THz SPECTROSCOPY FOR FUNDAMENTAL SCIENCE AND APPLICATIONS

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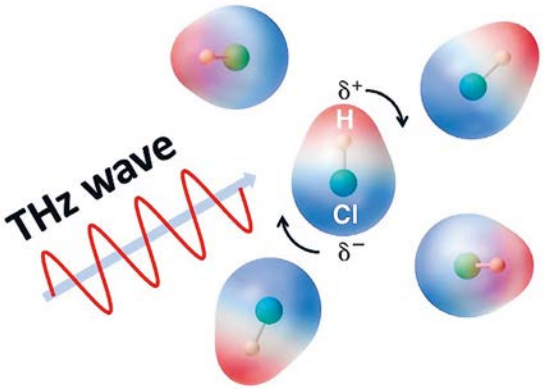

Many elementary process in matter, such as the interaction of electrons, spins and phonons as well as rotational modes of molecules possess resonances frequencies in the THz spectral range (1 THz = 10^{12} Hz) and dynamics on (sub)-picosecond time scales. Therefore, THz spectroscopy has become an exciting technique for probing and characterizing a variety of low-energy physical phenomena [1], which makes it very attractive for a wide range of disciplines including physics, chemistry, astronomy, and medicine.

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THz SPECTROSCOPY EXPERIMENTS

THz spectroscopy is based on the interaction between the electromagnetic field and the electric or magnetic dipoles contained in matter. These interactions with matter affect the propagation of THz waves, which yield a spectral signature that permits to identify matter and to understand its properties (Fig. 1). The majority of THz spectroscopy systems can be divided into three types: time-domain, frequency-domain systems and interferometric techniques.

TIME-DOMAIN SPECTROSCOPY

THz time-domain spectroscopy (THz-TDS) measures the time-resolved electric fields of THz radiation propagating through a medium and compared to a reference beam. These systems are based on ultrafast optical lasers that provide a set of femtosecond (fs) pulses centered around 800 nm. The pulse train is split in two optical beams (Fig. 1a). One optical beam is focused onto a photoconductive antenna or a nonlinear crystal (the THz emitter). The optical excitation gives rise to transient current or optical rectification that results in the emission of THz pulses. The emitted THz pulses are focused by paraboloidal mirrors onto the sample and then onto a THz detector. The second optical beam passes through a delay line (that modifies the path length) and is also focused onto the THz detector that synchronously probes the transient THz electric field. The detector is usually a photoconductive antenna or an electro-optic crystal. By delaying the timing of the optical probe pulse to the optical pulse which drives the THz emitter, • • •

the temporal waveform of the THz pulse incident on the detector is recorded with fs resolution (Fig. 1b). Both the amplitude and the phase of the THz radiation are obtained by a Fourier transform (Fig. 1c). The complex refractive index of the sample under investigation (*i.e.* the absorption and the dispersion) is then directly obtained without requiring the use of Kramers-Kronig relation [2].

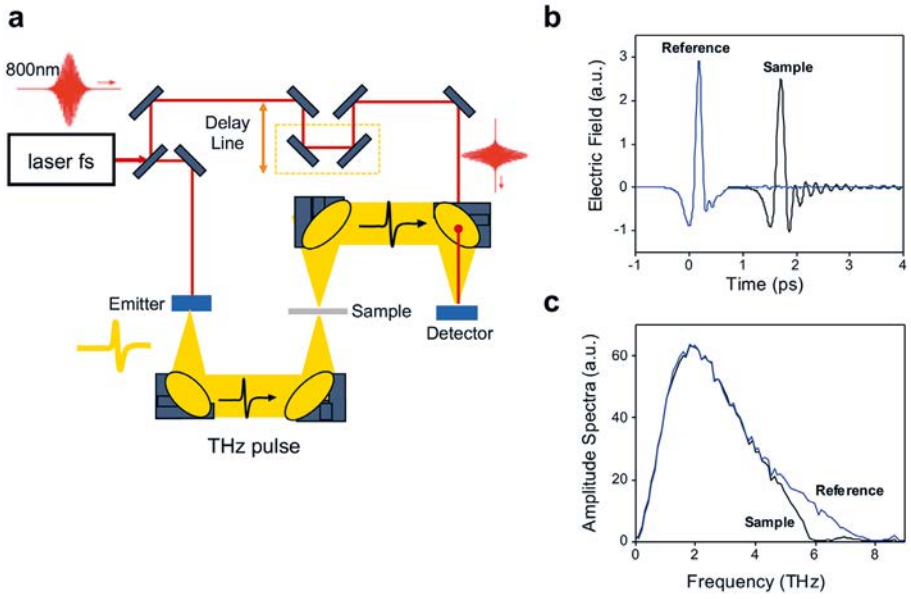
Starting from this basic spectroscopic technique and exploiting its time-gated coherent nature, a set of dynamical spectroscopy experimental techniques can be implemented in pump-probe configuration, multidimensional THz spectroscopy and THz emission spectroscopy. Special set-ups were also designed to allow the measurement of small quantities of material which is useful for biosamples [3].

