Fast Scan Submillimeter Spectroscopy Technique (FASSST):
A New Analytical Tool for the Gas Phase

Siegward Albert* and Frank C. De Lucia b

Abstract: A new Fast Scan Submillimeter Spectroscopic Technique (FASSST) for analytical applications is described. It is based on voltage tunable backward wave oscillators (BWOs), a fast scan 'freeze' frequency instability, and optical calibration methods. FASSST, due to its high resolution, is used to record the gas phase rotational spectra of mixtures of molecules (e.g. aromatic or heterocyclic compounds). This technique provides an unambiguous identification of the individual component compounds. The combination of FASSST with gas chromatography is expected to be an excellent method for qualitative and quantitative analysis.

Keywords: Fast scanning technique · Gas phase spectroscopy · Rotational spectroscopy · Submillimeter spectral region

1. Introduction

A new Fast Scan Submillimeter Spectroscopy Technique (FASSST) [1] is described which makes the lower part of the electromagnetic spectrum, the submillimeter region (100 GHz–1 THz) accessible for analytical applications. The potential for use of microwave spectroscopy in chemical analysis has been recognized since its beginning [2]. However, successful spectrometers operating in this region have not yet been introduced due to the size, cost and complexity of such instruments.

The Fast Scan Submillimeter Spectroscopy Technique (FASSST) described here overcomes these limitations. In addition, it offers significantly greater generality, speed, and detectability. This has been achieved by the use of 1) the submillimeter (~100–1000 GHz) spectral region, 2) a fast scanning 'optical' technique rather than the more traditional microwave phase-lock methodology, and 3) modern data acquisition, signal processing, and computing. Here we give a brief introduction into the field of submillimeter spectroscopy, followed by a detailed discussion of the FASSST system. We will discuss how FASSST makes it possible to identify the individual components in a mixture of sulfur dioxide, cyclopentene oxide and trimethylene sulfide. Finally, we present an outlook of further developments of the FASSST system and possible combinations with other analytical techniques.

[1] J.E. Jarvis, A.L. Gray, R.S. Houk, 'Handbook of Inductively Coupled Plasma Mass Spectrometry', Blackie, Glasgow, 1992.
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ment die Kontrolle der Blindwerte zum einzig relevanten Beitrag wird, um noch tiefere Nachweisgrenzen zu erreichen. Die Analyse von geologischen Proben zeigt, dass die Methode durch die spektrale Auflösung bis weit über 10.000 tatsächlich für viele bisher interferierte Elemente dramatische Verbesserungen bringt. Die hohe Empfindlichkeit kann aber nur für die Elemente tatsächlich ausgenutzt werden, bei denen nicht gleichzeitig die hohe Auflösung benötigt wird. Zudem gibt es weiterhin Interferenzen, die nur mit noch höherer Auflösung getrennt werden könnten. In solchen Fällen können bewährte Methoden wie Aerosol- trocknungen eingesetzt werden, um zum Beispiel die Bildung von Oxiden zu reduzieren. Im Routinebetrieb kann auch der etwas höhere Aufwand für Optimierungen ins Gewicht fallen. Trotz dieser Einschränkungen bringt die ICP-MS mit Sektorfeld-Massenspektrometer durch die spektrale Abtrennung von Interferenzen und die dadurch erweiterte Elementpalette wesentliche Vorteile gegenüber den Geräten mit Quadrupol-Massenspektrometern.

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2. Rotational Spectroscopy in the Submillimeter Spectral Region

Although the difficulties of developing appropriate technology in the submillimeter spectral region have until now precluded its use for general analytical purposes, the underlying physics is very favorable. Briefly stated, the FASSST system is orders of magnitude more sensitive than systems operating in the adjacent microwave region, is significantly faster and less complex than other submillimeter systems, provides absolute quantitative analysis traceable both to fundamental theory and/or straightforward calibration, and provides orders of magnitude greater resolution and requires smaller samples than infrared systems (especially those of comparable size and complexity). The latter attributes result from the much smaller Doppler width in the submillimeter region, which makes the optimum sample pressure for both sensitivity and resolution 10-100 mTorr.

Fig. 1 shows an example of a FASSST spectrum of a molecule of moderate size and spectral complexity, pyridine, which can be used to illustrate the nature of the submillimeter rotational spectra observed with a FASSST system. Because a single FASSST scan contains \( \sim 10^6 \) frequency resolution elements, it is not possible to graphically display a complete, full band spectrum. Consequently, Fig. 1 shows a series of enlargements in both frequency and sensitivity which provides a good perspective. The 40 GHz scan shown at the top was recorded in a single \( \sim 1 \) sec scan, with the 300 MHz segment shown at the bottom recorded in \( \sim 0.01 \) sec.

