HIGH RESOLUTION SPECTROSCOPY IN THE MICROWAVE AND FAR INFRARED

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ABSTRACT

High resolution rotational spectroscopy has long been central to remote sensing techniques in atmospheric sciences and astronomy. As such, laboratory measurements must supply the required data to make direct interpretation of data for instruments which sense atmospheres using rotational spectra. Spectral measurements in the microwave and far infrared regions are also very powerful tools when combined with infrared measurements for characterizing the rotational structure of vibrational spectra. In the past decade new techniques have been developed which have pushed high resolution spectroscopy into the wavelength region between 25 μm and 2 mm. Techniques to be described include: (1) harmonic generation of microwave sources, (2) infrared laser difference frequency generation, (3) laser sideband generation, and (4) ultra high resolution interferometers.

INTRODUCTION

The rotational spectra of molecules provide a very sensitive probe for remote sensing in the atmospheres of planets and the interstellar medium. The rotational lines are very narrow and uniquely characteristic of the species observed. Since the lines can be observed in thermal emission, temperature can can often be determined. In addition, the profiles of the lines can be used to infer pressure and species abundance. When observations are made close to the planet, limb observations can be made with great sensitivity. Weight and power limitations have made limb observations impractical for observations of planets other than the Earth. However, nadir observations are still of great utility provided that there is sufficient contrast between sources of continuum emission (ground and clouds) and the molecular emission. A consequence of this limitation is that observations are most sensitive to areas of planetary atmospheres which are at a different temperature than the ground or the cloud tops.

To interpret the data, or indeed to determine the sensitivity of a potential instrument, it is essential for laboratory spectroscopy to determine the transition frequencies of the lines, their pressure broadening coefficients, and their strengths. It is also important to determine the spectra of all plausible molecules so that interfering lines are avoided. These needs are common to all regions of the spectra where high resolution observations are made. In fact, determinations of rotational spectra and infrared vibrational spectra have been combined in a powerful way to provide more accurate information for use in both spectral regions.[1]

The trend for planetary instruments which observe rotational lines is to evolve to higher frequency. The antenna optics become smaller with smaller wavelength and the absorption

coefficients of molecules generally become larger. Thus, there is both a size premium and a sensitivity premium in moving to higher frequency. In addition, many of the hydride molecules such as NH_3, PH_3, H_2O, HDO, CH_3D, and HCN have their predominant spectra in the far infrared. Other molecules such as CO and SO_2 have strong spectra throughout the far infrared. The difficulty with this region is that water in the Earth's atmosphere absorbs strongly, and so observations are best made from space. Technology for high resolution submillimeter and far infrared instruments is evolving rapidly and will form an important part of planetary observations in the future. In the next decade, application will be found in high altitude observatories, aircraft and balloons. Astrophysics missions such as the Large Deployable Reflector (LDR) and its precursors will provide significant measurement capability in the submillimeter wavelength region. Such measurement capability will be of little use to the planetary community unless an adequate laboratory spectral data base exists.

The emphasis of this paper will be on the new techniques for submillimeter and far infrared laboratory spectroscopy which have appeared in the past decade. With encouragement, these techniques can become important tools for laboratory measurements of planetary molecules.

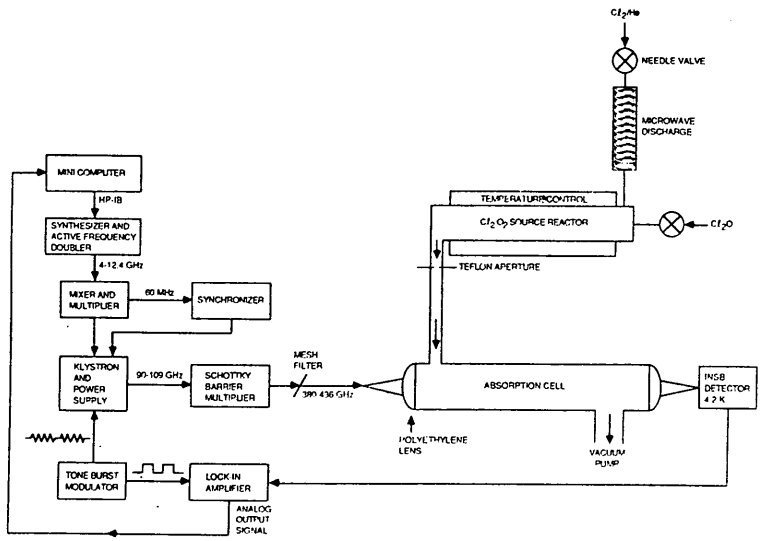

Fig. 1: Submillimeter Spectrometer Using Harmonic Generation

HARMONIC GENERATION

Harmonic generation is one of the oldest of the far infrared spectral techniques, and was developed by Walter Gordy and his students at Duke University.[2] Recently, several developments have made this technique more sensitive for routine measurements. The

