Tunable Far Infrared Spectroscopy

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Introduction

In this paper we describe the generation of far infrared (FIR) radiation with the metal-insulator-metal (MIM) diode and the operation of a spectrometer employing this diode. This technique is an extension of the use of the MIM diode from its use in the measurement of frequencies to the generation of far infrared radiation between 0.3 and 6.0 THz. The MIM diode has previously been used in frequency measurements yielding a definitive value for the speed of light and in the measurement of the frequency of visible radiation.

The MIM diode is the non-linear device used in the direct frequency measurement of the 88 THz (3.39 micron) helium-neon laser stabilized on methane. This frequency when multiplied by the wavelength of that laser, gave a value of the speed of light which was a hundred times more accurate than the previous values [1].

We have used the MIM diode to measure frequencies up to 200 THz (1.5 microns), which is about the upper frequency limit of the MIM. To reach the visible, bulk doublers were used, and two accurate values of molecular iodine absorptions were measured [2, 3]. These led the way to the redefinition of the meter: "The meter is the length of the path travelled by the light in vacuum during the time interval 1/299 792 458 of a second" [4]. This definition fixes the value of c at exactly 299 792 458 meters per second and permits the use of the laser in realizing the meter.

The MIM Diode

In the FIR we couple radiation in or out of the MIM diode by using long wire antenna coupling. When the wavelength of the radiation becomes comparable to the diameter of the whisker (in the IR) we use conical antenna coupling [5].

In the measurement of frequencies, the MIM diode is used as a harmonic-generator and mixer, and a radio frequency heterodyne difference (a beat note) is generated. In the measurement of methane, the radio frequency signal is generated from 3 times the frequency of CO_2 plus the microwave heterodyning with the methane stabilized He-Ne radiation [6]. The diode is used in this case to actually generate the radio frequency difference.

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Generation of FIR Radiation

We have observed very large signals when we mix the radiation from two CO_2 lasers a few MHz apart. These signals led us to speculate that FIR radiation might radiate from the diode if we selected CO_2 laser lines differing by a far infrared frequency. Using about 500 milliwatts of CO_2 radiation i.e., 250 milliwatts from each laser, we were able to radiate 0.2 microwatt of far infrared radiation [7]; we have now increased that to 0.7 microwatt from 100 mW from each CO_2 laser. We have generated radiation from 0.3 to 6.3 THz. The tunability of the FIR radiation results from the use of a high-pressure wave guide CO_2 laser tunable by about 150 megahertz. By using three isotopes of CO_2 most of the far infrared can be covered using various pairs of CO_2 lasers.

To demonstrate the fact that we had produced tunable far infrared radiation,we took spectra of a rotational line of CO. Figure 1a shows one of our first traces.

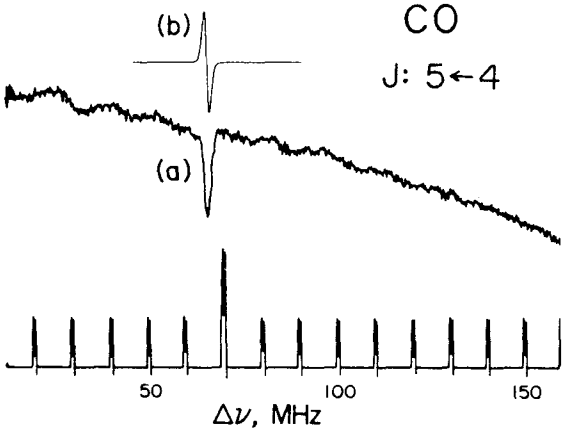

Fig. 1. CO ground state absorption at 576 GHz. Trace (a) is the first trace made using CO_2 difference radiation, and trace (b) is a recent trace using the spectrometer shown in figure 2.

FIR Spectroscopy

The FIR region had been a fairly inactive region because there were neither good sources of radiation nor good detectors. That situation is now changed: first, there are over a thousand fixed frequency FIR laser lines; second, very good detectors have become available which are limited by room temperature blackbody radiation. With these advances, radio astronomy expanded into the FIR, and measurements made on our atmosphere from balloons or high-flying airplanes are also made in the FIR region.

Two types of transitions lie in this region: fine structure transitions in atoms and molecules (these are magnetic dipole transitions), and rotational transitions in lighter molecules. The latter are very strong transitions and yield a high sensitivity. For example, FIR transitions are some 10^5 times stronger than microwave transitions. They are about an order of magnitude stronger than infrared transitions (vibrational), but they are about a hundred times weaker than electronic transitions in the visible. (These relative strengths are based on the absorption per molecule at a pressure of 133 Pa.)

