TUNABLE FAR INFRARED LASER SPECTROSCOPY

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Tunable far-infrared (FIR) radiation has been generated with four different techniques (1,2): harmonics of microwave oscillators; CO_2 laser difference frequency generation in GaAs; FIR laser plus microwave sidebands; and the CO_2 laser difference generation in a metal-insulator-metal diode. We are using the latter technique to measure highly accurate FIR frequencies of stable species to serve as frequency and wavelength calibration standards (3); to measure frequencies of transient species (including molecular ions) for astronomical searches (4-8); and to study line broadening and line shape parameters especially for atmospheric measurements (9,10). Sub-Doppler FIR spectroscopy has also been achieved using a CO_2 laser to selectively populate a narrow velocity subgroup which is then observed in the FIR (11). The technique has also been used; to directly measure the frequency of lasing gases (12), to measure the Stark effect in $^{13}CH_3OH$ (13), and to measure the K doubling frequencies in $^{12}CH_3OH$ (14). In all, six papers on these subjects are being presented at this conference (9-14).

Two FIR laser spectrometers are now in operation at the National Bureau of Standards, Boulder Laboratories in which the FIR radiation is synthesized in two ways: either from the difference between the CO_2 laser frequencies (i.e. in 2nd order), or, from the difference between two CO_2 lasers with the addition of microwave sidebands (ie. in 3rd order) (1,2). In 2nd order, tunability is achieved by using a waveguide CO_2 laser with about ±120 MHz of tunability for one of the CO_2 lasers; or, in 3rd order, microwave (tunable) sidebands are added to the FIR difference between two CO_2 lasers. Different MIM diodes are used in each spectrometer. In the second order spectrometer, a tungsten whisker contacts a nickel base and the normal oxide layer on nickel serves as the barrier. In the 3rd order spectrometer, a cobalt base with natural cobalt oxide is used with a tungsten whisker. The best 3rd order cobalt diodes produce about 1/3 as much FIR as the best 2nd order nickel diodes.

In the 2nd order spectrometer, the common isotope of CO_2 is used in the waveguide laser and one of four isotopic species are used in the fixed frequency CO_2 laser. Ninety-percent of all frequencies from 0.3 to 4.5 THz can be synthesized, and the coverage then decreases to a few percent at 6 THz. Ninety megahertz opto-acoustic modulators are used in the output beams of each CO_2 laser and serve to both increase the tunability by an additional 180 MHz and to isolate the CO_2 lasers from feedback from the MIM diode. Feedback reduction decreases the amplitude noise in the FIR radiation by an order of magnitude; hence, the spectrometer sensitivity increases by this amount. Two fixed frequency CO_2 lasers stabilized to saturated fluorescence signals in CO_2 are used: the radiation from one is focused on the diode, and the other serves as a frequency reference for the waveguide laser. The CO_2 radiation is coupled to the whisker by a 25 mm focal length lens using the conical sharpened tip of the 25 μm diameter tungsten whisker as a conical antenna

(15). The 3 to 10 mm long whiskers (from the tip to a right angle bend) radiates the FIR radiation in a long wire antenna pattern (15). The FIR radiation is collimated using a 10 mm focal length off-axis segment of a parabolic mirror.

The figure illustrates the 3rd order spectrometer. CO_2 lasers I and II are stabilized to CO_2 sub-Doppler saturated fluorescence features using separate (not shown) low pressure cells (16), to an uncertainty of 25 kHz in the spectrometer. The overall uncertainty in the FIR frequency is thus: $\sqrt{2} \times$ 25 or 35 kHz. The frequencies of these lasers are known to about ±3 kHz (16,17); however, without special baselines slope correction and special locking techniques described in references 16 and 17, our lasers were line center locked to a one sigma uncertainty of this 25 kHz. The largest contributor to the overall uncertainties in the measurement of a transition frequency comes from finding the line centers of these Doppler broadened lines, about 0.1 of the line width (0.05 to 1 MHz).

