THz Spectroscopy – Techniques and Applications

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Abstract **Spectroscopy and related applications have accounted for a large proportion of the work in the THz spectral region. These have included laboratory studies of the radiative and collisional properties of molecules, ions, and radicals, as well as field applications such as atmospheric remote sensing and molecular radio astronomy. This paper will review established techniques and discuss new approaches.**

I. INTRODUCTION

The genesis of microwave, and ultimately THz spectroscopy, was the war time development of microwave radar. However, this development was greatly aided by a fortuitous (for microwave spectroscopy at least!) accident that placed a previously unknown transition of water in the middle of the spectral region that was being developed at the end of the war as the next new radar band. Not only did this make vast quantities of sophisticated equipment immediately available, but it also established the 'relevance' of the field.

Technology advanced rapidly, reviews were published [1], and by 1954 the submillimeter threshold at 300 GHz had been passed[2]. This drive toward ever higher frequencies was aided by the rapidly increasing absorption strengths of the transitions of many of the most important small fundamental molecules.

A strong argument can be made that this scientific focus led spectroscopists towards the development of practical and robust 'THz' technologies, including the crossed waveguide harmonic generator[3], electronic frequency control systems[4], quasi-optical propagation, and the exploitation of sensitive detectors to compliment the harmonic generation sources[5].

While microwave spectroscopy had a number of other streams, in the end this drive to higher frequency to observe the most fundamental molecular species provides the enduring legacy for the field. Because these small species are not only scientifically fundamental but also pervasive in many physical and chemical systems, the strong interactions in the THz region have led to a number of important applications.

II. SPECTROSCOPIC TECHNIQUES

Because low pressure gases have line Q's ~ 10^6, spectroscopic applications place a high premium on spectral purity and calibration accuracy. We will begin by briefly mentioning a number of approaches and providing references to more detailed discussions.

The first technique which provided access to the submillimeter spectral region was harmonic generation[2]. Key developments where the crossed waveguide harmonic generator[3] and its combination with cryogenic detector techniques[5] to significantly increase the sensitivity and reliability of spectroscopic systems. Even today, in their modern microelectronic form, this approach is the technology of choice for many applications.

It has also long been recognized that difference frequency mixing of 'optical' sources can be used to produce THz radiation[6]. Mixing elements have ranged from point contact MIM diodes[7] to fabricated photoconductive switches[8]. Because the THz radiation produced represents a small difference between two large numbers, spectral purity and frequency calibration have been a major emphasis. One approach has used lamb-dip stabilized CO_2 lasers[7], while another uses cavity stabilized cw diode lasers[9].

The generation of tunable sidebands from fixed frequency FIR laser sources is in some sense a combination of the first two approaches. Implementations include those based on both FIR discharge[10] and optically pumped lasers[11-13].

Femtosecond techniques based on the Fourier Transform relation between short pulses and THz radiation have also been reported. These have included both high resolution methods based on a periodic train of pulses[14, 15] as well as broadband techniques[16].

Fundamental electronic oscillators have also been successfully used in the THz. The most successful of these have been Backward Wave Oscillators (BWOs)[17], which have ordinarily been used in high resolution, phase locked implementations[18, 19].

Finally, we will discuss in somewhat more detail a relatively new approach to THz spectroscopy, the FAst Scan Submillimeter Spectroscopy Technique (FASSST)[20] shown in Fig.1. Like the spectral region itself, it adopts

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methodologies from both the neighboring microwave and infrared regions.

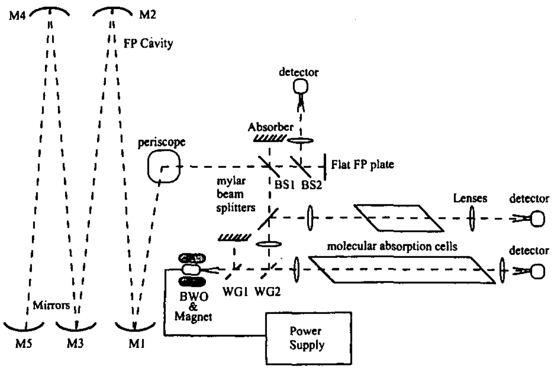

Fig. 1. The FASSST spectrometer.

