TUNABLE FAR INFRARED LASER SPECTROSCOPY*

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ABSTRACT. Tunable far-infrared (FIR) radiation has been generated
using CO_2 laser difference generation in metal-insulator-metal diodes
either from the difference between a fixed frequency CO_2 laser and a
tunable waveguide laser, or from the difference between two fixed
frequency CO_2 lasers plus microwave sidebands. Our tunable FIR source
is being used to make highly accurate FIR frequency measurements of
stable species to serve as frequency and wavelength calibration
standards; to measure frequencies of transient species (including
molecular ions) for astronomical searches; and to study line broadening
and line shape parameters especially for atmospheric spectroscopy
applications.

INTRODUCTION

Tunable far-infrared (FIR) radiation has been generated with four
different techniques: harmonics of microwave oscillators (1), CO_2 laser
difference frequency generation in GaAs (2), FIR laser plus microwave
sidebands (3), and the CO_2 laser difference generation in a metal-
insulator-metal diode (4,5) described in this paper. We are using our
tunable FIR source to make highly accurate FIR frequency measurements
of stable species to serve as frequency and wavelength calibration
standards (6), to measure frequencies of transient species (including
molecular ions) for astronomical searches (7-11), and to study line
broadening and line shape parameters (12) especially for atmospheric
spectroscopy applications.
We are using two related techniques of synthesizing tunable far
infrared radiation: either from the difference between a fixed

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An earlier version of this paper was submitted to the 11th
International Conference on Infrared and Millimeter Waves, and was
available only to delegates at the conference.

frequency CO_2 laser and a tunable waveguide laser (i.e., with second order generation), or from the difference between two fixed frequency CO_2 lasers plus microwave sidebands (i.e., with third order generation). In the first of these, a tungsten-nickel diode is used as the nonlinear element and in the second, a tungsten-cobalt diode is used. The tungsten-nickel diode generates very little third order radiation, and the tungsten-cobalt, very little second order. In second order, tunability is achieved by using a waveguide CO_2 laser with about ± 120 MHz of tunability; and in 3rd order, tunable microwave sidebands are added to the fixed FIR frequency difference from two CO_2 lasers. The best 3rd order cobalt diodes produce about 1/3 as much FIR radiation as the best 2nd order nickel diodes. The current-voltage curves of these two different diodes predict their corresponding 2nd or 3rd order behaviors. Typical FIR powers of a few tenths of a microwatt are obtained from 200 mW of CO_2 power.

SECOND ORDER SPECTROMETER

In the 2nd order spectrometer, shown in figure 1, 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 (I). Eighty-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 to isolate the output beams of the CO_2 lasers from the MIM diode and also to increase the tunability by an additional 180 MHz. 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 (I and II) stabilized to saturated fluorescence signals in CO_2 (13) 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 an antenna (14). 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 (14). The FIR radiation is collimated using a 10 mm focal length off-axis segment of a parabolic mirror.

THIRD ORDER SPECTROMETER

Figure 2 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 (13). Their radiation is focused on the diode along with that of a frequency-synthesized, microwave (2-20 GHz) source used to add the tunable sidebands to the
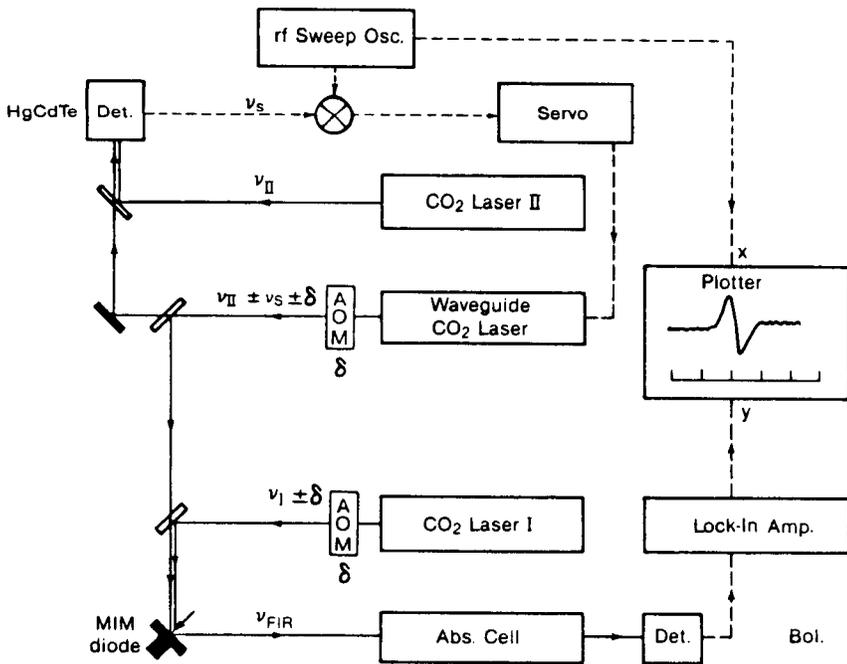
TuFIR SPECTROMETER