method involves illuminating a diode with microwave power and detecting absorption with the harmonics of the microwave source. The general scheme for this is illustrated in Fig. 1.

The first development has been to replace the W-Si point contact diodes with monolithic Schottky diodes. The diodes we have used most successfully for this application have been produced by R. Mattauch at the University of Virginia.[3] Interestingly, the best types have been high frequency mixer diodes. Varactor diodes, while theoretically better for multiplication, suffer from excess diode capacitance. The best mount for high harmonic generation is still the simple crossed waveguide mount originally developed by Gordy. While more efficient mounts can be made for doubling or tripling, the task of terminating all the harmonics and idler frequencies becomes a very difficult design problem at higher multiples. Our experience is that the harmonic power in the simple crossed waveguide mount drops by 6-10 dB per harmonic.

The second development has been the use of sensitive liquid He cooled detectors. The best in the 0.3 - 2 mm region is the InSb hot electron bolometer.[4] Unlike most bolometers, the InSb bolometer has its limiting thermal conductance between the conduction electrons (which are heated by the far infrared radiation) and the lattice. Because of this the InSb bolometer is best mounted in good thermal contact with the liquid He cold surface. The response time is $< 1\mu$sec, making the detector more immune to 1/f noise in the source, but the sensitivity falls off above 20 cm^{-1}.

The third development has been the use of a dichroic plate to filter out the lower harmonics of the harmonic generator. These plates are designed after similar but much larger plates used to separate S and X band at the JPL Deep Space Network. In our application the plates are made of 1-2 mm thick aluminum and have a close-packed array of circular holes. Each of the holes act like a small circular waveguide. The plate reflects frequencies which are below the cut-off frequency of the waveguide. The plates have better than 80% transmission up to about twice the cut-off frequency, where diffraction starts becoming important. The highest frequency cutoff filter we have made has a 500 GHz (16.7 cm^{-1}) cutoff employing about 2000 holes of 0.25 mm diameter.

These developments have allowed us to make many studies of spectra in the 10-30 cm^{-1} region. An unretouched example is shown in Fig. 2. It is the J,K = 3,3 inversion transition of ammonia in the $\nu_2 = 1$ excited state at 1073 049.708 MHz (35.79308 cm^{-1}).

LASER DIFFERENCE FREQUENCY GENERATION

Laser difference frequency generation is a technique developed by Ken Evenson and his co-workers at NBS (now NIST) in Boulder, CO.[5] The apparatus for two photon generation is shown in Fig. 3. Central to this technique is the W-NiO-Ni tunnel junction called a MIM diode which provides the non-linearity for mixing the two CO_2 lasers. One of these lasers is fixed in frequency and Lamb dip stabilized to an accuracy of 10 kHz. The second waveguide laser can be tuned over $\sim$ 100 MHz. Its frequency is determined by beating a portion of the output with a Lamb dip stabilized laser, which is lasing on the same CO_2 line, in a HgCdTe high speed detector. By choosing different laser transitions wide