FREQUENCY-DOMAIN SPECTROSCOPY

In contrast to THz-TDS, frequency-domain THz spectroscopy systems do not require fs lasers but they are based on continuous-wave (CW) lasers. The CW photomixing THz spectroscopy technique relies on superimposing two continuous optical laser beams on an ultrafast photodetector for the generation of CW THz waves. The two lasers are tuned to two different wavelengths, then a beat appears at the frequency equal to the difference between the two laser frequencies. This beat is easily tunable between zero and several THz by tuning one of the lasers. The photocurrent follows the variation of the laser light intensity induced by this beat and flows in a broadband antenna which radiates a CW THz beam in free space. This photomixing technique can be used also for the detection of the beam with the same kind of device thanks to a homodyne setup. CW THz-TDS systems are usually less complex and less expensive than a typical THz-TDS setup and are used to perform high resolution broadband THz spectroscopy (the spectral resolution can be of the order of 1 MHz or less). It is well suited for narrow spectral features in gas-phase spectroscopy, but is also used for the spectroscopy of solid or liquid samples in amplitude and phase thanks to the homodyne setup [4].

The photocurrent follows the variation of the laser light intensity induced by this beat and flows in a broadband antenna which radiates a CW THz beam in free space. This photomixing technique can be used also for the detection of the beam with the same kind of device thanks to a homodyne setup.

Figure 1.
(a) Schematic illustration of a THz-TDS system showing the fs laser excitation source, optical delay line, THz source, THz detector and THz coupling optics. (b) Time-domain scans of a THz pulse with and without a sample of Teflon. The sample delays, disperses, and attenuates the pulse. (c) Amplitude spectra of the reference and the sample pulse calculated by Fourier transform.



More recently, THz Quantum Cascade Lasers (QCLs) have been used as powerful sources for THz spectroscopy systems. THz QCLs are compact semiconductor sources exploiting III-V quantum wells for direct laser action in the THz range [5]. Laser action arises from transitions between engineered electronic sub-bands and by 'cascading' a number of such active regions together. THz QCLs have shown remarkable performances over the 1–5 THz range, with demonstration of high peak (> 1 W) and (> 10 s of mW) average powers. These advances have permitted THz QCLs to be made commercially available, with operation recently demonstrated on Peltier coolers. QCLs are particularly interesting for astronomy where their large output powers, tunable emission and compact geometry are particularly advantageous compared to bulky CO_2-pumped gas lasers. Future developments related to QCL based spectroscopy will take advantage of recently demonstrated mode-locked QCLs where ultrafast, coherent and sensitive detection is expected using dual frequency comb spectroscopy.

