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Terahertz spectroscopy: The renaissance of far infrared spectroscopy

Mantsch, Henry H.; Naumann, Dieter

Abstract

This article does not attempt to offer an exhaustive assessment of the current status of terahertz technology, nor does it endeavour to cover all the anticipated applications of terahertz science, rather it is an attempt to raise the awareness of this tool among those molecular spectroscopists who may not yet have considered the emerging opportunities offered by this window in the electromagnetic spectrum.

Keywords: Terahertz spectroscopy and imaging; Vibrational spectroscopy; Far infrared spectroscopy; Structure elucidation

1. Introduction

Those of us who use molecular spectroscopy as an investigative tool for the study of molecular structures are increasingly confronted with the term of “terahertz spectroscopy”. This term is not commonly found in the standard spectroscopy textbooks, nor does it appear in the classical molecular spectroscopy “bible” of Gerhard Herzberg [1]. The term “far infrared spectroscopy”, on the other hand, has been around for a long time and is well documented in the spectroscopic literature [2]. Yet another term, that of “submillimeter spectroscopy”, is also utilised by the molecular astrophysics community. Today, however, the majority of spectroscopists have adopted the increasingly fashionable term of “terahertz spectroscopy”. Still, regardless of which terminology is used, we are basically dealing with the same window in the electromagnetic spectrum that spans the range from 0.3 to 3 THz, or for those who prefer wavenumbers, from 10 to 100 cm^{-1} and for those who like wavelengths, from 1 to 0.1 mm. A recent query on the search engine Google turned up barely 754,000 entries for the new term of “terahertz spectroscopy”, versus 1,510,000 entries for the old term of “far infrared spectroscopy”, hence the idiom “renaissance” in the title of our article.

2. Terahertz radiation

The electromagnetic radiation known as terahertz waves, T-rays, T-lux, or simply THz, fills the frequency gap between microwaves and infrared radiation. There is no consensus as to the precise delimitation of the terahertz spectral domain and the range of this region is not uniquely determined: some define it as the region between 0.1 THz (100 GHz) and 10 THz, most people, however, restrict it to the spectral range 0.3–3 THz (10–100 cm^{-1}). One terahertz corresponds to a photon energy of 4 meV (that is 33.3 cm^{-1}). Terahertz radiation is non-ionizing and as submillimeter microwaves they share with microwaves the capability to penetrate a wide variety of non-conducting materials. Terahertz rays can pass through clothing, paper, wood, masonry, plastic and ceramics and also go easily through smoke or dust (if particle size is small), but they cannot penetrate metal or water. Nowadays the traditional terahertz “frequency domain” spectroscopy has been augmented with the powerful terahertz “time domain” spectroscopy. In contrast to optical and infrared spectroscopy, which measure only the intensity of light at specific

frequencies, time domain terahertz spectroscopy is able to determine both the amplitude and the phase of the terahertz pulse, thus allowing the evaluation of both the absorption coefficient and the refractive index.

3. Terahertz sources and detectors

The reason for the frequently used expression of “terahertz gap” arises from a “gap in” or conversely, a lack of good sources and detectors for this spectral region when compared with the sources and detectors abundantly available for both the low-frequency or electronic end and the high-frequency or optical end of the terahertz gap. The current difficulty of generating and detecting terahertz radiation is also to blame for the paucity of commercially available terahertz spectrometers and explains why this window in the electromagnetic spectrum has not yet seen the technical and commercial developments afforded by the many infrared/optical and microwave spectrometers.

The generation and detection of terahertz radiation has remained technically challenging well into the 1990s. Early terahertz research was spearheaded by optical generation of terahertz radiation that uses pulsed or continuous-wave lasers to generate an ultrafast photocurrent in a photoconductive switch or semiconductor by applying electric field carrier acceleration. Today, terahertz waves are commonly generated by nonlinear optical effects such as optical rectification, difference-frequency generation or optical parametric oscillation. Popular nonlinear media include GaAs, GaP, ZnTe, CdTe and LiNbO₃, though research continues to find more effective materials. An intriguing optical method of generating terahertz radiation, ambient air plasma generation, is receiving considerable attention particularly with respect to security application. Herein, an intense pulsed laser produces an air plasma that emits terahertz waves and the source can be controlled remotely by a distant laser beam [3]. As far as detectors are concerned, conventional bolometers or deuterated triglycine sulphate crystals are still in use, however, more recently low-temperature grown GaAs has established itself as one of the best materials because of its high carrier mobility, fast carrier capture time, high breakdown voltage and high resistivity. Sensing of terahertz radiation by means of nonlinear optical processes is one of the most commonly used techniques for pulsed terahertz waves. Photoconductive antennae are used both as terahertz emitters and as terahertz detectors; their performance depends on the carrier mobility and the trapping time in the antennae. Terahertz radiation can be focused using lenses prepared from various materials such as teflon or silicon, while gold-coated mirrors are used for collimation and focusing of the terahertz beam. The imaging resolution is defined by the beam diameter of the terahertz wavelength, with higher frequency components giving better imaging resolution.