In this example, an ISTOK OB-30 BWO is used to cover the 240 - 375 GHz region. The first wire grid polarizer provides a well defined polarization from the output of the overmoded BWO. The second polarizer is used to split the output power of the BWO, with ~90% being directed quasi-optically through the molecular absorption cell and detected by an InSb hot electron bolometer operating at 1.5 K. The remaining ~10% of the power is coupled into a Fabry-Perot (FP) cavity via a Mylar beamsplitter, which provides fringes for frequency interpolation between reference spectral lines of known frequency. In order to provide a highly accurate basis for the analysis of the frequency-voltage characteristic of the BWO, a folded FP cavity of length ~38.89 m is used to provide modes every ~3.854 MHz.

The philosophy behind this system is based on the fact that the source linewidth (short-term stability) of the BWO oscillator is much less than the Doppler width of a spectral line. Thus, phase-lock is needed not to improve spectral purity, but rather to stabilize against thermal and power supply induced long term (≥ 0.01 sec) drift and ripple. It is straightforward to show that a combination of power supply development and a fast frequency scan can 'freeze' these instabilities, so long as a frequency reference can be provided which will allow the BWO's frequency instability to be calibrated in software[20].

The size of the FP cavity is dictated by the need to interpolate between adjacent FP cavity modes and the details of the small scale structure of the frequency-voltage characteristic of the BWO. Fig. 2 shows a typical example. These fluctuations are caused by standing wave phenomena both within and external to the tube.

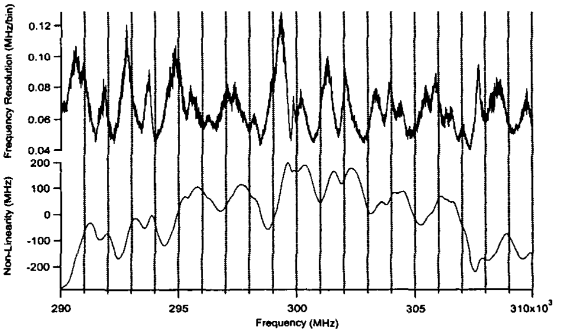

Fig. 2. Small scale variation in frequency-voltage characteristic (lower trace) and frequency differences between adjacent digitized points (upper trace) as a function of frequency for a typical BWO.

The FASSST approach makes it possible to measure thousands of spectral lines per second, with a frequency accuracy of a small fraction of a Doppler width (~0.1 MHz/3 x 10^{-6} cm^{-1}). Signal averaging is straightforward, and for equivalent integration times the sensitivity is the same as for slow-sweep, synthesized phase locked systems. Finally, FASSST is very simple in both concept and execution.

III. ANALYTICAL CHEMISTRY

Almost from the beginning of microwave spectroscopy, its potential for the chemical analysis of gases has been recognized (e. g. Chapter 18 of the classic monograph by Townes and Schawlow "The Use of Microwave Spectroscopy for Chemical Analysis")[21]. However, while techniques based on the ultraviolet, optical, and infrared regions of the electromagnetic spectrum have become standard analytical tools, this early promise has not been realized at longer wavelength.

In the late '50s and early '60s a commercial instrument, operating in the general frequency region between 10 and 40 GHz was developed and marketed by Hewlett-Packard. This instrument experienced some commercial success, being sold primarily to spectroscopists with interest in molecular structure. In hind sight, its modest success with the analytical community was due to the instrument's size, cost, and complexity.

However, analytical systems based on the FASSST concept overcome these limitations. In addition, they offer significantly greater generality, speed, and sensitivity.

As an example, consider Figure 3. It shows the FASSST spectra obtained with an ISTOK OB-80 BWO in an ~ 30 GHz region centered near 500 GHz that results from first adding 10 mTorr of Pyrrole (C_4H_5N) to the sample cell (upper trace), then 20 mTorr of pyridine (C_5H_5N) (middle trace), and finally 20 mTorr of SO_2 (lower trace). Fig. 4 shows an expansion of the ~ 0.2 GHz region near 511.8 GHz in Fig. 3. The spectral region in Fig. 4 is ~0.1% of the BWO bandwidth and represents ~0.01 second of data acquisition. In each figure the sensitivity is such that no noise can be displayed on the graph.