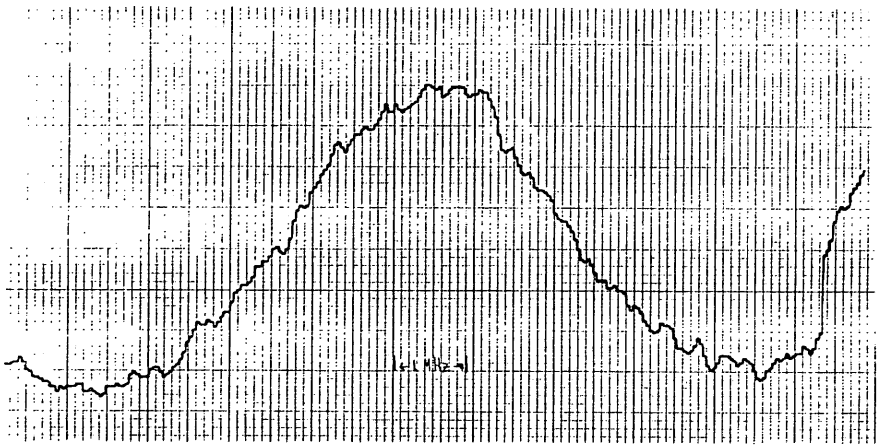

Fig. 2: NH_3 ν_2 inversion line for J,K = 3,3 at 1073 049.708 MHz

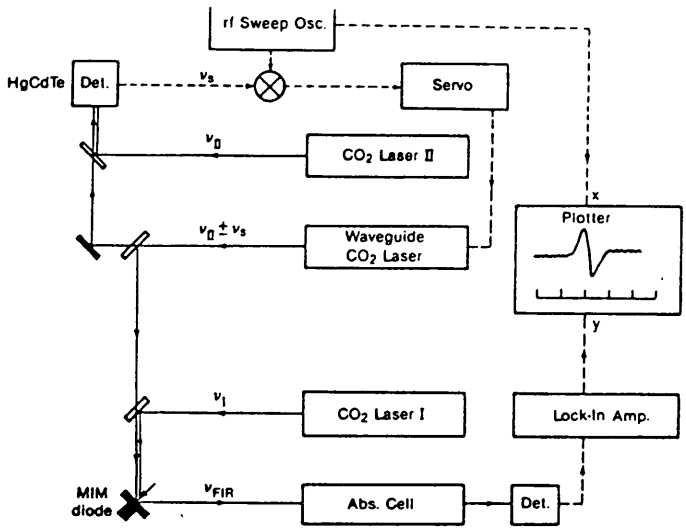

Fig. 3: Two Photon Laser Difference Generation

frequency coverage can be obtained in selected 100 MHz patches. Frequency accuracy is limited by ability to measure the peak position of the far infrared absorptions or $\sim$ 200 kHz.

In order to fill in the frequency coverage, Evenson has developed a three photon method in which two mid-infrared photons are combined with a microwave photon.[6] In this method, the two CO_2 lasers are both Lamb dip stabilized, and the tuning comes from the microwave

source. The optical layout is shown in Fig. 4. Frequency accuracy is comparable to the two photon method, but getting three wave mixing from the MIM diode is much more difficult.

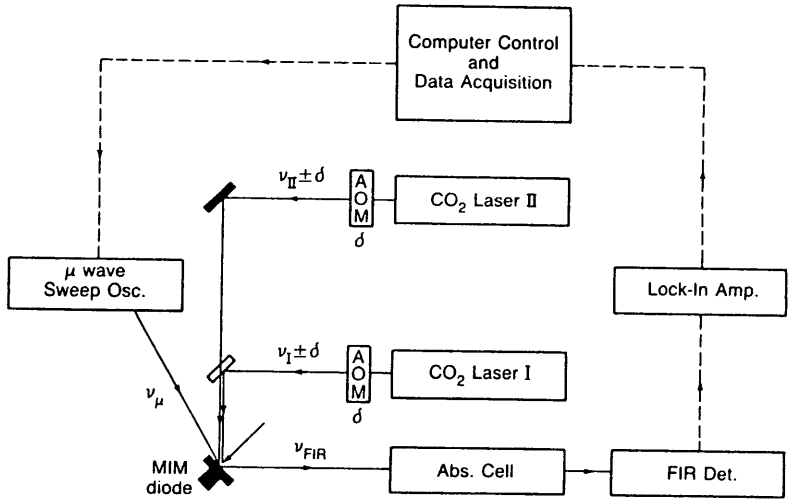

Fig. 4: Three Photon Laser and Microwave Difference Generation

Actually three far infrared frequencies are generated: one from the difference of the two infrared lasers, and two which are above and below the two photon frequency by an amount equal to the microwave frequency. These are readily distinguished by frequency modulating one of the lasers and observing the sense of the first derivative lineshape obtained under phase-sensitive detection while sweeping the microwave source.

