

# Terahertz spectroscopy

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Last year we discussed gigahertz spectrometry, so I thought it would be a step up for 2014 to go one further and look at Terahertz Spectroscopy. OK, so one is nuclear magnetic resonance spectrometry and the other is an optical spectroscopy technique, but they both actually have one common endearing feature, and that is a phenomenal rate of technological development revolutionising their respective application fields in the last ten years.

## Where spectrometers fear to tread!

Unless you are familiar with the term Terahertz Spectroscopy and maybe have worked with the technique, a brief scan through the common electromagnetic spectrum diagrams could well leave you stumped as to what we are referring to. Those who immediately dive for Wikipedia will see that we are talking about a frequency which seems to be orphaned between infrared and microwave regions. Historically, even before the advent of the Fourier transform spectrometer age, those working with conventional infrared spectroscopy may well have used high-end spectrometers which offered the capability to be able to work down to terahertz frequencies. For many years the more common term for this region was the far-infrared region, although this was often defined as running from the end of the infrared spectral region at  $400\text{ cm}^{-1}$  down to about  $10\text{ cm}^{-1}$ . To confuse matters even more in the literature it is also relatively common to come across the use of the term "T-wave" indicating essentially the same wavelength range. Trying to push the boundaries of conventional infrared spectrometers could be enor-

mously frustrating as there was a singular lack of good radiation sources and detectors for this frequency range. Some top-of-the-range research grade spectrometers could be equipped to operate in the so-called terahertz gap. Well into the last decade publications were describing the need to use polyethylene terephthalate or Mylar beam splitters, as well as replacing the conventional globar (silicon carbide), whose energy peters out at around  $100\text{ cm}^{-1}$ , with high pressure mercury lamp sources and potentially looking to liquid-helium cooled bolometers for high sensitivity. Of course analytical spectroscopists could also look to synchrotron radiation sources such as are currently available on beamlines at Diamond in the UK. Clearly, the investment and instrumentation requirements hampered the more wide-spread adoption of terahertz spectroscopy despite some rather unique advantages open to analysts harnessing the unusual possibilities this wavelength range has to offer. Fortunately, lasers have come to the rescue of analysts hoping to exploit information previously hidden in the terahertz gap!

## But why come over to the dark side?

There are many good reasons for spectroscopists and others to want to explore the capabilities of this region of the electromagnetic spectrum. Many substances show typical long-range phonon modes here, helping to characterise bulk properties in a way not possible in other wavelength ranges. In stark contrast to mid-infrared radiation, plastics, cloth and semiconducting materials are broadly transparent, opening up opportunity for *in situ* chemical and

biological imaging applications with a radiation type which is non-ionising and therefore inherently safer than x-rays. There are also specific signals accessible in this region which give information on structural features not available from more common spectroscopies.<sup>1</sup>

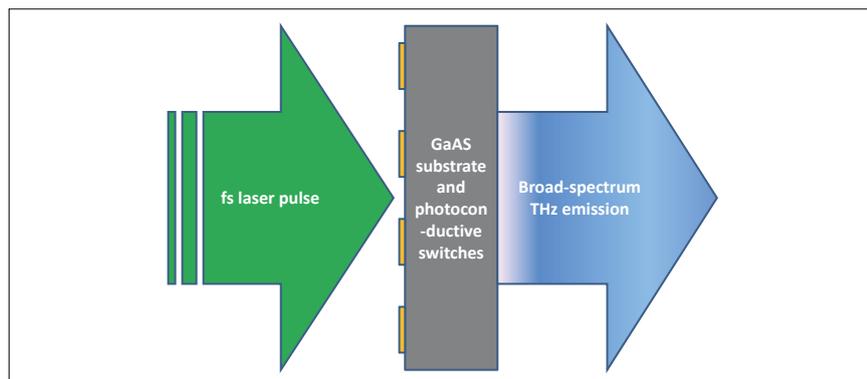
Fortunately, there has been a revolution in terahertz spectroscopy brought about by the development of stable femtosecond laser driven semiconductor sources and detectors.

## Hardware which revolutionises spectroscopy

At a very simple level the technology development which is capable of revolutionising this area of spectroscopy revolves around the development of an emitter consisting of an array of photoconductive switches on a Gallium-Arsenide (GaAs) substrate. These commercially available sources of THz radiation function through the stimulation of the semiconductor substrate by the arrival of femtosecond pulses creating optically excited carriers which are then accelerated by an electric field between the switches which give rise to a broad emission spectrum of terahertz frequency radiation. These sources can also be "broad" in geometry with the possibility of building arrays of microstructured switches on the semiconductor which produce a large area source (Figure 1). Bigger devices also have the advantage of offering greater target areas for the fs laser avoiding some alignment and saturation issues.

