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# Laser Spectroscopy in the Submillimeter and Far-Infrared Region

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## 40.1 INTRODUCTION

Research in the submillimeter and far-infrared (SM-FIR) regions of the electromagnetic spectrum (1000 to 150 $\mu$m, 0.3 to 2.0 THz; and 150 to 20 $\mu$m, 2.0 to 15 THz, respectively) had been relatively inactive until about 25 years ago. Three events were responsible for enhanced activity in this part of the electromagnetic spectrum: the discovery of far-infrared (FIR) lasers [1], the development of background-limited detectors [2], and the invention of the FIR Fourier transform (FT) spectrometer [3]. Following these developments major discoveries have taken place in laboratory spectroscopic studies [4,5], in astronomical observations [6], and in spectroscopic studies of our upper atmosphere [7].

Rotational transition frequencies of light molecules (such as hydrides) lie in this region, and the associated electric dipole transitions are especially strong at these frequencies. In fact they are 10 000 times stronger than at microwave frequencies because they are 100 times typical microwave frequencies and their peak absorptivities depend approximately on the square of the frequency. Fine structure transitions of atoms and molecules also lie in this region; however, they are much weaker magnetic dipole transitions. The observation of fine structure spectra is very important in determining atomic concentrations in astronomical and atmospheric sources and for determining the local physical conditions. Bending frequencies of larger molecules also lie in this region, but their transitions are not as strong as rotational transitions.

Spectral accuracy has been increased by several orders of magnitude with the extension of direct frequency measurement metrology into the SM-FIR region [8]. Transitions whose frequencies have been measured (including absorptions and laser emissions) are useful wavelength calibration sources ($\lambda_{\text{vac}} = c/\nu$) for FT spectrometers. FIR spectra of a series of rotational transitions have been measured in CO [9], HCl [10], HF [11], and $CH_3OH$ [12] to be used for FT calibration standards. These lines are ten to a hundred times more accurately measured than can be realized in present state-of-the-art Fourier transform spectrometers; thus, they are excellent calibration standards. High-accuracy and high-resolution spectroscopy has permitted the spectroscopic assignment of the SM-FIR lasing transitions themselves [13] resulting in a much better understanding of the lasing process.

Astronomical spectroscopy in this region [6] may be in emission or absorption and is performed using either interferometric [14] (wavelength-based), or heterodyne (frequency-based) [15] techniques to resolve the individual spectral features.

Most high resolution spectra of our upper atmosphere have been taken with FT spectrometers flown above the heavily absorbing water vapor region in our lower atmosphere. Emission lines are generally observed in these spectrometers [7].

## 40.2 EXPERIMENTAL TECHNIQUES USING COHERENT SM-FIR RADIATION

The earliest sources of coherent SM radiation came from harmonics of klystron radiation generated in point-contact semiconductor diodes [16]. Spectroscopically useful powers to about one terahertz are produced. This technique is being replaced by electronic oscillators which oscillate to over one terahertz [17]. Spectroscopy above this frequency generally is performed with either lasers or FT spectrometers (see Chap. 39).

Laser techniques use either tunable radiation synthesized from the radiation of other lasers, or fixed-frequency SM-FIR laser radiation and tuning of the transition frequency of the species by an electric or magnetic field. Spectroscopy with tunable far-infrared radiation is called TuFIR spectroscopy. Spectroscopy with fixed frequency lasers is called either laser electric resonance (LER) or laser magnetic resonance (LMR). LMR is applicable only to paramagnetic species and is noteworthy for its extreme sensitivity. LMR spectroscopy has been more widely applied than LER, and is discussed in this chapter.

