

Technological advances in terahertz pulsed systems bring far-infrared spectroscopy into the spotlight

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Introduction

Far-infrared spectroscopy explores low-frequency motions in molecular systems. These motions are either flexing of the individual molecules themselves or inter-molecular interactions, either via strong hydrogen bonds or weaker van der Waals bonding between nearest neighbours. These large amplitude vibrations can provide insight into the structural dynamics of biomolecules, such as proteins, or formation of polymorphs and hydrates of crystalline materials; which is of great interest to the pharmaceutical industry. However, working in the far-infrared region of the electromagnetic spectrum has long been problematic due to availability of only weak incoherent sources and low sensitivity detectors or liquid helium-cooled bolometers.

Although other methods can generate far-infrared radiation of high intensity or brightness, for example, free-electron lasers or synchrotrons, these large devices are not very convenient for typical research laboratories. In addition, the 1970s saw the development of the optically-pumped far-infrared gas laser to generate single frequency continuous wave or pulsed radiation, but these lasers tended to be large and temperamental to use.

To get an idea of the problems of working in the far-infrared it is useful to

consider the black-body radiation maxima corresponding to different wavelengths. The Wien's displacement law gives the relationship $\lambda_{\max}T = 0.2898 \text{ cmK}$, where λ_{\max} is the wavelength in cm and T is the temperature in Kelvin. From this, one can deduce that at a frequency of 300 GHz (10 cm^{-1} in wavenumbers) the corresponding black-body temperature is 3 K. With a spectrometer at about 300 K, one can see that the black-body emission from the spectrometer can dominate and overwhelm any experiments; thus the requirement to use helium-cooled detectors to detect tiny changes in the overall radiant intensity. This, coupled with weak sources, has made working in the far-infrared inconvenient in the past.

Recent advances in turn-key ultra-short pulsed lasers and semiconductor emitters and receivers have made working in what is now fashionably called the "terahertz gap" as straightforward as, if not easier than, working in other parts of the spectrum. Turn-key instruments are now available. These instruments routinely access the frequency region from 0.05 to 3 THz, corresponding to 1.2 to 100 cm^{-1} , with very high signal-to-noise ratios and without the use of any cryogenic liquids. In addition they require no user alignment and are insensitive to vibration making them

accessible for the first time to non-laser specialists.

Generation and detection in terahertz pulsed systems

Traditionally, globars or mercury lamps operating as black-body emitters have been used to generate incoherent radiation in the far-infrared region. By contrast, at the heart of a terahertz pulsed spectroscopy (TPS) system is an ultra-short pulsed laser, which generates a stream of near infrared (NIR) (800 nm) pulses at 80 MHz, with each pulse typically lasting about 70 fs. The other essential component is a semiconductor device known as an Auston switch, a very fast optical device developed by David Auston's group at Bell Laboratories in the 1980s.¹ By focusing the laser pulses onto the Auston switch, electron-hole pairs are generated at the surface of the semiconductor. With a carefully-designed antenna arrangement on the semiconductor, the electron-hole pairs are accelerated by a DC electric field applied across the device. The resulting effect is to induce emission of short bursts of broad band coherent terahertz radiation with each laser pulse. The light generated by this technique can then be collected using silicon lenses and utilised for spectroscopy or other terahertz applications, such as imaging and

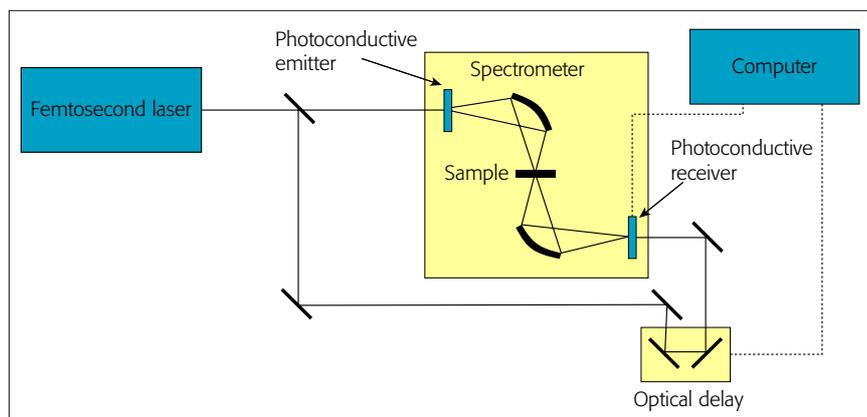


Figure 1. Schematic diagram of the principal components within a terahertz spectrometer.

mapping analysis. The terahertz pulses can either be focused onto surfaces for reflection spectroscopy or configured for a transmission spectrometer system as shown in Figure 1.