Figure 1 : The Second Order Tunable Far Infrared Spectrometer:
$\nu_{FIR} = (\nu_{II} \pm \nu_S \pm \delta) - (\nu_1 \pm \delta)$.

3rd ORDER
TuFIR SPECTROMETER
$$\nu_{FIR} = (\nu_I - \nu_{II}) \pm \nu_\mu$$
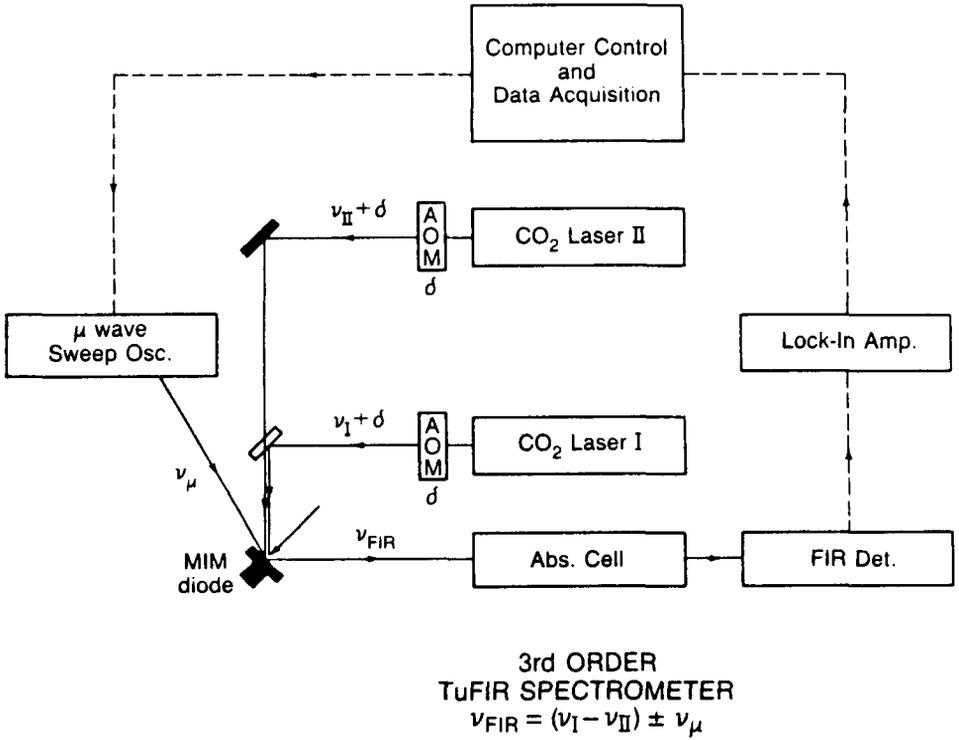
Figure 2 : The Third Order Tunable Far Infrared Spectrometer.

CO_2 difference frequency. Its accuracy is a few hertz, and it does not contribute to the uncertainty of the source.

EXPERIMENTAL TECHNIQUE

In each spectrometer both CO_2 reference lasers are frequency modulated at a 1 kHz rate using piezoelectric drivers on the end mirrors and are then servoed to the line center of the saturated fluorescence signals obtained from the external low-pressure CO_2 cells. The FIR detectors and lock-in amplifier detect at the modulation rate; hence, the derivatives of the absorptions are recorded. The depth of the frequency modulation of CO_2 laser I can be increased up to 7 MHz to enhance the FIR frequency modulation, thereby increasing the sensitivity for the broader lines.