Technical improvements in the mid 1990s have led to the development of novel semiconductor-based terahertz sources such as the terahertz quantum cascade laser, which generates terahertz waves by means of electron relaxation between sub-bands of quantum wells. Subsequent advances in photonics paved the way for the development of solid-state electronic devices like the uni-travelling-carrier photodiode which uses a photo-mixing technique to generate the terahertz waves by the optical beat of the light from two different wavelength laser diodes. It is certainly challenging to keep up with the many new developments in solid-state electronic devices (for example the advent of resonant tunnelling diodes or the arrival of terahertz single-

photon detectors), which continue to drive advancements in terahertz technology. For more details, “Terahertz Spectroscopy: Principles and Applications”, edited by Susan Dexheimer [4] provides a solid background on instrumentation and methods. The fundamental principles of terahertz technology, including some historic achievements are described in earlier reviews [5], [6], [7] and [8]. Here one must also mention such terahertz sources as free electron lasers like the free electron laser at the Jefferson Laboratory in Newport, Virginia [9], which is able to generate extremely high-power terahertz beams (up to 10 Watt or more). These powerful, but expensive broadband terahertz sources are ideal for fundamental research and are well suited to the study of molecular structures. On the other hand, the growing commercialization potential of terahertz technology is also driving the development of compact, inexpensive terahertz sources (and detectors). An interesting approach among these attempts is the use of a dielectric image line coupled with a terahertz whispering gallery mode disk resonator [10]. The latter efforts represent an important step towards developing low-cost terahertz instruments suitable for off-site applications in hospitals, point-of-care medical practices or private homes.

4. Selected applications of terahertz technology

As far as molecular science is concerned the applications of terahertz technology, both fundamental and applied, can be separated into two categories: spectroscopy and imaging. In addition to this, there are many terahertz applications that cannot be sorted into either of these two categories, such as detection of electron dynamics (in semiconductor or other materials), non-spectroscopic imaging, and of course the use of terahertz rays in communications. In this article, however, we concentrate on terahertz spectroscopy and imaging and focus on those applications that are of interest to the readership of this journal.

4.1. Molecular spectroscopy using terahertz radiation

Since the interpretation of terahertz spectra is basically the same as that of infrared and Raman spectra it can be easily appreciated by the general practitioners of vibrational spectroscopy.

4.1.1. Biomolecular systems

A number of biological and biomedical systems have already been successfully investigated by terahertz spectroscopy [11], [12], [13], [14], [15] and [16]. The analysis of terahertz spectra yields structural information which complements that offered by classical mid-infrared spectra. Furthermore, terahertz spectroscopy is well suited to explore the low frequency vibrational modes that define the incipient motions of large scale conformational changes which generally occur along the torsional degrees of freedom. These low-frequency vibrations are accountable for the flexibility of the polypeptide-, polynucleotide- and polysaccharide backbone in complex biopolymers. Given the long-range and collective nature of these vibrational modes they are highly sensitive to intermolecular interactions, particularly to the nature of intermolecular hydrogen bonds and thus provide a unique fingerprint of the molecular structure.

Moreover, since these vibrational modes probe the collective motions that extend over a large portion of the molecular framework, they can be used to investigate biomolecular dynamics, and to determine the mechanical anharmonicity in such large amplitude motions. It has even been

suggested that natively folded proteins exhibit characteristic vibrational modes at terahertz frequencies, and that these collective motions are critical indicators for the functionality of the protein. This hypothesis has yet to be validated.

4.1.2. Probing water binding (hydration) and its dynamics

As already mentioned terahertz spectra are particularly sensitive to intermolecular hydrogen bonds and therefore well suited to investigate the binding of water to large biomolecules [17], [18] and [19]. The recently developed kinetic terahertz absorption spectroscopy technique was successfully applied to explore real-time detection of protein–water dynamics upon protein folding. This type of spectroscopy provides a means of probing protein folding at a time resolution of less than a millisecond [19]. Short terahertz pulses were used to obtain signatures of water dynamics related to protein folding events: it was shown that in less than 10 ms after initiating protein refolding the dynamics of the water network changed as the protein regained its native structure. Since the two processes are highly correlated, the terahertz spectra could be used to determine the size of the dynamic hydration layer around the protein. It was concluded that these hydration shells significantly contribute to the structure and energetics of the native protein, suggesting that the coupling between the hydration dynamics and the protein dynamics plays an important role in the processes of protein folding and unfolding.