Time-domain systems can be built using the same technology for the detectors through the addition of a scannable delay to the fs laser pulse triggering the

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**Figure 1.** A very simplified schematic of the THz emitter for converting femtosecond laser pulses into broad spectrum wide area THz source.

detector along the lines of an interferometer in Fourier transform spectroscopy. For a very simplistic schematic, see Figure 2.

We also must not ignore the key development of vastly more stable fs lasers. Early reports in the literature had compared different lasers whose stability issues had given rise to annoying reproducibility issues and artefacts within the resulting spectra.

So with a new generation of massively improved sources and detectors available, we are lucky enough to have the hardware to start turning terahertz spectroscopy into a more mainstream technique with analysts looking to these (now commercially available) wavelength ranges to solve more analytically oriented problems rather than

spectroscopists building instruments to carry out research into spectroscopic effects.

At the meeting of the Royal Society of Chemistry, Molecular Spectroscopy Group on Recent Advances in Spectroscopy at Terahertz Frequencies in Cambridge, UK, ably organised by Brian Woodget at the end of 2013, it was clear from many speakers that a real focus of the applicability of terahertz spectroscopy to solving difficult analytical problems existed. Phase transitions such as crystalline to amorphous and differences in drug substance polymorphs are easily studied in this region. Long-distance coupling effects play a substantially greater role in influencing the observed spectra than in mid-infrared spectroscopy. Bernd Fischer and other speakers

discussed the problems of modelling terahertz spectra with programmes such as Gaussian, where modelling yields pretty good information for simulating/interpreting data from the mid-infrared region. If you try to model down to terahertz regions a single molecule is insufficient, yielding band predictions which often have no similarity to observed data. You will likely need to go to many repeating units before the models can get close to predicting what is observed experimentally. This could be frustrating for modellers, but it is a clear affirmation of the strength of the technique for differentiating longer range structural differences. Timothy Korter from Syracuse brought a very good example looking at the changes in the polymorphic form of a particular AIDS drug. Terahertz spectroscopy tracked the change in the polymorphic form of the drug after manufacturing during storage which yielded an inactive polymorph of the active ingredient.

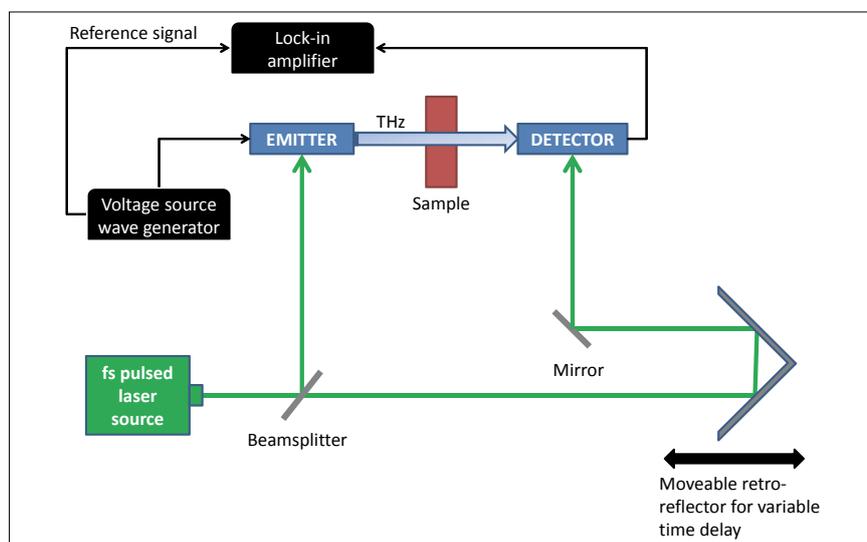
There are numerous other examples where terahertz spectroscopy can now regularly deliver results for complex questions and should be on the radar/in the toolkit of all analytical spectroscopists when considering how to solve particularly difficult analytical questions. You might just find the correct answer on the dark side!<sup>2</sup>

## Conclusions

So hopefully this brief article can awaken a flicker of interest in those who for many years had written off far-infrared spectroscopy as something of an oddity studied by people who like driving spectrometers into areas where they really are not designed to operate. Maybe when you are next standing in an airport gate being asked to hold your hands in the air while a 2.5m tall machine rotates around you, think of all the other applications that terahertz radiation can be put to.

## References

1. F. Platte and H.M. Heise, "Substance identification based on transmission THz spectra using library search", *J. Mol. Struct.* (2014). doi: <http://dx.doi.org/10.1016/j.molstruc.2013.12.065>
2. R.J. Falconer, "Terahertz spectroscopy's application to protein chemistry", *Spectrosc. Europe* **24**(2), 12 (2012). <http://bit.ly/11Dsxss>



**Figure 2.** Simplified schematic diagram of a time-domain terahertz spectrometer.