LASER SIDEBAND GENERATION

Laser sideband generation involves mixing the output of a fixed-frequency far infrared laser with a microwave source to produce sidebands above and below the laser frequency. Early demonstrations of this technique were made by Dymanus in the Netherlands[7] and by a group at Lincoln Laboratory.[8] Our improvement of the technique at JPL proceeded concurrently with Evenson's work using infrared lasers. The goal of our work was to produce a source which had an accuracy of 100 kHz and had adequate power to make sensitive spectroscopic measurements. The far infrared laser is obtained by pumping a molecule such as methanol with a high power CO_2 laser and observing lasing from rotational transitions in the pumped vibrational state. While the output frequency is nominally at the rotational frequency, cavity and pump pulling effects make the laser frequency uncertain by as much as several MHz. Our strategy was to measure "today's" laser frequency by measuring a transition of known frequency before or after the unknown transition is measured. This required development of a very stable far infrared laser using Invar and active temperature stabilization.[9] A diagram of it is shown in Fig. 5. Interestingly, this laser also turned out

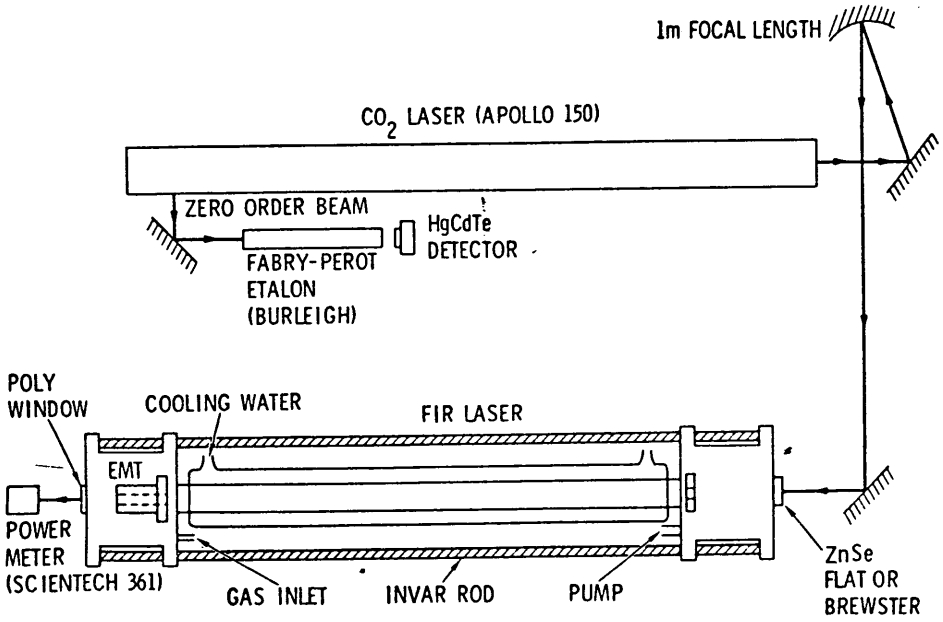

Fig. 5: Far Infrared Laser

to be a very high power laser, and our measured power of 1.25 W at 118 μm wavelength is probably a far infrared world record. More importantly, the frequency stability is < 100 kHz / hour.

In order to have usable sideband output power, it is essential to have a good way of separating sidebands from the laser. The way we chose to do this is shown in Fig. 6.[10] The

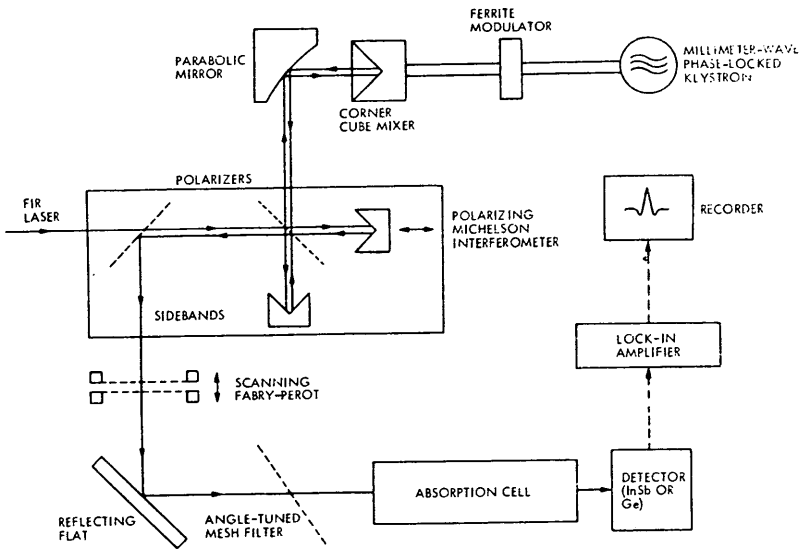

Fig. 6: Laser Sideband Generator

output from the laser passes through the analyzer polarizer and the polarizing Martin-

