Submillimeter Wave Spectroscopy and the Search for Life on Planets

Brian J. Drouin, Ken Cooper, Robert A. Stachnik and John C. Pearson
Califronia Institute of Technology, Jet Propulsion Laboratory, Pasadena, CA 91109 USA

***Abstract*—Absorption and emission of gases in the submillimeter wavelengths is currently exploited for laboratory spectroscopy as well as remote astronomy and limb sounding. We are developing a field-ready submillimeter spectrometer that will enable in-situ sensing with a goal for characterization of biogenic gases and life tracers.**

I. Introduction And Background

AT the Jet Propulsion Laboratory's Millimeter and Submillimeter Spectroscopy Laboratory we are developing a heterodyne spectrometer that will enable fieldwork with sensitivity and dynamic range that rivals the demonstrated laboratory spectroscopy and complements *in-situ* mass spectroscopy.

Options for *in-situ* exploration are limited by instrument size, power and lifetime. We are addressing each of these issues in the laboratory system with technology developed for the remote sensing instruments MLS and Herschel.

The size of the laboratory system is not optimal due to 1) a desire for long absorption path-length coupled with needs for flexibility in bandwidth; 2) The general usage of liquid helium detectors to achieve high sensitivity; and 3) Cumbersome supporting electronics designed for high performance and versatility. We will optimize the size of the *in-situ* instrument by 1) fixing the frequency range and designing compact, folded optics; 2) replacing the liquid helium cooled detectors with either room-temperature Schottky diode detectors or heterodyne mixers; and 3) designing custom electronics for targeted high-performance signal processing.

Traditional millimeter and submillimeter spectrometers generally have a wasteful power source such as a Klystron or Backward Wave Oscillator (BWO) which is weakly coupled into the high-sensitivity detection system. At JPL we have pioneered the usage of submillimeter multiplier chains that operate with higher efficiency than the free-running oscillators and reduce the number of supporting electronics[1]. In this configuration the stable reference oscillator is directly multiplied to the band of interest, rather than used as a locking source for the oscillator. With the removal of the Klystron/BWO from the system the synthesizer/multiplier chain(s) become the dominant power consumer(s) in the system. An ideal system will have a modest power (~100 μW) source with nearly 100% quasi-optical coupling of the light through the absorption path into the heterodyne mixer in concert with sufficient pumping (~10 mW) of the mixer. A well designed system will achieve this goal across the source/detector bandwidth. With streamlined electronics the only way to reduce power consumption further is to reduce system performance. Since performance increases with source power (until saturation occurs) a mission configuration will ultimately be driven by the science goals and engineering constraints. Following this path, at some level of the performance, the heterodyne method will become less competitive versus an optimized direct detection method using a Schottky diode. This less sensitive, alternative configuration would reduce power consumption because of the need for only one oscillator.

Laboratory experiments with liquid helium cooled detectors are inherently limited by the hold time of the Dewar. Usage of a cryostat increases the power consumption and complexity of the instrument. Therefore we have decided to implement room-temperature mixer/diode technology for the *in-situ* system. The heterodyne detection scheme will require attention to the phase of the intermediate frequency. Classical systems have implemented mechanically tuned bridges to achieve this balance. We will digitally process the intermediate frequency to allow phase adjustments to be compensated digitally.

II. Results

A prototype heterodyne system at 100 GHz is under construction and 300 and 600 GHz diode detection systems are in routine use for science programs. The Figure shows data acquired at 556 GHz and 547 GHz for water and ^{18}O water (natural abundance) measured with a JPL built multiplier chain and a Virginia Diodes Schottky detector.