Tunable SM-FIR radiation has been generated either by adding microwave sidebands to radiation from a SM-FIR laser [18] or by using a pair of higher frequency lasers and generating the frequency difference [19]. The sideband technique was first reported by Dymanus [18] and uses a Schottky diode as the mixing element. It has been used up to 4.25 THz and produces a few microwatts [20]. The $CO_2$ laser frequency-difference technique with difference generation in the metal-insulator-metal (MIM) diode covers the FIR region out to over 6 THz and produces about 0.1 $\mu$W. This technique uses fluorescence-stabilized $CO_2$ lasers whose frequencies have been directly measured, and it is about two orders of magnitude more accurate than the sideband technique. However, it is somewhat less sensitive because of the decreased power available. There are several review articles on the laser sideband technique [20, 21], and only the laser difference technique is described here.

### 40.2.1 Tunable FIR Spectroscopy with $CO_2$ Laser Difference Generation in a MIM Diode

There are two different ways of generating FIR radiation using a pair of $CO_2$ lasers and the MIM diode. One is by second-order generation, in which tunability is achieved by using a tunable waveguide $CO_2$ laser as one of the $CO_2$ lasers; it is operated at about 8 kPa (60 Torr) and is tunable by about ±120 MHz. The second technique uses third-order generation, in which tunable microwave sidebands are added to the difference frequency of the two $CO_2$ lasers. The complete spectrometer which can be operated in either second or third order is shown in Fig. 40.1.

The FIR frequencies generated are:

$$\text{second-order: } \nu_{\text{fir}} = |\nu_{1,\text{CO}_2} - \nu_{\text{W},\text{CO}_2}| \tag{40.1a}$$

$$\text{third-order: } \nu_{\text{fir}} = |\nu_{1,\text{CO}_2} - \nu_{\text{W},\text{CO}_2}| \pm \nu_{\text{mw}} \tag{40.1b}$$

where $\nu_{\text{fir}}$ is the tunable FIR radiation, $\nu_{1,\text{CO}_2}$ and $\nu_{\text{W},\text{CO}_2}$ are the $CO_2$ laser frequencies, and $\nu_{\text{mw}}$ is the microwave frequency.

Different MIM diodes are used for the two different orders: in second-order, a tungsten whisker contacts a nickel base and the normal oxide layer on nickel serves as the insulating barrier; in third-order, a cobalt base with its natural cobalt oxide layer is substituted for the nickel base. The third-order cobalt diodes produce about one third as much FIR radiation in each sideband as there is in the second-order difference; hence third-order generation is not quite as sensitive as second-order. The much larger tunability, however, makes it considerably easier to use.

The common isotope of $CO_2$ is used in both the waveguide laser and in laser 2; in laser 1, one of four isotopic species is used. Ninety percent of all frequencies from 0.3 to 4.5 THz can be synthesized, and the coverage between 4.5 and 6.3 THz decreases. Ninety megahertz acoustooptic modulators (AOMs) are used in the output beams of the two $CO_2$ lasers which irradiate the MIM diode; they increase the frequency coverage by an additional 180 MHz and isolate the $CO_2$ lasers from the MIM diode. This isolation decreases amplitude noise in the generated FIR radiation, caused by the feedback to the $CO_2$ laser from the MIM diode, by an order of magnitude; hence, the spectrometer sensitivity increases by an order of magnitude.

The radiations from laser 1 and the waveguide laser are focused on the MIM diode. Laser 2 serves as a frequency reference for the waveguide laser; the two lasers beat with each other in the HgCdTe detector and a servosystem offset-locks the waveguide laser to laser 2. Lasers 1 and 2 are frequency modulated using piezoelectric drivers on the end mirrors, and they are servoed to the line center of 4.3 $\mu$m saturated fluorescence