To avoid using cryogenic liquids, traditionally needed for sensitive detection of far-infrared radiation, in terahertz pulsed spectroscopy a small portion of the NIR laser pulse is cleverly used in the detection process. This is focused onto a second semiconductor device; again electron-hole pairs are generated at the surface. However, on this device the electric field is provided by the coincident terahertz pulses, inducing a photocurrent that

can be measured. The femtosecond laser pulse effectively acts as an optical gate, which is open only for the <200 fs lifetime of the electron-hole pairs in the semiconductor. By sweeping the time delay between the arrival of the femtosecond laser pulse and the terahertz pulse, a waveform comprising the terahertz signal as a function of time can be reconstructed. Figure 2 shows two waveforms obtained from a terahertz system. The black waveform is the reference while the red waveform is that obtained with a sample. The sample waveform is

displaced in time from the reference due to the presence of material in the beam path with higher refractive index. By mathematical Fourier transform of the waveforms in Figure 2 the spectra in Figure 3 are obtained with a wavenumber scale covering the range 1.2 cm^{-1} to 150 cm^{-1} . The reference spectrum shows some residual water vapour absorption in the instrument, while the sample spectrum shows a series of strong absorption bands. These are due to phonon vibrations in the material under investigation. The y-axis in Figure 3 is shown on a logarithmic scale to indicate the very high dynamic range of the measurement (>40 dB can be achieved). The waveform signals shown in Figure 2 are directly proportional to the electric field of the terahertz pulse, meaning that it is possible to directly recover phase and amplitude information from the data, providing a direct measurement of the spectral absorption coefficients $[\alpha(\nu)]$ and the refractive indices $[n(\nu)]$. The electric field is related to absorption coefficient and refractive index by

$$\left(\frac{E_s}{E_r}\right) = T(n) \exp\left(-\frac{\alpha d}{2} + \frac{i n \omega d}{c_0}\right)$$

where E_r and E_s are terahertz electric field strengths before and after transmission, respectively, d is the sample thickness, ω the angular frequency of the radiation, c_0

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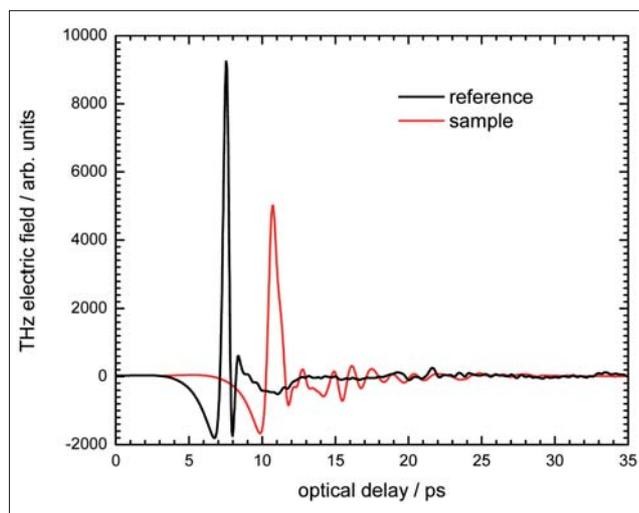


Figure 2. The terahertz electric field recorded as a function of time. The black curve is the reference waveform and the red curve is the waveform obtained after the terahertz beam has passed through 4 mm thick sample. The red waveform is displaced in time from the black due to the presence of material in the beam path with higher refractive index.

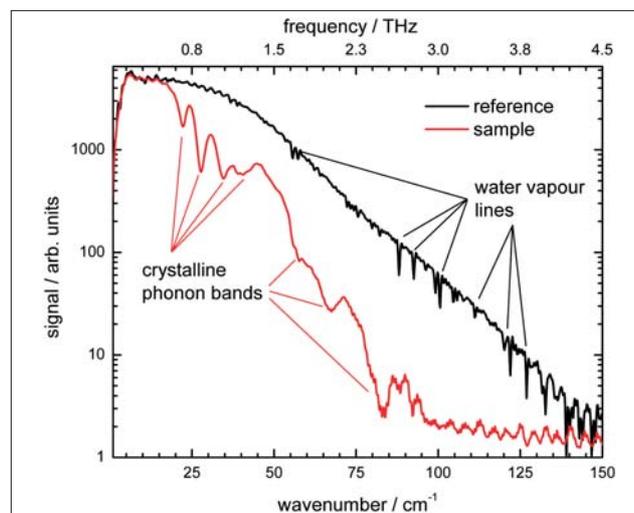


Figure 3. Fourier transforms of the two time-domain waveforms shown in Figure 2. Highlighted in the reference spectrum are lines due to water vapour, these can be used to calibrate wavenumber scale of the spectrum. Also, shown are the bands due to crystalline phonon modes. The signal is plotted on a logarithmic scale to show the dynamic range of the instrument.

the speed of light in vacuum and $T(n)$ is the Fresnel reflection loss at the sample surface.