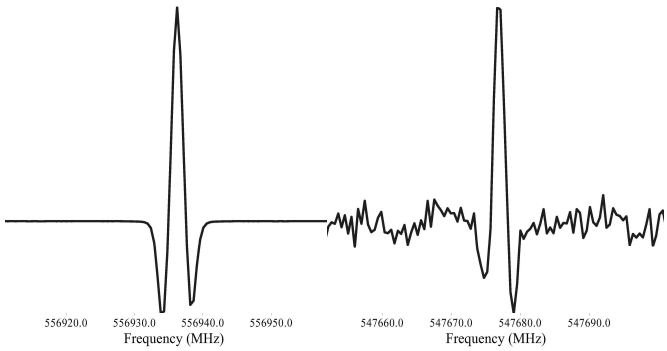

Figure 1. Modulated absorption spectra of water (left - 50%T) and ^{18}O water (right - 0.25%T) recorded with 100 kHz frequency modulation of a 10 μW source coupled into a Schottky diode detector in a 10 cm path. Each scan shows 100 co-added 25 ms sweeps with 125 measurements across 30 MHz.

III. Planetary Science Potential

This *in situ* system will mirror the operation of other gas phase techniques, *i.e.* gas from the ambient atmosphere, or an onboard gas generating experiment, is pulled into a chamber and analyzed. Frequency coverage over a gigantic range of

978-1-4244-2120-6/08/$25.00 ©IEEE.

specific gases creates huge discovery potential, and the high sensitivity allows trace species (e.g. 1 ppm or $2x10^{12}$ molecules/cm^3 at 0.1 Torr and 300 K) to be probed for isotopic ratios (an H/D ratio of $1x10^{-4}$ is 10 ppt in 1 ppm carrier). This realizes science experiments such as searching for potentially biogenic gases.

A premier feature of the technique is high sensitivity and specificity for detection and identification of small organic species and associated isomers and isotopologues. This may enable future exploratory missions to accomplish a number of significant questions for astrobiology, including whether or not biological systems were once, or continue to be, active at *in-situ* probe sites.

In-situ techniques currently take advantage of atomic and molecular spectral signatures from gamma-rays through the infrared. The longer wavelengths, where gas-phase rotational spectra can be probed, provide high sensitivity and specificity for gas phase species. However, these wavelengths have not been utilized for *in-situ* studies primarily due to technical issues which have now been overcome. Typical limitations of existing *in-situ* gas analysis techniques are, (1) sensitivity; such as the mass spectroscopy limit of a few ppm for most species, and (2) selectivity; such as fluorescence spectroscopy which requires chromophores. Infrared spectroscopy provides the promise of high sensitivity and a broad range of absorbing species that may be detected. However, a practical system such as the Tunable Laser Spectrometer on the Sample Analysis at Mars has expensive requirements for each additional science product and demonstrates that these systems are inherently limited to a few selected species. Our technique has extensive molecular coverage, high sensitivity and innate selectivity thanks to several coincidental physical realities.

1) A submillimeter spectrum can be measured when molecular rotation creates an oscillating electric or magnetic field (dipole interactions). Typical dipole moments are ~1 Debye, which are large enough to produce absorptions of 10^{-4} per cm.

2) Rotation is typically the lowest energy mode of the molecule. Rotational spectra have a common origin at zero frequency and spectra appear in the millimeter and submillimeter wavelengths.

3) At low density, pressure broadening can be neglected and spectra exhibit Doppler limited linewidths, providing the high resolution required to separate spectral features.

4) Spectral features have unique positions that are dependent on molecular inertial moments, therefore every molecule, isomer and isotopomer has a unique spectrum.

A submillimeter gas detector takes advantage of this by probing a spectral region that is rich with every kind of molecular species. Furthermore, the bandwidth of a tunable submillimeter source is gigantic in comparison with the width of each spectral feature, and is also large enough to encompass at least one transition of each diatomic (non-hydride) species. Additionally, polyatomic molecules tend to have many transitions available. Because each spectrum is unique, overlap and spectral confusion can be treated with an algorithm that ensures a confident detection.

