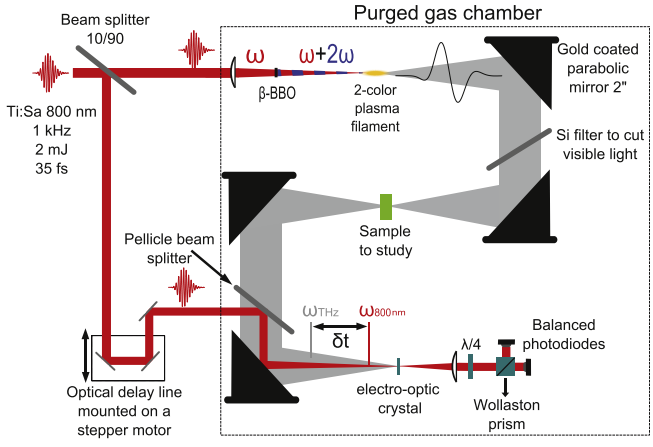

Fig. 1. Schematic representation of the experimental set-up.

3. System performances and tunability

Using the THz setup described above, we measured the electric field emitted from the 2-color filament. The measured THz electric field with the electro-optic setup depends on the crystal used for the detection. Two examples are shown in Fig. 2a, where the same emitted signal has been recorded with a thick ZnTe crystal (1 mm) and a thin GaP crystal (100 μm). The recorded electric field will inherently depend on the crystal thickness (phase matching between the two pulses) and the presence of longitudinal optical (LO) phonon modes which will burn holes in the broad spectrum. In the case of GaP, which is thinner and has a LO phonon mode at 11 THz compared to the 6.17 THz LO phonon of ZnTe, the recorded electric field is much shorter and in turn exhibits a larger frequency band. On the other hand, the electro-optic coefficient of ZnTe is bigger and since the crystal is thicker a signal with higher signal to noise ratio is recorded as one can see in Fig. 2a where both recorded signals using the two different crystals are plotted on the same scale. By applying a Fourier transform to these electric fields, one obtains the spectral distribution of the pulse (Fig. 2b). As one can see, the detected THz pulse duration clearly depends on the measurement technique. Recently, a new approach has been developed based on the cross term mixing within a second plasma string [24], which demonstrates the possibility to measure frequency components up to 30 THz from a 2-color plasma based source, similar to the one discussed here.

An estimation of the THz peak electric field can be directly deduced from the time domain trace, the measured energy and the estimation of the focused beam diameter [25]. Using a commercially available THz-sensitive pyroelectric detector, we have measured the THz pulse energy to be 80 nJ for an input laser pulse energy of 1.3 mJ. In order to measure the diameter of our focused THz beam, a knife edge technique is used where a razor blade is scanning across the focused THz beam and the respective THz power is measured by the aid of the pyroelectric detector. For a Gaussian-like beam profile, the extracted full width half maximum (FWHM) is equal to 205 μm and a $1/e^2$ diameter equal to 435 μm. This size corresponds to a diffraction limited spot for a THz beam at 1.7 THz, which is in good agreement with the THz spectra presented above. Using the time trace measured with the thin GaP crystal (Fig. 2b) and the full bandwidth measurement of the energy, the THz electric field is estimated to be equal to 200 kV/cm.