Applications Spectroscopy

Since the terahertz pulses generated from the semiconductor are broadband in nature, they are ideal for spectroscopic applications. However, as this region of the electromagnetic spectrum has been difficult to access until now there have been few calculations undertaken to explain the spectral modes observed and our theoretical understanding is much poorer than for established infrared spectroscopy. With the availability of terahertz pulsed spectroscopy systems, scientists are now able to readily probe the spectroscopy of materials in this spectral region and published work on the subject is increasing rapidly. The basic understanding is that for solids many of the terahertz spectral features are due to phonon vibrations in the crystalline lattice. Strachan *et al.*² and Walther *et al.*³ have carried out terahertz spectroscopy studies and shown features in this spectral region require a high level of crystalline structure. Taday *et al.*⁴ were able to use the unique sensitivity of the technique to

changes in crystalline structure to distinguish between the two main polymorphs of the drug ranitidine hydrochloride. Quantitative analysis of materials using terahertz pulsed spectroscopy combined with chemometric techniques such as partial least squares and principal components analysis has also been demonstrated.⁵

All measurements in this paper were made in transmission using a TPI™ spectra1000 spectrometer (TeraView Limited, Cambridge, UK). Nitrogen purge of the terahertz beam path readily removed sharp absorption features due to atmospheric water vapour. The water lines can also provide a useful wavenumber calibration check, although other calibration standard materials are being investigated. Terahertz spectral data were acquired and processed using OPUS™ software (Bruker Optics, Germany).

The instrument generates broadband terahertz pulsed radiation in the range 50 GHz to 4 THz (1.4 cm^{-1} to 130 cm^{-1}). All the optical components are mounted in a bespoke casing, giving mechanical stability to the instrument with very little day-to-day adjustment required. Spectroscopic measurements can be recorded in one of two modes: (i) in rapid-scan mode the optical time delay is generated

by rapidly moving mirrors, and (ii) step-scan mode where a cube-corner retro-reflector mirror is translated by a stepper motor to generate the time delay. In rapid-scan mode, spectra are acquired at the rate of 30 per second with a spectral resolution of 30 GHz (1 cm^{-1}). For step-scan mode the measurement time depends on the resolution required and integration time to achieve the desired signal-to-noise; the highest spectral resolution is 3 GHz (0.1 cm^{-1}). No matter what spectral resolution is required all radiation from the source can be used, unlike FT-IR where the field-of-view must be reduced by aperturing down the system to achieve high resolution, thus causing a loss of signal. TPS thus has a unique throughput (étendue) advantage over FT-IR. The instrument is capable of accommodating a 100 mm pathlength gas cell or a standard liquid cell. For the gas and liquid cells some consideration must be given to window materials; useful materials include TPX® [poly (4-methyl pentene-1)], polyethylene, polypropylene and z-cut quartz.

Absorbance (decadic) spectra were calculated from all measured sample and reference terahertz spectra using $A(\tilde{\nu}) = \log_{10}[I(\tilde{\nu})/I_0(\tilde{\nu})]$, where $I(\tilde{\nu})$ is the sample spectrum and $I_0(\tilde{\nu})$ is the back-

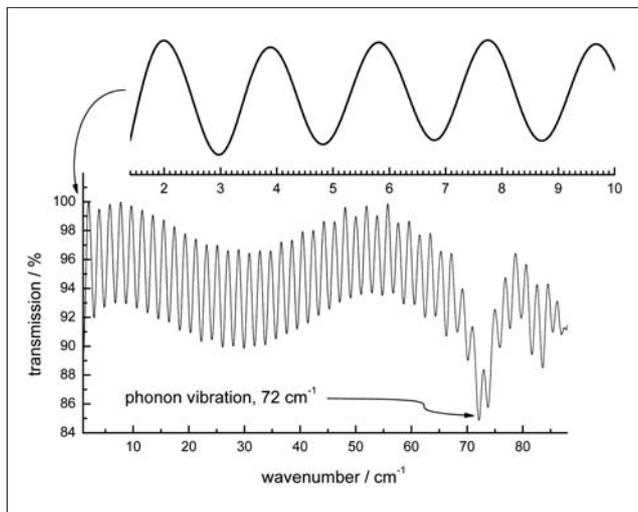


Figure 4. The terahertz transmission spectrum of a 3 mm thick piece of parallel-sided high density polyethylene. The insert shows the 1.5 cm^{-1} to 10 cm^{-1} region. The fringes are due to etalon reflection in the polyethylene and these extend down to at least 1.5 cm^{-1} .