Puplett interferometer such that it is not attenuated and arrives at the corner cube diode mount with the correct polarization. At the diode, the laser is mixed with the output of a mm wavelength klystron. The sidebands and the unused laser power are reflected from the corner cube back through the interferometer. If the optical path difference is $\sim \frac{1}{4}\times$ the wavelength of the microwave source, then the sideband polarization is rotated by 90° with respect to the laser. As a consequence, the sidebands are reflected off the analyzer polarizer toward the sample cell and detector. Frequently we use a Fabry-Perot resonator to discriminate between the sidebands and to provide further rejection of the laser. A typical length scan of this Fabry-Perot, shown in Fig. 7, clearly shows the two sidebands and the original laser frequency.

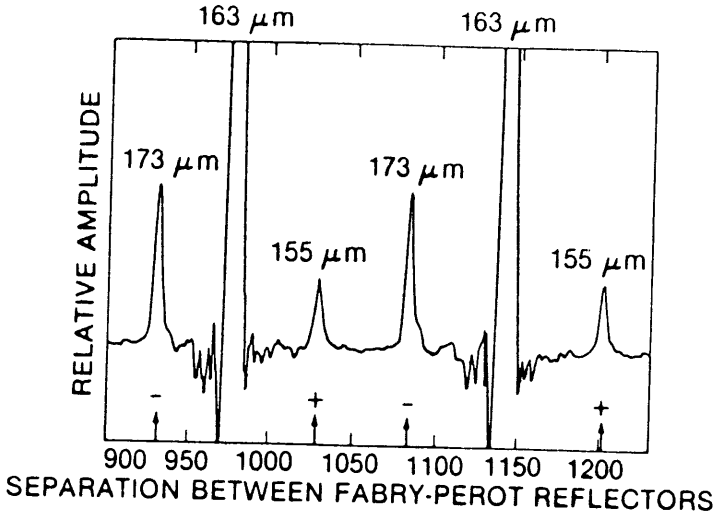

Fig. 7: Fabry-Perot Scan of Laser Sideband Output

Fig. 8 shows spectra obtained of ammonia and HDO using two cells in series. Accurate frequency measurements require a reference gas whose frequencies are known to the 100 kHz level, and whose doppler width facilitates accurate measurements. HDO is not a good reference gas in this sense, but CO is better since extensive laser difference measurements have been made on this gas.[11] An even better choice is a gas like SO_2, which has a narrower doppler width and a denser spectrum. We have calibrated SO_2 against the CO standard, and in addition have made several measurements of two SO_2 lines in the same laser sideband scan. In many cases, for example if the lines are P and R branch lines of different K, the difference in frequency is almost as valuable to the fit as the absolute frequency. The fit combining these far infrared determinations with microwave data is providing a very useful secondary standard for the laser sideband technique which is accurate to the level of our ability to measure the frequencies.