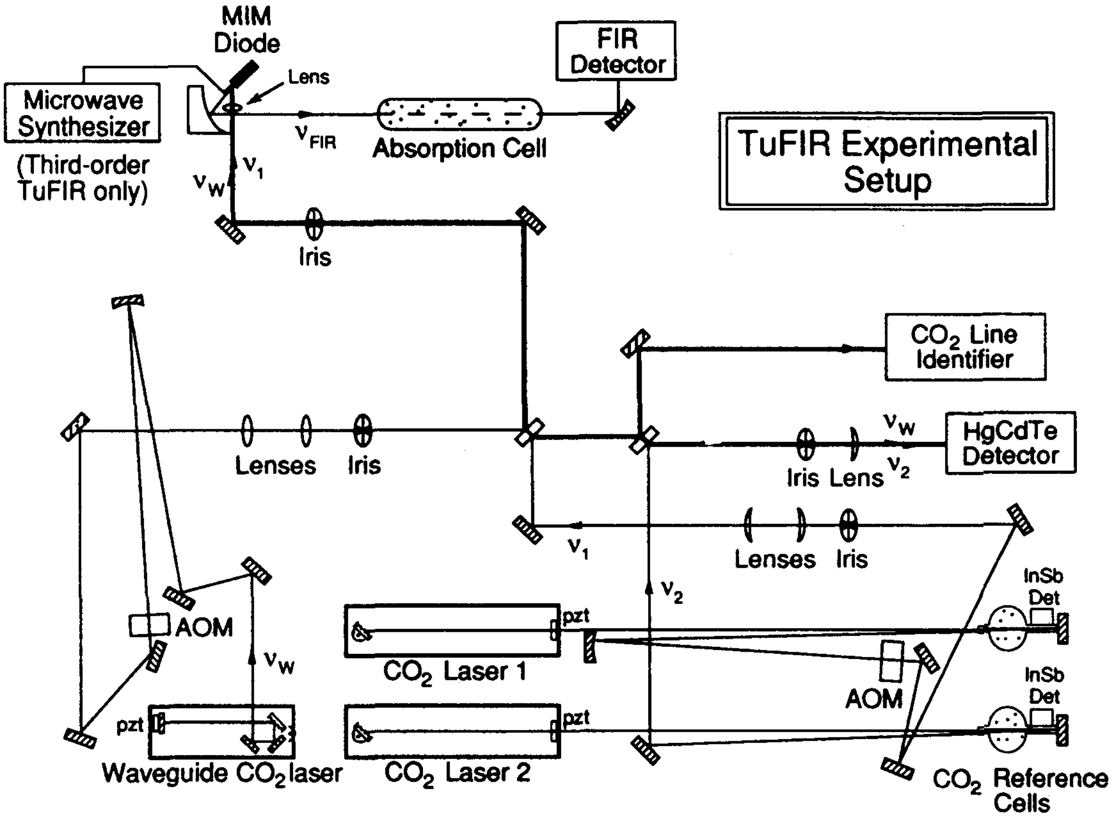

**Figure 40.1.** Tunable far-infrared spectrometer for second or third order operation using $CO_2$ laser difference frequency generation in the MIM diode.

signals obtained from the external low-pressure $CO_2$ reference cells. In both second and third order, the $CO_2$ reference lasers are stabilized to line center with an uncertainty of 10 kHz. The overall uncertainty in the FIR frequency due to two lasers is thus $\sqrt{2}$ x 10 or 14 kHz. This number was determined experimentally in a measurement of the rotational frequencies of CO out to $J = 38$ (4.3 THz), with the analysis of the data set determining the molecular constants [9].

The $CO_2$ radiation is focused by a 25 mm focal length lens onto the conically sharpened tip of the 25 $\mu$m diameter tungsten whisker. The FIR radiation is emitted from the 0.1 to 3 mm long whisker in a conical long-wire antenna pattern. Then it is collimated to a polarized beam by a corner reflector [22] and a 30 mm focal length off-axis segment of a parabolic mirror.

The largest uncertainty in the measurement of a transition frequency comes from finding the centers of the Doppler broadened lines. This is about 0.05 of the line width for lines observed with a signal-to-noise ratio of 50 or better and coresponds to about 0.05 to 0.5 MHz. A linefitting program [23] improves the line center determinations by nearly an order of magnitude. The FIR radiation is frequency modulated due to a 0.5 to 6 MHz frequency modulation of $CO_2$ laser 1; this modulation is at a rate of 1 kHz. The FIR detector and lock-in amplifier detect at this modulation rate; hence the derivatives of the absorptions are recorded.