The rotational energy levels of a molecule result from the quantization of its rotational kinetic energy:

\[
E_j = \frac{1}{2} \left( \frac{P_j^2}{I_1} + \frac{P_j^2}{I_2} + \frac{P_j^2}{I_3} \right)
\]

where the \( P_j \) are the components of the molecular angular momentum and the \( I_i \) are the components of the principal moments of inertia. All real molecules have additional effects (e.g., centrifugal distortion, perturbations, and internal rotations) which significantly complicate the spectroscopic problem [3] but which have minimal impact in analytical applications and will not be considered further here.

The fundamental underpinnings of the high specificity of FASSST are that the rotational degree of freedom is unique in that many levels are thermally populated and the strong fundamental rotational transitions which arise from these levels are not associated with functional groups which may be constituents of many similar molecules. Rather they depend upon the global moment of inertia tensor \( I \) of the molecule. Since submillimeter spectroscopy is sensitive to changes in each of the \( I_j \) of \( < 10^{-7} \), each molecule has a unique signature even if only a few of the lines of its rotational structure can be detected and measured.

3. The FASSST System

The FASSST system, shown in Fig. 2, is simple in concept and straightforward in execution. Its power is derived from the physics which governs molecular interactions in the submillimeter region and the use of modern computational techniques to coordinate and exploit the capabilities of the elements of the system. In this example a Backward Wave Oscillator (BWO) tube (ISTOK OB-30) is used to cover the 240–375 GHz region. Similar tubes are available for the 100–1000 GHz region [4]. The beam splitter is used to split the output power of the BWO, with 90% being directed quasi-optically through the molecular absorption cell of length 1–10 m and detected by an InSb hot electron bolometer [5]. The remaining 10% of the power is coupled into a Fabry-Perot cavity via a mylar beam splitter, which provides fringes for frequency interpolation between reference spectral lines of known frequency.

In order to maximize the dynamic range of the spectrum, the low frequency roll off in the analog amplifiers between the detector and the A/D input to the computer is adjusted to provide an approximately first derivative lineshape and to generally suppress the recording of the power variations of the BWO and multipath interference effects. The con-
volution of the recorded first derivative lineshape with a reference first derivative lineshape in the signal processing software results in the approximately second derivative lineshape shown in Fig. 1. For the study of weaker lines, additional analog gain is used at the expense of the measurement of the amplitude of the stronger lines. In the current system (which is not optimized for sensitivity), strongly absorbing lines are of S/N $10^6$ in 1 MHz of bandwidth (1 usec of integration time). Comparison of spectra obtained on phase locked systems with FASSST spectra shows that they too are Doppler limited.

Here we will provide an overview of the physics of the BWO system and focus on those aspects most important for analytical systems: The characteristics of the BWO submillimeter source and the 'optical' frequency calibration scheme. Additional details are provided in a recent Review of Scientific Instruments article [6].

3.1. The BWO Characteristics

There are two requirements for the submillimeter sources which are necessary for a FASSST system. The first and most important requirement is that the spectral width of the source, averaged over the time required to sweep through the line (typically $10^{-3}$ sec) be much less than the spectral linewidths. Since studies done over many years have shown that the short-term width of free-running ISTOK BWOs is < 20 kHz [7] and Doppler widths near 300 GHz ~ 1 MHz, this requirement is easily met. The second requirement is that the sources be voltage tunable over an 50% frequency range. This tunability is necessary both for the desired spectral coverage and for the optical calibration scheme employed. This range contains $10^3$ spectral resolution elements (Doppler limited) and $10^4$ distinct measurable line frequencies. For the large majority of molecules of analytical interest, many (100–10000) of the resolution elements will be filled with strong, fully resolved 'fingerprint' lines.

The BWO is a classical device in which a beam of electrons interact with a periodic slow wave structure, which supports the propagation of an electromagnetic wave in the opposite direction [8–10]. To accomplish a net transfer of energy from the electrons to the electromagnetic wave and support oscillation, the electrons must be bunched and the interaction between the bunches and the wave organized so that the bunches always interact with a phase of the wave which produces deceleration. Because the electron velocity has a first order effect in this phase relationship, the frequency of oscillation is strongly dependent on the electric potential between the cathode and slow wave structure, thus providing broad electrical tunability.