There are several other techniques of generating FIR radiation. Some backward wave oscillators operate up to a little above 1 THz [8]. The oldest technique is that of generating harmonics from a klystron or backward wave oscillator [9, 10]. A more efficient technique is that of generating a far infrared laser sideband [11,12]. Difference frequency radiation between CO_2 lasers can be generated using either non-linear crystals [13] or the MIM diode [7]. Although the MIM diode does not provide as much power as the other techniques, it is convenient and by using CO_2 stabilized lasers, it provides an accuracy of 35 kHz and a spectral purity of about 10 kHz.

The Spectrometer

The complete spectrometer (which we call a TuFIR spectrometer) is shown in fig. 2. The two drive CO_2 lasers (CO_2 laser number I and the CO_2 waveguide laser) are combined on the beam splitter and then are focused on the MIM diode where the far infrared radiation is generated. Laser I is frequency-modulated and the derivative of the absorption signal is observed following lock-in detection. Laser II is used to control the frequency of the waveguide laser with the radio frequency sweep. Opto-acoustic modulators are used to isolate the lasers from the MIM diode and to provide an additional 90 MHz of tunability. The improvements in the spectrometer are indicated in Fig.1b in which the same transition as in Fig. 1a was recorded. The signal to noise is much improved; the noise level now corresponds to a fractional absorption of about 1×10^{-4} with a 1 s time-constant.

Seven CO lines have been observed and the rotational constants calculated. These are used to predict the rotational frequencies with uncertainties from about 30 kHz for low J lines to about a 100 kHz on the high J lines. These frequencies are very useful as calibration standards and will be published elsewhere. The first four rotational frequencies of HF which are about 12 times those of CO, have also been measured, and their rotational constants have also been calculated.

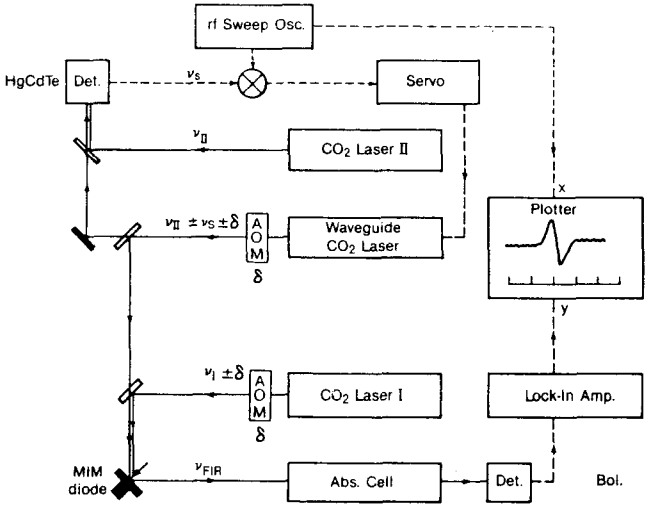

Fig. 2. Tunable Far Infrared spectrometer using a MIM diode to generate the difference frequency from two CO_2 lasers.

The high sensitivity of the technique is demonstrated by the observation of the spectra of the OH free radical. The rotational constants have been calculated and then used to predict the rotational frequencies to an accuracy of about ± 100 kHz. The result is an improvement in the accuracy of these lines by about two orders of magnitude. These OH transition frequencies can now be used by radio astronomers and by aeronomers to detect and study this species important in our atmosphere and in interstellar space. Another important application of this spectroscopy will be in line broadening studies of OH so that atmospheric spectroscopic data can be used to yield the concentrations of OH in our atmosphere as a function of altitude.

Two recently observed transient molecules are NaH and MgH. We have observed six rotational transitions of NaH in the $v = 0$ manifold and six transitions in the $v = 1$ manifold. The data are being analyzed and will be published elsewhere. MgH is a very important astronomical molecule and the observation of more lines will allow the prediction of its frequencies for astronomical searches.

The exciting uses of FIR spectroscopy have been indicated, and we have shown some of the interesting molecules which are available for future studies.

Future

How efficient is the MIM diode? The I-V curve of tungsten-nickel is nearly a straight line; but its small non-linearity allows the MIM diode to detect and to generate difference frequencies. Because of its small non-linearity, it is not a very efficient device. By comparison, the Schottky diode (which does not operate well above 1 THz) has a very sharp bend in its I-V curve. Are there other more efficient devices that will also work at this high speed? Klaus Siemsen from the Canadian National Research Council tested a tin telluride diode in our NBS laboratory. It is about five times more efficient than nickel; however, it is less stable, and we still prefer nickel as a base.