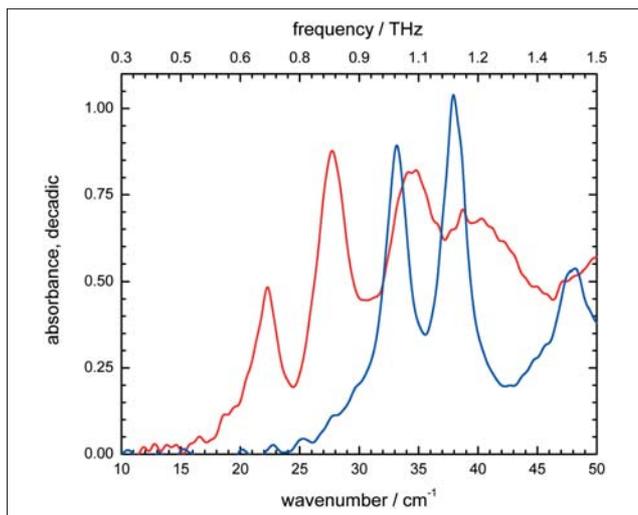


Figure 5. The terahertz absorption spectra of two polymorphs of sulfathiazole. The red spectrum is due to polymorph II while the blue is due to polymorph V. There are considerable spectral differences between these spectra.

ground (reference) spectrum, both generated by Fourier transform of the raw time-domain signal.

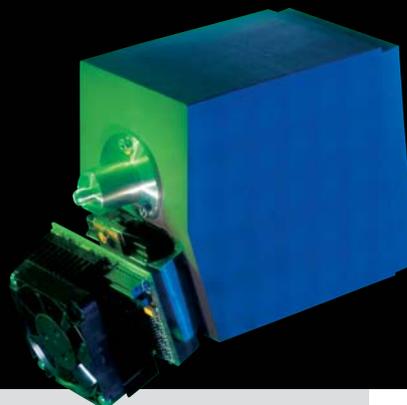
To give an indication of the longest wavelength measurement achievable, we measured a 3 mm thick piece of high-density polyethylene (PE) with plane parallel sides. The terahertz transmission spectrum, acquired in less than a second, is shown in Figure 4. The oscillations are due to interference between reflections from the front and back surfaces of the sample. The response of the terahertz spectrometer allows the observation of oscillations down to 1.5 cm^{-1} , which corresponds to a wavelength of 6.6 mm. Also shown in Figure 4 is the weak absorption band centred at 72 cm^{-1} due to the phonon B_{1u} mode of PE.



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The sensitivity of terahertz absorption spectroscopy to the crystalline structure of materials has been described previously. As an example, Figure 5 shows the terahertz absorption spectra of two polymorphs of the antibiotic sulfathiazole, form II (red curve) and form V (blue curve). The spectra of the two forms show considerable differences. The three other known polymorphs of sulfathiazole have also been studied and show differences. This discrimination opens terahertz applications in the pharmaceutical industry such as polymorph screening.

Medical terahertz mapping

As the terahertz radiation is emitted from a diffraction-limited point source on the semiconductor device it is easy to manipulate. This opens up the possibility of new applications such as terahertz mapping where either the terahertz beam is raster scanned across the sample or the sample is moved in the terahertz beam.

In recent studies,⁶ terahertz pulsed imaging (TPI) has been used to investigate basal cell carcinomas and has shown that there is a significant difference between the tumour and healthy tissue in this spectral region. The contrast mechanism is believed to be increased water content in cancerous skin. Water has very strong absorption features in the terahertz region making it an excellent molecular

marker for diseased tissues. To begin to understand the contrast mechanism in skin, *in vivo* studies of healthy volunteers has been undertaken.⁷ In this study finite difference time-domain modelling was successfully used to describe how the terahertz pulses interacts with healthy living tissue.

Security

Kemp *et al.*⁸ have shown that all the major plastic explosives have discrete, well-described terahertz spectral signatures and this coupled with the fact that most items of clothing and common packing materials are semitransparent to terahertz radiation has opened the opportunity for applications in the security screening area.

Summary

Recent advancement in the development of plug-and-play terahertz systems capable of 24–7 (24-hour/7-day continuous) operation are opening new opportunities for the far-infrared region of the electromagnetic spectrum, until recently difficult to access in areas of pharmaceuticals, security and medical science.

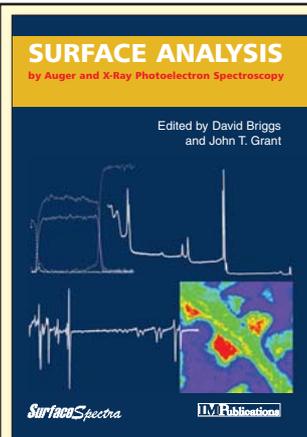
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