Terahertz spectroscopy was also applied to examine the dynamics of water surrounding various low- and high molecular weight biomolecules, including carbohydrates [20], small peptides [21] and DNA oligomers [22].

4.1.3. Pharmaceutical applications

A number of pharmaceutical companies already use terahertz spectroscopy routinely as a tool to characterize pharmaceutical products [23], [24] and [25]. Since most pharmaceuticals have to be administered at very low doses, these small quantities require that the drug is formulated in a proper pharmaceutical dosage, known as the drug delivery system. The correct formulation of the drug in an optimal pharmaceutical dosage is critical for any pharmaceutical product. Whereas information obtained from infrared or Raman spectra is predominantly at the molecular level, the properties that need to be monitored for drug delivery are at the intermolecular- and lattice level. Thus, there is a need for a non-destructive analytical technique able to monitor intermolecular interactions in pharmaceutical formulation and production technology. This can be terahertz spectroscopy. Since drug solubility and dissolution rates are influenced by such factors as polymorphism and degree of crystallinity, terahertz spectroscopy, with its sensitivity to intermolecular effects, is almost ideally suited to address these issues. After purification, drug molecules often crystallize in different polymorphic forms which can be rapidly and effectively identified by terahertz spectroscopy. Unlike their mid-infrared spectra, terahertz spectra of the various polymorphs are markedly distinct, illustrating the sensitivity to the intermolecular hydrogen bonding networks which characterize the different polymorphic forms. Furthermore, unlike their spectra in the mid-infrared region the terahertz spectra can also distinguish between the hydrated and dehydrated forms. A number of laboratories have already introduced terahertz pulsed spectroscopy in the production line, for instance to discriminate between samples with different hydration levels in pharmaceuticals like carbamazepine, piroxicam, or phylline [26] and

[27], or to differentiate enantiomers, for example to distinguish L- from D-tartaric acid and from L,D-tartaric acid [28].

4.1.4. Trace gases

Both frequency domain and time domain terahertz spectroscopy have been applied for the detection of trace gases. Continuous-wave terahertz spectra obtained by photo-mixing different laser beams were used to analyse mainstream cigarette smoke [29]. Characteristic terahertz spectral signatures were observed in the 0.5–2.4 THz range for hydrogen cyanide (HCN), carbon monoxide (CO), formaldehyde (H₂CO), and water (H₂O) allowing investigators to identify and quantify the individual gases, achieving direct concentration measurements from the pure rotational transitions. The detection limit of trace gases approached 9 ppm. It is expected that hazardous gas detection using terahertz sensing is likely to become even more common, for example to spot carbon monoxide at fire sites where the infrared detection is blocked by concrete walls.

4.2. Spectroscopic imaging with terahertz radiation

Terahertz technology is not only attractive for new applications in molecular spectroscopy but also as a novel imaging modality. Many common materials and living tissues are transparent or semi-transparent to terahertz radiation and exhibit “terahertz fingerprints” permitting them to be imaged and identified. Terahertz imaging provides a higher resolution than microwave imaging as the resolution is defined by the beam diameter at the terahertz wavelength. Scanning near-field microscopy with a modulated terahertz field is likely to further improve the resolution to yield terahertz images at a resolution of tens of microns.

4.2.1. Security applications

Much of today’s applied terahertz imaging research is linked to security applications with the majority focusing on safety in public spaces. Long lines for security screening at airports only underline the need for quick, reliable and safe personal screening. Because terahertz radiation has a low photon energy and is non-ionizing, it presents a suitable option for non-invasive imaging of humans, offering the possibility to screen for and locate concealed objects or materials [30], [31], [32] and [33]. Moreover, terahertz cameras with focal-plane arrays can be used to read letters in unopened envelopes as images of objects can be obtained regardless of the background illumination.

Terahertz imaging has also been successfully employed to screen for hazardous materials such as explosives. Explosives, as well as narcotics, have distinct signatures in their terahertz spectra making it straightforward to non-invasively screen for and identify individual explosives and drugs. The terahertz absorption spectra of TNT (2,4,6-trinitrotoluene) and RDX (cyclo-1,3,5-trimethylene) for instance are quite different and the strong RDX peak at 0.81 THz (27 cm⁻¹) can clearly be seen in the spectra of commercial plastic explosives, providing identification of RDX-based explosives even through common clothing materials. It is therefore only a matter of time before terahertz-based technology will be used regularly in airports and other public spaces. To probe more deeply into applications of terahertz technology to security and defence topics

readers may wish to consult “Terahertz Science and Technology for Military and Security Applications” edited by Woodland et al. [34].