In order to maintain the required phasing, the spatial periodicity of the slow wave structure must be on the scale of the distance traveled by the electron bunch in one oscillation of the electromagnetic wave. For an accelerating voltage of a few thousand volts and $\lambda = 1$ mm, this distance is on the order of 100 $\mu$m. Although this is large by modern microfabrication standards, energy handling capabilities decrease and circuit losses increase rapidly with decreasing wavelength and circuit size. As a result, the manufacture of BWOs and other electron beam tubes for $\lambda < 1$ mm has been a challenge. Nevertheless, in spite of these small dimensions and highly energetic electron beams, years of development work on these sources have resulted in a high level of reliability for the ISTOK BWOs used in this work. In three years of operation (more than 1000 h), we have not had a BWO burn out or experienced any noticeable deterioration in performance. This result is consistent with the experience of others.

The high spectral purity and frequency tunability of the BWOs can only be exploited in the context of a power supply and calibration scheme with complimentary properties. Typically, a BWO tunes 100 GHz with a voltage variation of 2000 V, a tuning rate of 50 MHz/volt. If it is desired that the voltage fluctuations of the power supply result in a frequency variation which is no more than 10% of a linewidth (0.1 MHz), the fluctuations must be less than 2 mV in the context of a power supply capable of sweeping several thousand volts. We have developed such a power supply, which is described in a recent article [6]. Alternatively, for the somewhat relaxed frequency calibration requirements of many analytical applications and for very fast scans, a number of simple commercial power supplies are satisfactory. More specifically, in a typical FASSST scan 10$^4$ Fabry-Perot fringes/second are recorded. Since the resulting 10 usec between calibration points is much less than the period of power supply ripple, thermal drift, and typical pick-up, these instabilities are 'frozen' and compensated for in the calibration software (see next section). For example, the spectrum of Fig. 1 was obtained with a simple Bertan 210-05R switching power supply.

3.2. The 'Optical' Frequency Calibration of FASSST

In a FASSST system the synthesized frequency reference and phase lock typical of high resolution submillimeter spectrometers is replaced by a system more typical of optical spectroscopy. If the frequency of a BWO as a function of voltage were linear, the frequency calibration scheme could be as simple as having two spectral lines of known frequency somewhere near the opposite ends of the frequency sweep range and using linear interpolation. However, the small scale structure is much more complex. If the effects of this small scale structure are not properly treated, the frequency accuracy of the FASSST system is 100 MHz, approximately 1000 times worse than that required for high resolution spectroscopy and 100 times worse than is desirable for analytical applications. However, with a small FP mode spacing (5 MHz) it is possible to use simple linear interpolation methods to measure line frequencies.
to 1/10 of the Doppler limited linewidth [6]. Based on these considerations, the basic FASSST calibration scheme is to:

a) take a fast (10^4–10^5 MHz/sec) scan over the spectral region of interest,

b) include two or more reference lines (typically 50 are available),

c) use the known frequencies of the reference lines to determine the FP cavity mode spacing and absolute frequency,

d) count FP modes to establish the frequency of each fringe, and

e) use linear interpolation between the two nearest FP modes to calculate molecular absorption frequencies.

4. The Characteristics of Analytical Spectroscopy in the Submillimeter Region

Fig. 3a shows the FASSST spectra obtained with an ISTOK OB-80 BWO in an ~2 GHz region near 513 GHz which result from first adding 10 mTorr of SO\textsubscript{2} to the sample cell (upper trace), then 20 mTorr of cyclopentene oxide (C\textsubscript{5}H\textsubscript{8}O) (middle trace), and finally 20 mTorr of trimethylene sulfide (lower trace). Fig. 3b shows an expansion of the ~0.2 GHz boxed region near 515.0 GHz. The spectrum in Fig. 3b 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.

The lines in the top trace of each Fig. are Doppler limited, whereas those in the middle and lower trace show modest pressure broadening. Trimethylene sulfide is a molecule of intermediate size and weight and shows both regions of widely spaced lines as well as more compact features. It is clear even in the small expanded spectral interval displayed in the figure that each molecule has a unique signature, as they do in almost any other randomly chosen small interval throughout the submillimeter region. On the other hand, SO\textsubscript{2} and cyclopentene oxide have only about 5–10 strong lines in the 2 GHz region near 514 GHz and two in the smaller 0.2 GHz expanded region. A region which contains a few of their several hundred strong submillimeter lines would need to be selected for their identification and quantitative measurement.