Absorption cells from 0.5 to 3.5 m in length with diameters ranging from 19 to 30 mm have been used in the spectrometer. The cells have either glass, copper, or Teflon walls and have polyethylene or polypropylene windows at each end. These long absorption cells naturally lend themselves to electrical discharges for the study of molecular ions. A measurement of the $HCO^+$ line at 1 THz exhibited a signal-to-noise ratio of 100:1 using a 1 s time constant; this is the same signal-to-noise ratio which was obtained using the laser sideband technique.

The instrumental resolution of the spectrometer is limited by the combined frequency fluctuation from each $CO_2$ laser (about 15 kHz). This is less than any Doppler-limited line width and, therefore, does not limit the resolution. The entire data system is computerized to facilitate the data recording and optimize the data handling.

Improvements in this TuFIR technique may come from either better diodes or detection schemes. The nonlinearity of the MIM diode is extremely small, and conversion efficiencies could be much larger if a more efficient diode is discovered. Differential detection (which requires more sensitive detectors) could also significantly improve the sensitivity and permit the detection of weaker lines.

### 40.2.2 Laser Magnetic Resonance

Laser magnetic resonance (LMR) is performed by magnetically tuning the transition frequencies of paramagnetic species into coincidence with the fixed frequency radiation from a laser. LMR is a type of Zeeman spectroscopy [24], and its chief forte is its extreme sensitivity. Approximately one hundred species have been observed in the SM-FIR region. These include atoms, diatomics (especially hydrides), polyatomics, ions, metastables, metastable ions [25], and many "first observations" of free radicals. These observations are summarized in several review articles on LMR [26, 27].

The FIR LMR spectrometer at NIST, Boulder is shown in Fig. 40.2. This spectrometer has an intracavity paramagnetic sample in a variable magnetic field which is labeled "sample volume" in the figure. A regular 38 cm EPR magnet with a 7.5 cm air gap is used. The laser cavity is divided into two parts by a Brewster angle polypropylene beam splitter about 12 $\mu$m thick. A $CO_2$ laser optically pumps the FIR laser gas. This pump beam makes many nearly perpendicular passes reflected by the walls of the gold-lined Pyrex tube. A 45° coupler serves to couple out the FIR radiation from the cavity to the helium-cooled detector. Mirrors each with an 89 cm radius of curvature are used in the nearly confocal geometry of the 94 cm cavity. One of the gold-coated end mirrors is moved with a micrometer to tune the cavity to resonance and also to determine the oscillating wavelength by moving the end mirror several half-wavelengths. The beam splitter is rotatable so that the polarization of the laser can be varied with respect to the magnetic field. Quartz spacers are used to minimize the thermal expansion of the cavity. This LMR spectrometer oscillates at wavelengths between 40 and 1000 $\mu$m. The technology of FIR lasers is reviewed by Nigel Douglas [28].

The LMR technique requires a close coincidence (typically within 20 GHz) between the absorption line and the frequency of the laser. Zero field frequencies which are 100 times more accurate than those obtained from optical spectra are obtained from the analysis of the Zeeman spectra observed (i.e. using the laser frequency and the magnetic field values). The accuracy is within 1 or 2 MHz and has permitted the far infrared astronomical observation of many of these species.

Atomic FIR LMR spectra are due to fine structure transitions and are magnetic dipole transitions; hence, they are several orders of magnitude weaker than electric dipole rotational spectra of molecules. The production of a sufficient atomic number density can be difficult; however, "atomic flames" have been very effective sources. and the high sensitivity of LMR has been the most successful spectroscopic technique for measuring these transitions. The atoms O, C, metastable Mg, S, Si, Fe, Al, $N^+$, $C^+$, and $F^+$ have been measured by FIR LMR. Atomic Zeeman spectra are relatively simple to analyze, and fine structure frequencies accurate to within 1 MHz can be determined.