Our lasers are locked with an uncertainty of 25 kHz; thus, the overall uncertainty in the FIR frequency is: $\sqrt{2}$ x 25 or 35 kHz. The frequencies of these CO_2 absorptions are known to about ±3 kHz (14,15); however, without special baselines slope correction and special locking techniques described in references 13 and 15, the overall uncertainties increase to the aforementioned 25 kHz level. 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).

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

Four different detectors have been used in the spectrometers: 1) an InSb 4K, 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 4K, with an NEP of 10^{-14}W/$\sqrt{}$Hz, operating from 2.5 to 6.0 THz.

RESULTS

FIR spectra of a series of rotational transitions have been measured in CO, HCl, and HF and will be published elsewhere (6). These lines, about ten times more accurately measured than what is needed in the present state-of-the-art Fourier transform spectrometers, 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 (8), NaH
(9), and MgH (10). 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 one megahertz, and the frequencies were used
for 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 ratio (100:1 with a 1 s time constant) equivalent to that
obtained using the laser sideband technique (16). Possible 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 for
possible sub-Doppler work. 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 using absorption and emission measurements
requires an accurate knowledge of its linewidth in the atmosphere.

Figure 3 shows a spectrum of methanol taken with our 3rd order
spectrometer. Spectra from both sidebands are observed simultaneously
and are superimposed; however, they are easily distinguishable because
the phases of the derivatives are opposite. That is: the absorptions
between 3 499 588.4 and 3 504 588.4 MHz start out positive (from left
to right in the figure); those on the other sideband (3 489 5884.4 and
3 484 588.4 MHz) start out negative. A corresponding scan taken with a
high resolution FTIR show a jumble of unresolved lines; in contrast,
this scan shows resolved lines even though two sidebands are
superimposed.

CONCLUSION

Improvements in these different techniques may come from either
improved diodes or detection schemes. The nonlinearities 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 which will result in larger FIR powers may be
found. 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. Laser magnetic resonance is useful only for paramagnetic

5 GHz

3,499,588.4

3,489,588.4

3,504,588.4

3,484,588.4
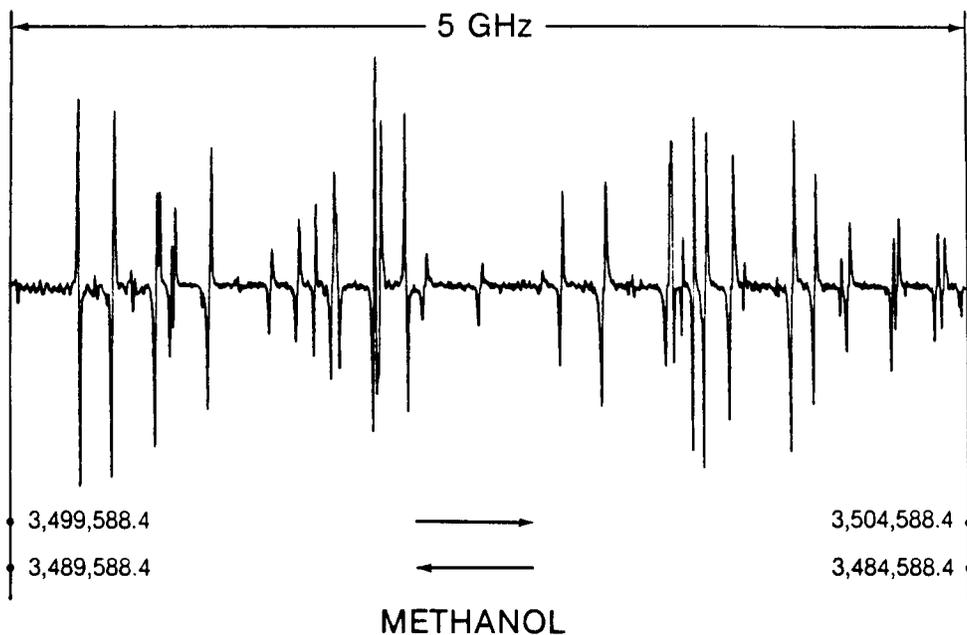
METHANOL

Figure 3 : A far infrared scan of methanol: a pressure of about 10 Pa of methanol and a frequency modulation of 2.5 MHz were used to record the spectrum. Both sidebands are shown: the lines which are positive on the left are those in the increasing frequency sideband and vice versa for those which are negative on the left. The frequencies are in megahertz.

species and is less accurate than the TuFIR technique by about an order of magnitude. 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

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