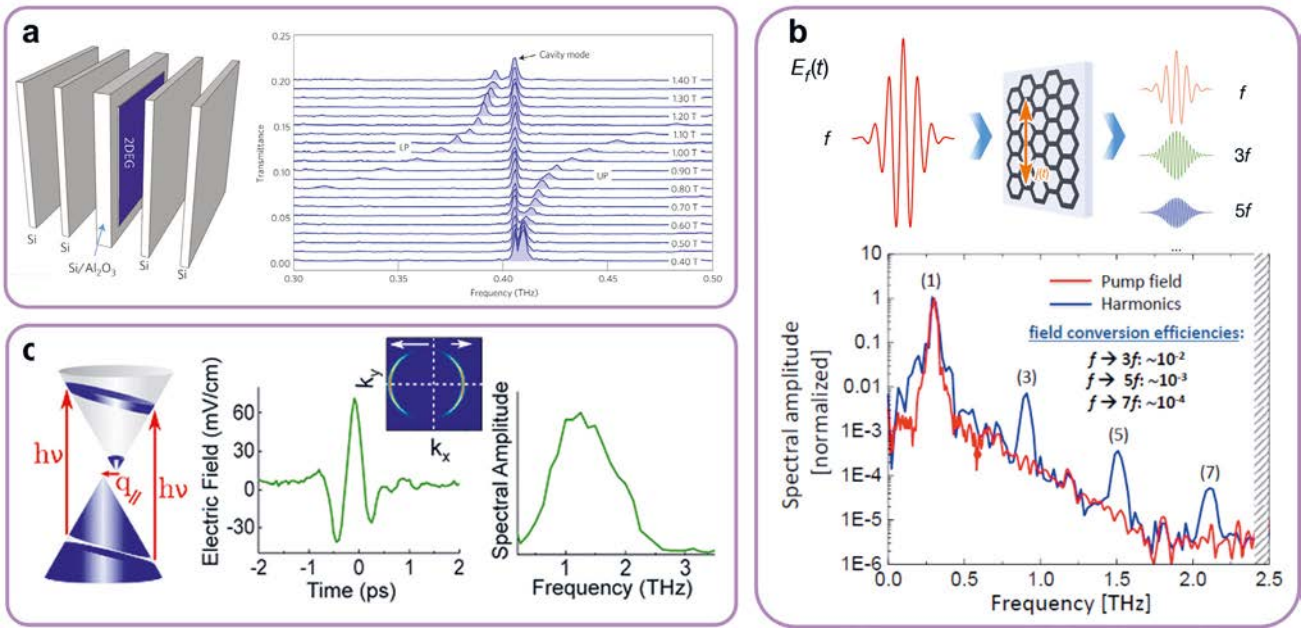


Figure 2. (a) (left) Collective non-perturbative coupling of 2D electrons gas with high-quality-factor THz cavity, from Ref [6]. (b) Extremely efficient THz high-harmonic generation in graphene by hot Dirac fermions, from Ref [7]. (c). Coherent THz emission by dynamical photon drag effect in graphene excited by fs optical pulses, from Ref [8].

The latter has revolutionized metrology in other spectral regions and has begun to be applied to the THz range, going hand-in-hand with recent developments in detector technology, such as THz quantum well infrared photodetectors (QWIPs).

INTERFEROMETRIC SPECTROSCOPY

Alternatively, THz Fourier transform infrared (FTIR) spectroscopy is a well-established method based on a Michelson interferometer providing Fourier transform of the interferogram of broadband incoherent radiation. A typical far-infrared FTIR consists of an incoherent high-pressure mercury arc lamp, a beam splitter, focusing and collimating optical beams, a motorized delay line and a thermal detector. FTIR spectrometers cover a wide frequency range from THz to visible with typically a better signal-to-noise ratio than THz TDS systems above 5 THz. In return, below 3 THz, their signal-to-noise ratio is lower by a few orders of magnitude than typical THz-TDS systems. Standard FTIR systems measure only the intensity of the THz waves and do not capture the phase information. As a result, they have the drawback over THz-TDS and CW THz spectroscopy systems to require • • •