In a FIR LMR spectrometer the sample is inside the laser cavity; hence, sub-Doppler line widths can be observed by operating the sample at low pressure and observing saturation dips in the signals. This has permitted the resolution of hyperfine structure in a number of hydrides. The observation of the resolved hyperfine structure is useful in the identification of the species involved and also yields accurate values of the hyperfine splittings.

Rotational spectra of most hydrides lie in this spectral region and many of the hydrides, such as OH, CH, SH, and NH have been observed. Others, such as CaH, MnH, TiH, and ZnH are excellent candidates for LMR studies. Ions are much more difficult because of their low concentrations; however, the use of a special microwave discharge operating in the magnetic field has proved to be an extremely productive source of ions for LMR studies [25].

The spectra of a number of polyatomic species has been observed by LMR: $NO_2$, $HO_2$, HCO, $PH_2$, $CH_2$, $CH_3O$, and CCH. The spectra of these polyatomic species are more difficult to analyze, resulting in a somewhat less accurate prediction of the zero-field frequencies. Spectra of the extremely elusive $CH_2$ and $CD_2$ have finally yielded to analysis with the simultaneous observation of FIR LMR spectra [29] and IR LMR spectra [30]. The data yield rotational constants which predict the ground state rotational transition frequencies and permit the determination of the singlet-triplet splitting in that molecule [31].

The sensitivity of TuFIR is only about 1% of that of laser magnetic resonance, but it is difficult to compare the two because the sample can be very large in the TuFIR spectrometer and is limited to about 2 cm in the LMR spectrometer.

### 40.2.3 TuFIR and LMR Detectors

Four different detectors have been used in the TuFIR and LMR spectrometers: (1) an InSb 4 K, liquid $^4$He-cooled, hot-electron bolometer, operating from 0.3