4.1. Sensitivity

The FASSST system described here operates at frequencies which are 10–100 times higher than the region historically referred to as the microwave. The distinc-
tion between systems operating in the microwave and the submillimeter regions is very important. Molecular absorption strengths increase with frequency with a functional dependence between $v^2 - v^3$, peaking somewhere in the submillimeter region. As a result, spectroscopic systems in this region are between $10^2$ and $10^6$ more sensitive than the much more common microwave systems. Additionally, the larger spectral region results in virtually universal coverage of molecular species, subject only to the requirement that the species have a dipole moment or a large amplitude vibration in the submillimeter. The only chemically stable species which is an exception is HF ($\sim 1200$ GHz). The molecules HCl ($\sim 600$ GHz), HBr ($\sim 500$ GHz), and NH$_3$ ($\sim 600$ GHz) are not observable by the use of the OB-30 BWO, but can be measured with the other BWOs (OB-32, 370–535 GHz; OB-80, 526–714 GHz) used in this work.

Sensitivity comparisons with infrared systems are more complex because of the diversity of infrared technologies which have been used for analytical purposes, as well as the variety of analytical applications. The FASSST system is inherently very sensitive, because it is based on powerful electronic oscillators which are fundamentally very bright and very quiet and, because quiet detectors are available at long wavelengths. In addition, noise due to microphonics is much reduced at long wavelengths and rotational transition moments are related to the total electric dipole moment.

The Table shows the absorption coefficients typical of lines for a number of molecules of interest. In the current FASSST system, which uses 1 µsec of integration time, the system S/N is $10^4$. Extensive experience with submillimeter spectrometers has shown that the full statistical gain associated with smaller bandwidths can be obtained out to at least 1 second of integrating time, with longer integrating times often used. The Table lists detection limits for a 1 second integration period, a fairly short period for most analytical applications. An absorption cell length of 1 m is nominal for submillimeter spectroscopy, unless absorptions are expected to be weak, in which cases long-path techniques can be used.

Effective Path Lengths (EPLs) of 100 m can be achieved by use of Fabry-Perot cavities or White-type cell configurations. Dilution ratios are calculated relative to a nominal total pressure of 10 mTorr. In the Doppler limit, the minimum detectable sample depends upon the cell cross section, but not its length. In the Table, the minimum detectable sample is calculated for a cell of cross section $10^2$ cm$^2$, somewhat larger than fundamental waveguide at $\lambda = 1$ mm (300 GHz).

### 4.2. Specificity and Rotational Spectroscopy

The large number of resolvable channels in the submillimeter region, the large number of thermally excited rotational lines which populate these resolvable channels, the high signal to noise attainable even with very short integrating times, and the absolute measurement of absorption coefficients available in the submillimeter make it possible in virtually all scenarios to set false alarm rates that are so low as to be considered absolutely specific.

Because Doppler limited lines for molecules whose masses are 100 AMU have line Q's of $3 \times 10^3$ independent of spectral region, any Doppler limited spectroscopic instrument has $\sim 10^5$ resolution elements in a 30% bandwidth ($Q=\Delta V/\nu$). However, if the rotational line density is comparable to or greater than the Doppler width so that adjacent lines overlap, the spectral resolution that can be used for analytical purposes is reduced to that of the width of the unresolved rotational bands or their 'features' rather than that of the Doppler width of the instrument itself. Even in Doppler limited infrared systems, this important transition occurs for molecules whose size/mass are greater than that of ClONO$_2$ [11].

### 4.3. Quantitative Analysis

Because the strengths of the molecular rotational transitions observed in the submillimeter region depend upon the permanent molecular dipole moment (which can be measured to great accuracy using the Stark Effect) and angular momentum quantum mechanics (for which 'exact' solutions are obtainable), measured fractional absorption can be translated into absolute concentration if the partition function is considered. Although rotational partition functions are straightforward to calculate, large molecules can have significant vibrational partition functions with significant contributions from largely unknown low lying vibrational modes. In these cases the calculations must be verified experimentally with known samples.