4.2.2. Biomedical diagnostics

It should come as no surprise that the medical research community has turned to terahertz spectroscopy and imaging in its relentless quest to improve cancer diagnosis [35], [36] and [37]. When terahertz pulsed imaging was used to examine excised basal carcinoma tissue slices, significant differences between the tumour and the healthy tissue were revealed in the terahertz images. However, similar to earlier studies that used infrared spectroscopy and imaging to diagnose cancer, the devices based on terahertz spectroscopy still require significant improvements and refinements before they can be accepted as non-invasive diagnostic tools by the medical community at large. One advantage of terahertz over infrared spectroscopy is that it can be applied to frozen tissues since terahertz transmittance of ice is much higher than that of water.

The high sensitivity of terahertz radiation to polar molecules such as water renders the terahertz imaging modality an excellent non-invasive tool for determining the hydration levels in skin tissue, both *in vitro* and *in vivo* [35]. In another interesting application, hydration measurements performed *in vivo* on the stratum corneum in the eye made it possible to determine the level of tissue hydration in the intact eye [38]. Since terahertz testing of human tissue hydration can be conducted *in vivo*, without any particular sample preparation or patient interference, it gives this imaging modality an obvious advantage over other diagnostic tools.

4.2.3. Commercial applications

The emergence of terahertz spectroscopy and imaging as both a new technology and as a candidate with commercial potential, has led to the creation of a number of commercial enterprises and firms.

For example, the “Center for Terahertz Research” set up at the Rensselaer Polytechnic Institute in Troy, has pioneered many applications of terahertz research and technology in areas ranging from basic science, material science, medical science to security monitoring and its director Dr. Zhang, a terahertz expert himself, predicts that the future “killer application” will be in biomedicine.

The high sensitivity of terahertz radiation to water also makes terahertz imaging an excellent tool for online screening of food and agricultural products, for example to evaluate the water content of vegetables or to monitor damage to fruits not visible to the naked eye. Such commercial applications, however, have to await the development of rapid, low-cost imaging systems based on terahertz radiation.

In another commercial application, terahertz imaging at a fixed frequency of 0.6 THz was tested as a modality for remotely assessing the water content of paper in an industrial setting [39]. Promising results were achieved with a good sensitivity to the water content, a high spatial resolution, and importantly, no interference from scattering at the paper surface.

There are even more esoteric applications of terahertz imaging, such as detecting defects (voids) in the heat-insulation panels used in the space shuttle [40].

It is very likely that applications of terahertz imaging in the areas of safety and security will dominate future commercial applications as terahertz imagers could soon supplement (or even replace) the common X-ray imagers. One could also envisage terahertz-based cameras being used to develop new human biometrics systems. The possibilities are only limited by the scope of human imagination.

In addition, there are also businesses that sell commercially available terahertz technology, for example the “Zomega Terahertz Corporation” in Troy NY which offers non-destructive testing of industrial materials, as well as various security and defence applications. Another commercial company, Microtech Instruments Inc., promotes a compact terahertz spectrometer based on millimeter backward wave oscillators combined with frequency multipliers and broadband pyroelectric detectors. In the UK, TeraView offers a commercial terahertz pulsed imaging system for applications in areas such as pharmaceutical innovation, material characterization, medical imaging and security screening.

It should also be mentioned here that the globalization of science and technology has led to the establishment of web-based terahertz networks like the “THz Science and Technology Network” (www.ThzNetwork.org), which are intended to foster global interactions amongst those interested in terahertz research and technology.

5. Final remarks

Now, what should the practitioners of molecular spectroscopy expect from the explosive growth of terahertz science and technology? Certainly, a great deal, but has terahertz spectroscopy finally come of age? There are numerous research labs and institutes in the US, in Europe, Japan and in the former Soviet Union which are at the cutting edge of terahertz research and scientists the world over are looking for better ways to generate and harness the potential of terahertz radiation. Regrettably, the signal breakthrough has not yet occurred, and the proponents of terahertz spectroscopy continue to praise its great promise. Yet, the portion of the electromagnetic spectrum referred to as the “terahertz gap” in no way constitutes a gap in the sense of there being something missing or lacking, but quite the opposite in fact. This gap has been opened up by a handful of scientists and as emphasized again in this paper, is poised to become a major player in the global arena of emerging technologies. Young enterprising scientists interested in molecular spectroscopic research are encouraged to turn their attention to this area as only the sky is the limit to imaginative new applications of terahertz spectroscopy and imaging.

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