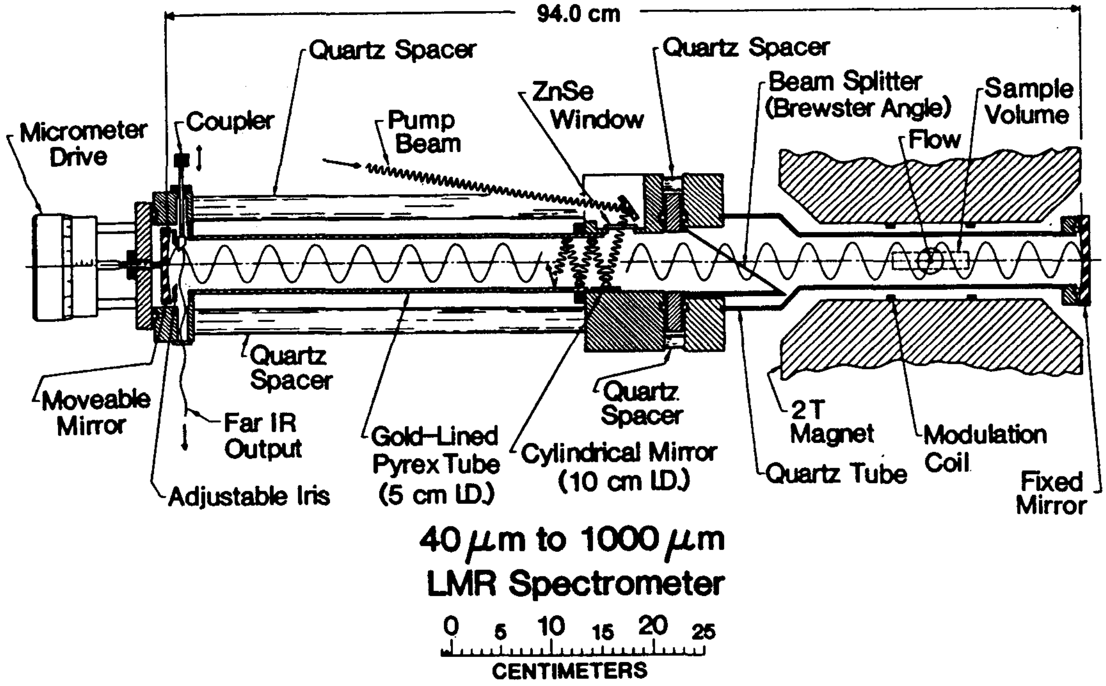

**Figure 40.2.** Far-infrared laser magnetic resonance spectrometer using an optically pumped FIR laser.

to 0.6 THz with a noise equivalent power (NEP) of about $10^{-13}$ W/$\sqrt{\text{Hz}}$; (2) a gallium doped germanium bolometer, cooled to the lambda point of liquid-helium, operating from 0.6 to 8.5 THz with an NEP of about $10^{-13}$ W/$\sqrt{\text{Hz}}$; (3) a similar, but liquid $^3$He-cooled bolometer, with a NEP two orders of magnitude smaller; and (4) an unstressed Ge:Ga photoconductor, cooled to 4 K, with an NEP of $10^{-14}$ W/$\sqrt{\text{Hz}}$, operating from 2.5 to 8.5 THz. The optimization of detector systems for this new technique has been responsible for a significant improvement in sensitivity of these spectrometers.

## 40.3 SUBMILLIMETER AND FIR ASTRONOMY

Submillimeter astronomy is reviewed in Ref. [6]. Many atomic species (both neutrals and ions) and more than 96 molecules have been detected in interstellar space; many were first observed in the submillimeter and FIR region. In the microwave and submillimeter region, radio (heterodyne) techniques are employed in the receivers. At higher frequencies, interferometric techniques are used [14]; however, heterodyne techniques recently have been employed at these higher frequencies and have resulted in the detection of CO [32] and OH [33] at 2.5 THz and methylene [34] at 30 THz. Submillimeter radio astronomy observatories (at high altitudes above much of the water vapor absorptions in our atmosphere) use laboratory determined frequencies. For example, the Kuiper Airborne Observatory and the submillimeter and FIR telescopes on Mauna Kea, Hawaii require frequencies accurate to about 1 MHz in their heterodyne receivers. For heterodyne detection, fixed frequency FIR gas lasers generally serve as local oscillators, and the frequencies of these lasers must be known. Nearly 1000 FIR laser lines have been directly frequency measured and are summarized in a review article [35].

There are four main goals of laboratory SM-FIR spectroscopy which serve the needs of the SM-FIR radio astronomy field:

1. to provide accurate frequencies of SM-FIR species for their detection,
2. to find new far infrared active species,
3. to measure the frequencies of FIR species which can be used to calibrate Fourier transform spectrometers, and
4. to measure frequencies of far-infrared lasers for use as local oscillators in radio astronomy receivers (and to be used in the analysis of laboratory LMR data).

## 40.4 UPPER ATMOSPHERIC STUDIES

A very impressive set of SM-FIR spectra of our upper atmosphere has been observed using balloon-borne

FT spectrometers flown at altitudes where the lines are narrow and the spectrometer is above the "black," heavily absorbing water vapor transitions [7]. A number of very important species with very strong SM-FIR spectra have been observed. They include: $O_2$, $H_2O$, NO, ClO, OH, $HO_2$, $O_3$, and O. Numerous lines have not yet been identified. It is difficult to calibrate these instruments absolutely because the spectra come from the species emitting at temperatures of about 200 K, and from an indeterminate path length. The high sensitivity of LMR might provide an alternate way of measuring the paramagnetic species in our upper atmosphere by flying an LMR spectrometer to high altitudes. A light-weight solenoid magnet could be used to increase the path length. Absolute concentrations of the paramagnetic species such as OH, $HO_2$, NO, and O could be obtained.

## *Acknowledgments*

I have benefitted invaluably from the help and collaboration of John Brown, Oxford University, England for his theoretical and experimental work over many years of collaboration, I.G. Nolt of NASA, Langley for his assistance with the detector technology, and Kelly Chance for his line shape fitting program and his assistance with our studies of upper atmospheric species.

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