THz SPECTROSCOPY FOR FUNDAMENTAL SCIENCE AND APPLICATIONS

Many elementary processes 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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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, multi-dimensional 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.

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**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 CO₂-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.
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...
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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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 Herschel 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 are isotopologue abundance at a pressure around 100 µbar in red (the black line is the base line).

Figure 4. Absorption signature of the transition $J = 56 \leftarrow 55$ of the rare isotopologue $^{18}$O$^{13}$C$^{35}$S in natural abundance at a pressure around 100 µbar in red (the black line is the base line).

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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