Most importantly, because of the high resolution of the FASSST spectra, any of many isolated rotational lines can ordinarily be used for quantitative purposes; thus providing massive redundancy and eliminating the possibilities of contributions from interfering and overlapping lines. For example, in Fig. 1, anyone of more than 100 lines could be used to determine the concentration. In real systems, moderate efforts at establishing the partition functions and fractional absorption of the submillimeter power should result in a quantitative uncertainty of about 10%, whereas 1% should be achievable for most species with modest effort.

### 5. Future Developments

The system described above has been configured as a general purpose laboratory instrument, with high resolution spectroscopic capabilities. For many applications modifications are appropriate. To give a sense of the possibilities, we will briefly describe six:

1) A smaller and more compact system: For analytical purposes, which require identification rather than state-of-the-art spectroscopic measurement, the frequency calibration requirements can be relaxed significantly. For example, frequency measurement accurate to a Doppler broadened linewidth would still...
leave $10^4$ distinct channels for identification rather than the $\sim 10^6$ channels of the system. This reduces significantly both the power supply stability and FP cavity size requirements. Additionally, for applications which do not require maximum sensitivity and spectral coverage, the system has an all solid state analog (FASSST-SS) based on chirped GUNN oscillators and Schottky diode detectors.

2) **Sampling of higher pressure environments:** The sensitivity and selectivity of a FASSST system is optimal when the sample pressure is 10–100 mTorr. It is common in many analytical applications to introduce samples into an instrument, which in turn changes the physical conditions before the fundamental measurement interaction occurs. For example, pressures in mass spectrometers are typically $<10^3$ Torr. These same techniques (including preconcentration methods) which have been developed for a wide array of analytical applications can also be used with FASSST systems.

3) **Automated identification and quantification of samples:** The existing software which is used for the calibration of the FP fringes is based on the automated assignment of spectral lines of a known reference gas. This algorithm, which is very robust, can easily be extended to compare a library of references gases for their identification and quantification. As the spectra above show, the information content of the high resolution FASSST spectra is very high and identification and quantification even in relatively complex mixtures is possible. Since absolute absorption coefficients for rotational transitions can be accurately calculated from measured dipole moments, the recovery of absolute concentrations is also straightforward.

4) **Larger molecules:** The study of the rotational structure of molecular spectra has ordinarily been limited to relatively small molecules. In the infrared, the rotational structure is ordinarily obscured by Doppler broadening for molecules of more than 5–10 atoms. In the microwave, the sheer number of rotational lines of heavier species has been incompatible with the relatively slow and/or narrow banded systems previously used. Because rotationally resolved spectra provide absolute specificity even in complex mixtures, the extension of FASSST to large molecules whose other physical properties are often similar will be important. Accordingly, we feel that the study of heavy organic/biological species with the FASSST system is a particularly exciting scientific opportunity.

5) **Additional sensitivity:** Under most circumstances, detectivity is proportional to the effective path length of the system. By the use of White-type cells, or other multiple pass/cavity schemes, about two orders of magnitude are obtainable. Also, the amplitude noise properties of the BWOs are not well characterized in the spectral region which is the fundamental of the FASSST signal detection channel (100 kHz). It is probable that significantly greater system S/N (currently $10^4$ for 1 sec of integration) can be obtained.

6) **Combination with gas chromatography:** For many applications it has been found to be advantageous to combine gas chromatography with a spectroscopic technique, usually infrared or mass spectrometry based [12][13]. Because the recording time of FASSST spectra is shorter than the separation time of the analytical column, the output of the column can be connected directly to the absorption cell of the spectrometer. In addition, because the optimum sensitivity of the FASSST system occurs at a much lower pressure (10 mTorr) than that of infrared or optical systems, significantly smaller sample separations from the column are required.

### 6. Conclusions

In summary, we describe a new technique based in the submillimeter spectral region, which makes this part of the electromagnetic spectrum accessible for analytical purposes. In this spectral region fingerprints arise from the rotational energy levels of molecules. These fingerprints are ordinarily complex and unique because many rotational levels are thermally populated. Additionally, in the submillimeter the underlying physical interactions between radiation and matter are strong and at low pressure the small Doppler broadening allows high resolution. Additionally, the FASSST methodology is fundamentally simple and powerful. It is based on electronically tunable sources of high spectral brightness and spectral purity. Fast scanning, ‘optical’ calibration, and modern data acquisition and computational techniques are used to replace the more complex phase lock techniques ordinarily used. The result is a system with a unique combination of speed, sensitivity, and specificity. We believe that these attributes along with FASSST’s generality and configurability will lead to a wide range of analytical applications.

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