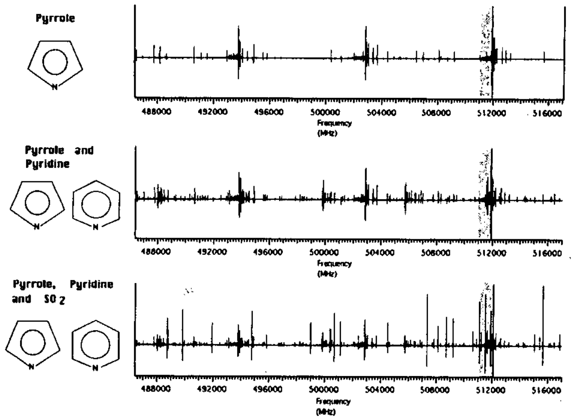

Fig. 3. FASSST spectra obtained with an ISTOK OB-80 BWO in an ~ 30 GHz region centered near 500 GHz which results from first adding 10 mTorr of Pyrrole (C_4H_5N) to the sample cell (upper trace), then 20 mTorr of pyridine (C_5H_5N) (middle trace), and finally 20 mTorr of SO_2 (lower trace).

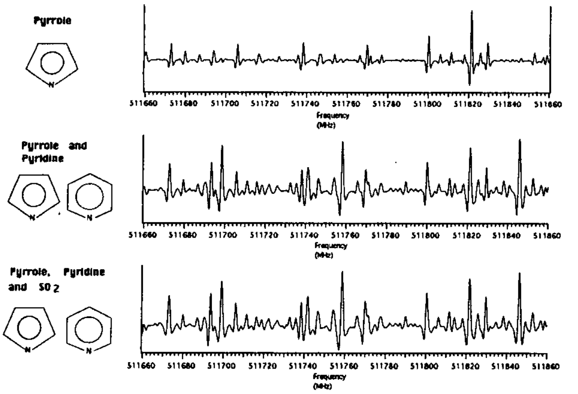

Fig. 4. An expansion of the ~ 0.2 GHz region near 511.8 GHz in Fig. 3. The spectral region in this figure is ~0.1% of the BWO bandwidth and represents ~0.01 second of data acquisition.

One way of viewing the information content and power of FASSST as an analytical tool is to recognize that if Fig. 3 were expanded to show all of its resolution elements in the horizontal and 1 mm of noise in the vertical, the resulting graph would be approximately 10 m high by 100 m long for each 1 second of data acquisition.

A more detailed discussion of a THz FASSST system used as an analytical instrument can be found in an A-pages article in *Analytical Chemistry*[22].

IV. THE FUTURE

While a number of developments have made the THz more accessible, probably the ones of greatest importance are those associated with microfabrication. This trend will clearly continue and probably accelerate as the mass market associated with wireless communication moves to ever higher frequency. As a brief example, consider the analytical chemistry application discussed above. While the implementation shown in Fig. 1 is very powerful, it is neither small nor inexpensive. However, work is underway to implement a solid state version of it which can be both. While the replacement of the high voltage tubes with solid state devices is an obvious extension, it is not a complete solution because of the large (~40 m) FP cavity used for frequency calibration. However, recall the need for this cavity was driven by the small scale frequency variation in the BWOs frequency-voltage characteristic. Since these variation must be driven by physics (e. g. standing waves and other reflections), their scale must be set by the size of the system which supports the reflections. For example, the output window of the BWO is ~15 cm from the slow wave structure. This sets a scale of 1 GHz for the small scale structure and much smaller scales are set by external reflections into the fundamental oscillator. However, solid state oscillators have orders of magnitude smaller sizes, thereby virtually eliminating small scale structure. Figure 5 shows an example, which verifies this supposition.

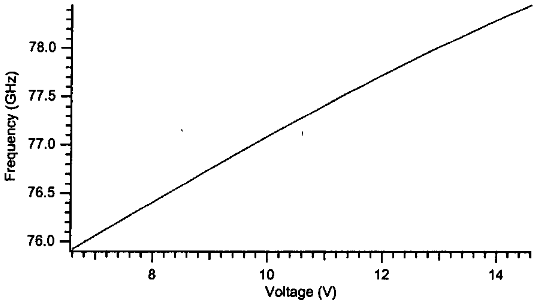

Fig. 5. Frequency-voltage characteristic of a solid state source.

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