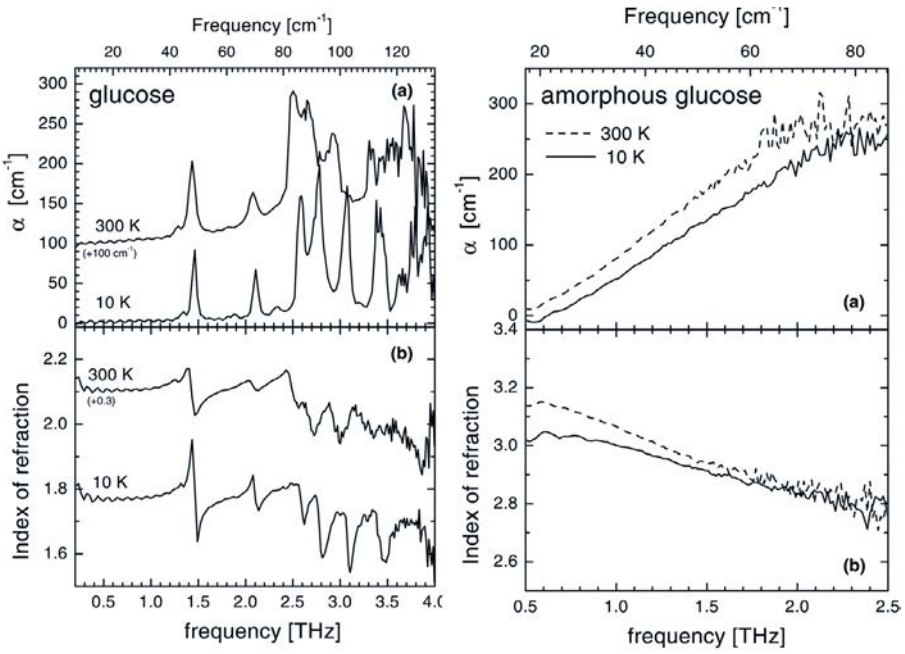


Figure 3.
(a) Absorption coefficient and (b) index of refraction of crystalline α-D-glucose (left panel) and amorphous glucose (right panel), from Ref. [9].

Kramers-Kronig analysis for extracting the complex-valued refractive index of the sample.

FUNDAMENTAL STUDIES

Over the last decade, THz spectroscopy has been investigated to explore fundamental excitations in matter. For instance, in the field of THz quantum optics and THz quantum electrodynamics, researchers have studied strong THz light-matter coupling (Fig. 2a), measured directly the spectral characteristics of vacuum field fluctuations and the squeezed states of the vacuum. Using THz spectroscopy emission schemes, several interesting works have reported ultrafast photoinduced spin currents and spin-to-charge conversion in magnetic metal multilayers as well as transient photon drag effect in graphene (Fig. 2c). Leveraging high power lasers and recent breakthroughs in THz generation, THz experiments with intense THz fields is an emerging area. This offers the possibility to perform time-resolved nonlinear studies and so to probe new fascinating physics in many materials. For example, extremely efficient generation of THz high harmonics has been demonstrated in graphene induced by the collective thermal response of background Dirac electrons to the driving THz fields (Fig. 2b). Further, the nonlinearity of transverse phonon modes has been recently explored providing insight on the interatomic potential of lithium niobate. Nowadays, ultra-broadband THz time domain spectroscopy can extend up to the mid-infrared, enlarging the field of physical phenomena that can be probed, such as the study of electronic correlations in van der Waals heterostructures. Another important recent area involves the THz near-field microscopy where individual nanostructures can be studied despite the extremely long wavelengths of THz photons. These examples illustrate the novel and unique fundamental studies that can be carried out with THz light and that will have an impact on the progress and development of future THz technologies.

APPLICATIONS

THz SPECTROSCOPY OF SOLIDS

The transparency of materials to THz waves depends critically on the polarity of the chemical bonds present in the material. It will also depend on the electrical conductivity of materials. Indeed if mobile electrons are present in the material they will oscillate under THz wave excitation and this will correspond to a loss of energy. Highly conductive metals such as copper do not allow transmission of terahertz waves, but they reflect them and can be used as mirrors. The semiconductors are more or less transparent depending on their doping, THz spectroscopy can therefore be used to probe the doping of semiconductors. Figure 3 shows an example of THz spectroscopy of a very common sugar: glucose. It shows the difference obtained between crystallized glucose and amorphous glucose. The spectrum features peaks only when glucose is crystallized, whilst in the amorphous case only a broad absorption is seen. Contrary to what happens in infrared spectroscopy that is mainly sensitive to localized vibrations between atoms and for which the two spectra would be very similar, THz spectroscopy is sensitive to low frequency vibrations of the whole crystalline structure which in this case is organised by the molecular hydrogen bonds. THz spectroscopy can also be used to identify different isomers, isotopologues or polymorphs of the same molecule and thus has applications in the pharmaceutical industry [10].