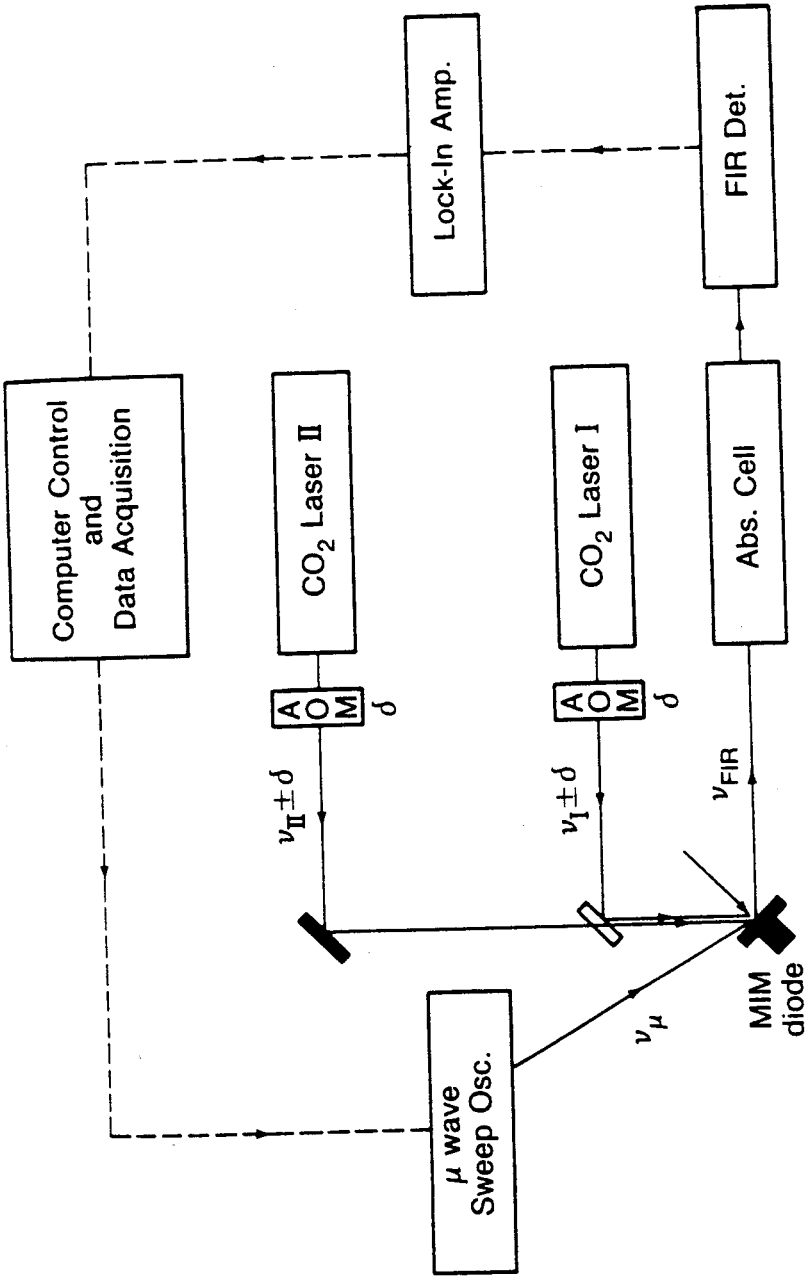
The FIR radiation was frequency modulated up to 3 MHz at a one kilohertz rate in order to minimize FIR amplitude noise and maintain bolometer sensitivity. Lasers I and II are frequency modulated using piezo-electric drivers on the end mirrors; they are then servoed to the line center of the saturated fluorescence signals obtained from the external low-pressure CO_2 cells. The frequency modulation on the radiation from laser II appears on the FIR radiation, and the FIR detectors and lock-in-amplifier detect at the modulation rate. Hence, the derivatives of the absorptions are recorded.

Absorption cells from 0.5 to 3.5 meters in length with diameters ranging from 19 to 30 millimeters have been used in each spectrometer. The cells have either glass or copper walls and polyethylene windows.

Four different detectors have been used in the spectrometers: 1) an InSb 4°K, liquid ^{4}He cooled, hot-electron bolometer, operating from 0.3 to 0.6 THz with an NEP of about 10^{-13}w/$\sqrt{Hz}$; 2) a gallium doped germanium bolometer, cooled to the lambda point of ^{4}He, operating from 0.6 to 6.5 THz with an NEP of about 10^{-13}w/$\sqrt{Hz}$; 3) a similar, but ^{3}He cooled bolometer, with a two-orders-of-magnitude smaller NEP; and 4) a Ge:Ga photoconductor, cooled to 4°K, with an NEP of 10^{-14} w/$\sqrt{Hz}$, operating from 2.5 to 6.0 THz.

FIR spectra of a series of rotational transitions have been measured in CO, HCl, and HF and will be published elsewhere (8). These lines are about ten times more accurately measured than what is needed in the present state-of-the-art Fourier transform spectrometers, they serve as excellent absolute calibration lines, and are the most accurate available.

Radio astronomy has been extended to the terahertz region and requires accurate frequencies of transitions in order to identify the species and to determine the Doppler shifts of the sources. Several astronomically interesting molecules have been studied: OH (5), NaH (6), and MgH (7). The OH had previously been studied by FIR laser magnetic resonance, but the new measurements decrease the uncertainties of the transitions by about an order of magnitude. Rotational spectra of NaH were studied in several vibrational levels and accurate rotational constants were obtained. The measurements in MgH are accurate to better than a megahertz, and the frequencies were used for



3rd ORDER
TuFIR SPECTROMETER
$\nu_{FIR} = (\nu_I - \nu_{II}) \pm \nu_\mu$

a preliminary astronomical search for MgH; further searches are necessary for a positive identification.

The long absorption cells naturally lend themselves to a hollow-cathode discharge configuration for the study of molecular ions. A preliminary experiment revealed the HCO^+ line at 1 THz with a signal-to-noise (100:1 with a 1 s time constant) equivalent to that obtained using the laser sideband technique (18). Transitions in H_2D^+ and OH^- have also been observed; however they are weak and only tentatively identified, and further work is underway.

The instrumental resolution of the spectrometers is limited by the combined frequency fluctuation from each CO_2 laser (about 15 kilohertz). This, of course, is less than any Doppler limited linewidth and, therefore, does not limit our resolution except possibly for the sub-Doppler work (11). This high resolution provides an excellent way of studying pressure shifts and line shape studies of spectral lines. The measurement of OH concentrations in our atmosphere as a function of altitude by absorption and emission measurements requires an accurate knowledge of its linewidth in the atmosphere. Such measurements in OH have just been completed and will be described in paper (9) at this conference. Similar studies have been made on HCl and will be described in paper (10).

Improvements in this different technique may come from either improved diodes or detection schemes. The non-linearities measured in the current-voltage curves of our MIM diodes are extremely small and conversion efficiencies could be 100 times larger. We are optimistic that better materials may be found which will result in larger FIR powers. Differential detection schemes would also significantly improve the sensitivity and permit the detection of weaker lines. The sensitivity, however, is still only about 1% of that of laser magnetic resonance (19).

We believe that this technique of laser difference spectroscopy in the FIR is now well established and we are looking forward to many exciting discoveries.

Acknowledgments

This work is partially supported by NASA contract W-15, 047 and the fluorocarbon panel of the Chemical Manufacturer's Association.

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