The integrated absorption intensity of any molecular gas transition at any wavelength is calculated from the following equations[2,3]:

$$I(\upsilon,T)=\Gamma(\upsilon)I(T),\quad \Gamma(\upsilon)=e^{-((\upsilon-\upsilon_0)/\Delta\upsilon_D)^2},$$

$$I(T)=\left(\frac{8\pi^3}{3hc}\right)\upsilon S\mu^2\left[e^{-E''/kT}-e^{-E'/kT}\right]/Q$$

I(ν,T) is the temperature and frequency dependent absorption intensity. Γ(ν) is the lineshape, given here as only the Doppler profile. I(T) absorbs the remaining quantum mechanical parameters. Here, *h* is Planck's constant, *c* is the speed of light, ν is the frequency, *E"* and *E'* are the upper and lower state energies, respectively, *k* is Boltzmann's constant, *T* is the temperature, *S* is quantum line strength, μ is the dipole moment and *Q* is the partition function. In rotational spectra the energy exponents are typically $e^{-E/kT} \sim 0.01\text{-}0.1$. Plugging in typical values for a generic species, of say 100 atomic mass units and a 1 Debye dipole moment, results in a peak absorption of $\Delta I/I = 10^{-4}$ cm^{-1}Torr^{-1} , *i.e.* the rotational transitions (at 1 Torr pressure) will be optically thick (>10% absorption) in 1 meter of absorption pathlength. Transition moments of infrared and electronic transitions are typically 1-5 orders of magnitude smaller than rotational transitions.

The intensity of a transition is distributed over the linewidth, $\Delta\nu_D$, and the peak absorption ΔI is proportional to $I(\nu,T)/\Delta\nu_D$. Other contributions to rotational linewidths include: spontaneous emission broadening (inverse of Einstein A coefficient or lifetime), Doppler (or thermal), and pressure broadening (collisional). Rotational spontaneous emission linewidths are a few kHz. The Doppler width ($\Delta\nu_D \propto \nu\sqrt{(T/m)}$ is typically 0.2 MHz in the millimeter wavelengths and < 1 MHz in the submillimeter wavelengths[3]. Pressure broadening (2-15 MHz/Torr) is independent of wavelength[3]. In the Doppler limit (no collisional broadening) the frequency dependence of the intensity is cancelled, resulting in peak line strength for any transition dependent only on the dipole, the energy factors and the partition function. This often results in the rotational band being the strongest peak absorption per unit path length in the entire electromagnetic spectrum. Since all absorption spectroscopy instruments detect peak absorption this is very favorable to rotational spectroscopy in the THz range.

The power transmitted per unit length *x* of gas cell is $P_x = P_0 e^{-\Delta Ix}$. All molecular transitions have a maximum absorption per unit length, but the line width is determined by the Doppler width in the low-pressure limit and by pressure broadening at higher pressure[3]. In the frequency range chosen the ideal pressure for detection is 5-100 mTorr.

The number of effective spectral resolution elements in rotational spectroscopy is determined by the Doppler width (~200-300 kHz) of the rotational transitions. This results in 500,000 effective resolution elements in a system bandwidth of 100 GHz. Since spectral frequencies in the rotational bands are unique (defined by moments of inertia), the high resolution

978-1-4244-2120-6/08/$25.00 ©IEEE.

will clearly distinguish different chemicals, isomers and isotopomers.

A THz transceiver optimized for high spectral purity measurements of small power fluctuations at specific frequency intervals is required to take advantage of the favorable molecular physics. The frequency calibration, frequency stability and frequency repeatability of a submillimeter system are defined by the lock of the oscillator to a reference[4] (1 part in 10^8 is reasonable for a simple quartz crystal). The instrument resolution and coherent detection limit is determined by the spectral purity of the fundamental oscillator multiplied by 20 log(N), where N is the total harmonic number to the output frequency. Typically, less than 100 Hz can be achieved in the submillimeter regime. The instrument will measure 10-20 points across each line shape (effective resolution element) allowing the line width and integrated intensity to be quantitatively determined.

The key figure of merit for a millimeter or submillimeter wave system is the smallest change in power that it can detect per unit time. For the spectrometer to make detections and to quantify absorption, the gas observed must absorb more power than the minimum detectable change of power in the observation time or it will not be detected.