The I-V curve of tungsten-cobalt is nearly symmetrical (tungsten-nickel's curve is asymmetrical). This diode does not detect well and does not produce difference radiation as predicted by its symmetrical I-V curve; however, it does generate a 3rd order signal very well. This permits the generation of the difference between two CO_2 lasers plus and minus microwave radiation. This is very exciting, because we now obtain nearly 100 times more tunability. For example, in 2nd order (CO_2 difference), a tunability of ± 300 MHz is possible, but in 3rd order with fixed CO_2 lasers and a microwave sweeper, the tunability is ± 20,000 MHz. Thus we can now cover the entire far infrared by using 150 pairs of CO_2 differences plus and minus microwave radiation.

The MIM diode is more and more perplexing. The mechanism responsible for the operation of the diode seems to be tunneling; however, we are not even sure of that [5].

Does the diode also radiate the sum frequency? It probably does, but this is in the region where blackbody room-temperature radiation swamp the potential IR radiation from the diode; we will need a heterodyne or interferometric technique to detect it.

Thin film metal-insulator metal diodes would be much more reliable. Some initial research has been done along this line [14], but more is

desirable. Communication's applications with terahertz bandwidth is a very exciting possibility with such devices.

The use of other metals may extend the operation of the MIM diode beyond 1.5 microns to the visible. Third-order diodes would be very useful in the visible so that one could directly heterodyne various pairs of visible oscillators with IR oscillators to obtain highly accurate frequency measurements across the visible.

Future Spectroscopic Measurements

The Rydberg will certainly be directly frequency-measured in the near future. The time standard itself presently is cesium in the microwave region: it will be improved by optically pumping cesium with a laser [15]. Further in the future, a stored ion standard in the visible [16] may become the frequency standard, then frequency multiplication from the microwave to the visible will be absolutely essential.

In closing, the future of this field of frequency measurement and synthesis looks very bright indeed!

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1. K. M. Evenson, J. S. Wells, F. R. Petersen, B. L. Danielson, G. W. Day R. L. Barger, and J. L. Hall, Phys. Rev. Lett., 29, 1346 (1972).
2. C. R. Pollock, D. A. Jennings, F. R. Petersen, J. S. Wells, R. E. Drullinger, E. C. Beaty, and K. M. Evenson, Opt. Lett., 8, 133 (1983).
3. D. A. Jennings, C. R. Pollock, F. R. Petersen, R. E. Drullinger, K. M. Evenson, and J. S. Wells, Opt. Lett. 8, 136 (1983).
4. "Documents Concerning the New Definition of the Metre", Metrologia 19, pp. 163-177 (Springer-Verlag, 1984).
5. K. M. Evenson, M. Inguscio, and D. A. Jennings, J. Appl. Phys. 57, 956 (1985).
6. K. M. Evenson, J. S. Wells, F. R. Petersen, B. L. Danielson, and G. W. Day, Appl. Phys. Lett. 22, 192 (1973).
7. K. M. Evenson, D. A. Jennings, and F. R. Petersen, Appl. Phys. Lett. 44 576 (1984).
8. A. F. Krupnov, "Modern Aspect of Microwave Spectroscopy", ed. G. W. Chantry (Academic Press, New York, 1979), p. 217.
9. P. Helminger, J. K. Messer, and F. C. DeLucia, Appl. Phys. Lett. 42, 309 (1983).
10. E. A. Cohen and H. M. Pickett, J. Mol. Spectrosc. 93, 83 (1982).
11. D. D. Bícanic, B. F. J. Zuidberg, and A. Dyamanus, Appl. Phys. Lett. 32, 367 (1978).
12. H. R. Fetterman, P. E. Tannenwald, B. J. Clifton, W. D. Fitzgerald, and N. R. Erickson, Appl. Phys. Lett. 33, 151 (1978).
13. R. L. Aggarwal, B. Lax, H. R. Fetterman, P. E. Tannenwald, and B. J. Clifton, J. Appl. Phys. 45, 3972 (1974).
14. K. M. Evenson, M. Inguscio, and D. A. Jennings, J. Appl. Phys. 57, 960 (1985).
15. R. E. Drullinger, private communication.
16. J. C. Bergquist, D. J. Wineland, W. M. Itano, H. Hemmati, H.-U. Daniel, and G. Leuchs, "Two-Photon Optical Spectroscopy of Trapped HgII" (chapter in this volume).