THz SPECTROSCOPY OF GAS PHASE

As early as 1955, C. H. Townes, Nobel Prize laureate in physics, stated that the use of rotational spectra of polar molecules, usually measured in the THz domain is an ideal tool for chemical gas phase analysis due to an exceptional degree of resolution (Fig. 4). The Doppler linewidths of pure rotational spectral signatures give rise to very sharp lines yielding the unrivalled degree of selectivity. As a result, many applications such as, breath analysis, environmental surveillance, food spoilage monitoring, or detection ● ● ●

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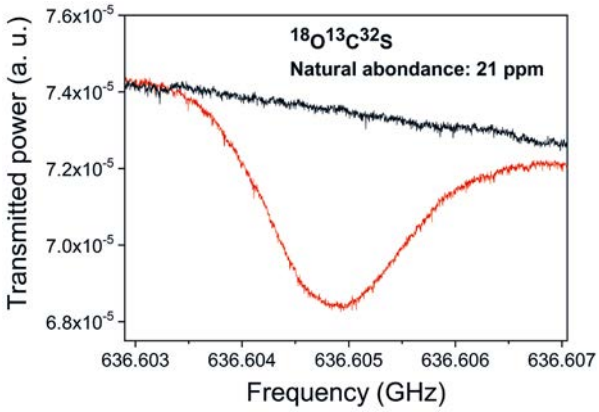

Figure 4.
Absorption signature of the transition J = 56 ← 55 of the rare isotopologue ^{18}O ^{13}C ^{32}S in natural abundance at a pressure around 100 µbar in red (the black line is the base line).

of explosive taggants have been proposed. Another successful application of THz waves is the continual study of the atmosphere (terrestrial, planetary or cometary) and the interstellar medium. THz astronomy is a hot topic for which a huge number of scientific groups over the world are engaged to obtain a large amount of information on "the cold Universe" and especially on organic molecules. Many observatory stations and/or satellite platforms, such as Hershel Space Observatory, Stratospheric Observatory for Infrared Astronomy (SOFIA) and Atacama Large Milli-metre Array (ALMA), are currently operated. All those applications require very sensitive THz gas phase spectrometers to be competitive with classical chemical analysis techniques or to obtain very accurate data for an efficient astronomical observation. Basically, increasing the interaction length between target gases and THz radiation improves the sensitivity and thus significance of all these latter applications. Up to very recently, THz gas-phase spectrometers were based onto single pass cells to reach an interaction length of several meters. Multiple pass cells provide higher sensitivities but are limited by a significant attenuation and generally require large volumes to reach distances typically not exceeding one hundred meters. A superior approach is to adapt the ultrasensitive techniques developed in the infrared domain, such as Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring Down Spectroscopy (CRDS) to the THz and submillimetre domain that require a high finesse cavity. This explicit requirement was recently achieved by use of extremely low loss oversized corrugated waveguide along with very high reflectivity Bragg mirrors [1]. Typically, a finesse around 3200, corresponding to a quality factor around 6×10^6, was experimentally demonstrated corresponding to a kilometre equivalent interaction length around 600 GHz, extending greatly the possibility and scope of applications described before and also opening others too.

CONCLUSION

In conclusion, the field of THz spectroscopy is rich and vibrant, with impacts in many areas of science. Thanks to on-going progress on the different THz spectrometers, their performances (such as spatial resolution, spectral range, electric field amplitude and time resolution) are significantly improved, opening exciting perspectives for fundamental research. Besides, THz spectrometers are already adapted for industrial requirements. Indeed, last achievements offer compact, broadband THz spectrometers that are easy-to-use, turnkey and flexible, meeting the needs for integration in industrial environment. As an example, some THz spectrometers are currently implemented in nondestructive testing industry to evaluate the properties of material components (polymers, semiconductor, ceramics and glasses, organic molecules, gas spectroscopy, conductive films, liquid crystals, composites, oil & gas), without causing damage.

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