Heterodyne absorption spectroscopy relies on detecting the small change of a large signal due to absorption by a trace concentration of some molecule. In heterodyne spectroscopy the sum of the signal voltage and the noise voltage are squared in the detector. The result is the noise observed is proportional to the square root of the input power. A simple sensitivity figure of merit can be obtained which is the square root of the carrier to noise ratio for the smallest change in power that can be detected. The minimum detectable absorption, $\alpha_{min}L = I(T)/\Delta\nu_D$, is given by the following equation:

$$\Delta P_{\min} = P_{rx}(1-e^{-\alpha L}) = \sqrt{2P_{rx}kT_{sys}\Delta\nu},$$

where P_{rx} is the power received, T_{sys} is the receiver system temperature, and $\Delta\nu$ is the fixed detection bandwidth. The absorption α is the gas absorption in cm^{-1} and L is the length of the absorption cell in cm. With a carrier power[5] of ~100μW and a noise temperature of 6000K, our system will achieve a carrier-to-noise ratio of approximately 10^{15} in a 1Hz bandwidth, resulting in a minimum fractional change in measured power of $\Delta P_{min}/P_{rx} \sim 4x10^{-8}$.

In comparison with direct detection (a simple diode) and large source powers the kT_{sys} term can be augmented through addition of the detector NEP. So, for a diode with low input power and low 1/f noise, the minimum detectable change in power is comparable to the NEP which is typically $1\text{-}10x10^{-12}$ Watts (the equivalent factor for the heterodyne system is $4x10^{-12}$). In theory a diode measurement of a small change in a 10 μW source can achieve a minimum fractional power measurement of $1x10^{-7}$. However a diode is limited by saturation from high input power as well as 1/f noise, therefore measurements approaching the NEP are unrealistic. In practice measurements of minimum fractional changes in power are one to three orders of magnitude above the NEP[5]. In our example shown in Figure 1 the measured absorption of $H_2{}^{18}O$ water is $2.5x10^{-3}$, in principle only 3 frequency measurements are required to determine the signal intensity, giving an equivalent measurement time of (3/125)0.25s, or 6 ms which gives a minimum fractional absorption measurement of $1.5x10^{-5}$ (in one second).

In these two comparable, and potentially *in situ*, techniques, the heterodyne detection is more sensitive when given no constraints for system mass and power, but the diode detection competes or wins when the available power source is weak.

IV. Discussion

There are other methods for development of a THz trace-gas detector. Currently the most viable technique is via photomixing of infrared or near-infrared lasers. The range, tunability and stability of these systems are transferred from the laser specifications. The photomixing technique has a broader frequency coverage than the typical multiplier chain, however this only increases molecular coverage for a small number of light molecules (mostly hydrides) which are readily detected by complementary techniques. The photomixing power output rivals harmonic multipliers above a THz, however, the primary spectral region for exploiting molecular spectra is 0.1-0.8 THz where the multiplier chains are still more powerful. Furthermore, beginning with high frequency components (lasers) inherently gives the system more phase-noise. The superior phase noise characteristics available with RF sources in the multiplier chain will allow full exploitation of coherent integrations.

Overall we see a clear path for the technique to be nurtured for its analytical potential and optimized for usage in remote environments. Life detection, *vis a vis* exploration of our neighboring planets and moons, will require highly capable tools such as this concept in order to piece together chemical and biotic information from alien environments.

Acknowledgement

This work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

References

[1] B.J. Drouin, F.W. Maiwald, J.C. Pearson, "Application of Cascaded Frequency Multiplication toMolecular Spectroscopy," in *Rev. Sci. Instr*, 76 (9): Art. No. 093113, 2005.

[1] Townes, C.H. & Schawlow A.L., 1975, Microwave Spectroscopy, Dover, New York.

[2] Gordy, W., & Cook R.L., 1984, Microwave Molecular Spectroscopy, John Wiley & Sons, New York.

[3] Best, R.E., 1984, Phase-Locked Loops Theory, Design, and Applications, McGraw-Hill, New York.

[4] Maestrini, A., Ward, J.S., Gill, J.J., Javadi, H.H.S., Schlecht, E., Tripon-Canseliet, C., Chattopadhyay, G., & Mehdi, I.,2005, "A 540-640 GHz High Efficiency Four Anode Frequency Tripler," IEEE Trans. Microwave Theory and Techniques, 53(9) 2835.

[5] Hesler, J. L. and Crowe T. W. "Responsivity and Noise Measurements of Zero-bias Schottky Diode Detectors" 18th Intl. Symp. Space Terahertz Techn., Pasadena, March 2007.