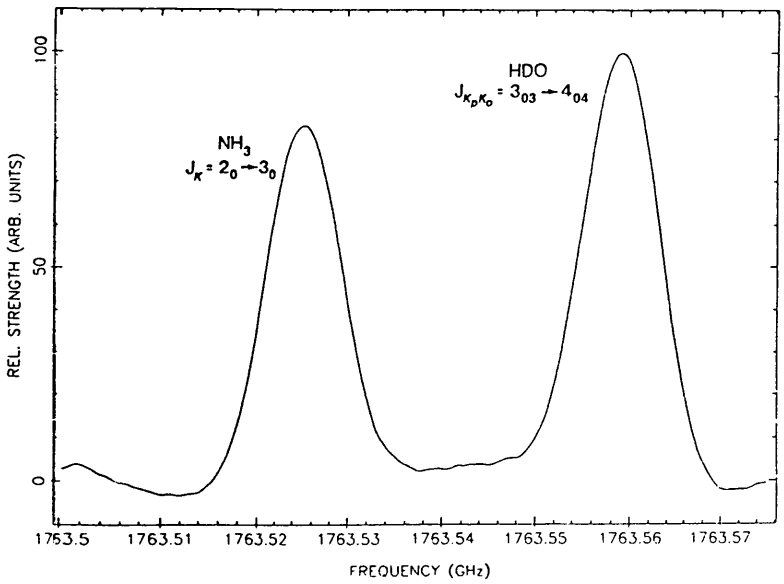

Fig. 8: Laser Sideband Spectrum of NH_3 and HDO

INTERFEROMETERS

There has been a steady improvement of both user-constructed and commercial far infrared interferometers. In the far infrared it is important to have large optics and high throughput so that resolution is not limited by diffraction. In the long wavelength region, the advantages of the polarizing Martin-Puplett design (in which a wire-grid polarizer forms the beam splitter) have been employed by B. Carli at IROE in Italy.[12] More common are the mylar beam splitter Michelson interferometers represented by the Bomem and Bruker instruments. The Bomem instrument in its highest resolution form has an optical path difference of 2.5 m, although J. Johns at the Hertzberg Institute in Canada has a modification to effectively double this difference.[13] The Brucker instrument in its highest resolution form has an optical path difference of 6 m, which represents a resolution of 0.0016 cm^{-1}. Last November JPL received delivery of the first Bruker of this resolution in this country. We are still in the process of characterizing this instrument, but an example of the spectra we have obtained is shown in Fig. 9. Unfortunately, the pressure is too high to display the spectra at the doppler limit, but an indication of the resolution is given by the splitting at 101.6 cm^{-1} which is 0.005 cm^{-1}. While the ultimate resolution of 50 MHz is not comparable to laser-based methods, it is very good for survey work and linewidth measurements.

CONCLUSIONS

The four techniques described here are both complementary and powerful. Harmonic generation is most useful for the millimeter wavelength end of the spectral region. High resolution interferometers are diffraction limited in this region, but are very accurate and

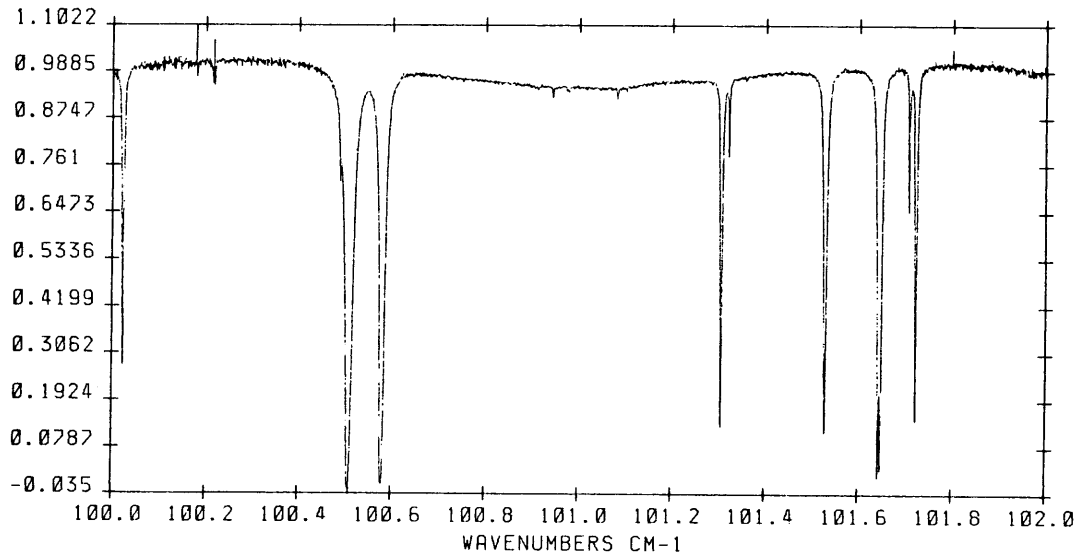

Fig. 9: Bruker Spectrum of HDO at 2 Torr Pressure

sensitive survey instruments at shorter wavelengths. The two methods for laser generation of tunable far infrared radiation are capable of higher resolution measurements on selected lines. Difference frequency generation has high absolute accuracy in frequency, but laser sideband generation is probably easier once suitable standards are available.

ACKNOWLEDGEMENT

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