

# TUNABLE FAR-INFRARED ABSORPTION SPECTROSCOPY OF CH<sub>2</sub>F<sub>2</sub>, CH<sub>3</sub>OH, AND <sup>13</sup>CD<sub>3</sub>OH LASER TRANSITIONS \*

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## ABSTRACT

Difference-frequency generation of tunable far-infrared radiation in a metal-insulator-metal (MIM) diode irradiated by two saturation stabilized CO<sub>2</sub> lasers allows nearly complete coverage of the region from 0.3 to 6 THz (1 mm to 50 μm). This work reports the use of this radiation for absorption measurements of laser transitions in CH<sub>2</sub>F<sub>2</sub>, CH<sub>3</sub>OH and <sup>13</sup>CD<sub>3</sub>OH in their excited vibrational states.

Difference-frequency generation of tunable far-infrared (TuFIR) radiation in a metal-insulator-metal (MIM) diode provides a highly accurate source of radiation for spectroscopic measurements.<sup>1,2</sup> This radiation was used by Inguscio et al.<sup>2</sup> to measure the frequency of the strong FIR methanol laser transition at 119 μm by measuring the laser transition in absorption in the excited vibrational state. This measurement is more accurate than measurements using the laser emission because it eliminates cavity-pulling and pump-pulling effects that can alter the shape of the gain curve leading to erroneous determination of its line center. In this work we extended the technique to important FIR laser transitions in CH<sub>2</sub>F<sub>2</sub>, CH<sub>3</sub>OH and <sup>13</sup>CD<sub>3</sub>OH, and improved the previous measurement technique<sup>2</sup> by using a White cell.

The radiations from two saturation-stabilized CO<sub>2</sub> lasers (one a conventional laser, the other a waveguide laser) and a tunable microwave source are mixed on a metal-insulator-metal (MIM) diode to generate far-infrared radiation in the 0.3 to 6 THz spectral region. The FIR frequency can be tuned either by varying the waveguide laser frequency (i. e. in second order), or by adding the radiation of a tunable microwave sideband source to the CO<sub>2</sub> difference (i.e. in third order). The frequency of the FIR radiation is known with an accuracy (1σ) of 15 kHz and has a spectral purity of about 10 kHz. Frequency modulation of one of the CO<sub>2</sub> lasers produces modulated FIR radiation; lock-in detection of the FIR radiation produces a first derivative of the absorption. A recently revised set of CO<sub>2</sub> laser frequencies<sup>3</sup> was used.

A one-meter long White cell fitted with high density polypropylene windows was

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used for the absorption cell. A maximum path length of 40 m could be achieved with a transmitted power of around 60% relative to a path length of 4 m. The optimum setting was usually in the range 16 m to 24 m. The White cell yielded a factor of five improvement compared to the 4 m cell used in the previous experiment<sup>2</sup>.

Since several of the laser lines to be measured in absorption were close to other absorption lines, an aid for the identification of the laser line was implemented: the beam of a free running CO<sub>2</sub> laser, tuned to the pump line of the laser transition, was focused into the viewport of the White cell to longitudinally excite the upper level of the absorption line. This leads to the observation of a sharp, induced emission spike on top of the absorption profile of the laser line. The width of the emission spike is determined by the jitter of the pump laser and the homogeneous width of the absorption medium. The signal has a phase opposite to that of the Doppler- and pressure-broadened absorption line.

To determine accurate center frequencies, a first-derivative Voigt profile was fit to every measured line using a least squares fitting program.<sup>4</sup> Due to baseline modulation, the overlap of strong ground-state absorption lines, and small signal-to-noise ratios, line centers of the laser transitions could be determined to typical accuracy ( $1\sigma$ ) of 80 kHz, (excluding the anomalously large one for the 242.847  $\mu\text{m}$  line of CH<sub>3</sub>OH).

The measured frequencies are displayed in Table I, along with the previous heterodyne frequency measurements.<sup>5</sup> A total of 15 "strong" or "very strong" FIR laser lines in CH<sub>3</sub>OH, <sup>13</sup>CD<sub>3</sub>OH and CH<sub>2</sub>F<sub>2</sub> were measured. Among them is the frequency of the 123  $\mu\text{m}$  line in methanol, pumped by the hot-band CO<sub>2</sub> line 9HP(20)<sup>6</sup>. This line is currently the most efficient FIR laser line that is now known. We also remeasured the frequency of the 119  $\mu\text{m}$  methanol laser line. The absorption measurements are in good agreement with the emission measurements to within the uncertainties except for the <sup>13</sup>CD<sub>3</sub>OH laser line at 281.388  $\mu\text{m}$ . In this case the discrepancy is probably due to the increased uncertainty resulting from using two longitudinally-pumped FIR lasers for that frequency measurement.<sup>7,8</sup>

In summary the direct absorption frequency measurements of these lasing transitions has confirmed the usefulness of this technique: the frequency measurement of strong and non-overlapping laser transitions in the far-infrared in absorption can improve the accuracy of line center determination by about an order of magnitude.

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**Table I - Frequency Measurements of Far-Infrared Laser Transitions by Absorption Spectroscopy**

Molecule	Pump Line CO <sub>2</sub> Laser	Wavelength FIR Laser  μm	TuFIR Frequency Measurement (Absorption) MHz	Previous Heterodyne Frequency Measurement (Laser Emission) MHz
CH <sub>3</sub> OH	9P(34)	70.512	4 251 674.56(10)	4 251 674.00(210)
CH <sub>3</sub> OH	9P(36)	110.716	2 707 749.40( 3)	2 707 749.30( 50)
CH <sub>3</sub> OH	9P(36)	118.834	2 522 782.74( 8)	2 522 782.46( 50) <sup>2</sup>
"	"	"	2 522 782.57( 7) <sup>2</sup>	"
CH <sub>3</sub> OH	9HP(20)	123.452	2 428 421.90( 5)	2 428 422.60( 50) <sup>6</sup>
<sup>13</sup> CD <sub>3</sub> OH	10P(08)	127.021	2 360 174.76( 7)	2 360 174.80( 50)
CH <sub>3</sub> OH	9P(12)	163.574	1 832 769.97(10)	1 832 768.60( 90)
CH <sub>3</sub> OH	9P(14)	164.508	1 822 362.05(15)	1 822 362.70( 90)
CH <sub>3</sub> OH	9P(16)	164.600	1 821 334.91(14)	1 821 335.20( 90)
CH <sub>3</sub> OH	9R(10)	164.783	1 819 313.37( 9)	1 819 314.00( 40)
CH <sub>2</sub> F <sub>2</sub>	9R(32)	184.306	1 626 601.18( 5)	1 626 602.60( 80)
CH <sub>2</sub> F <sub>2</sub>	9R(34)	214.579	1 397 117.66( 5)	1 397 118.60( 70)
CH <sub>2</sub> F <sub>2</sub>	9R(06)	236.601	1 267 081.78(10)	1 267 081.50( 60)
CH <sub>3</sub> OH	10R(32)	242.847	1 234 489.80(18)	1 234 490.40( 20)
<sup>13</sup> CD <sub>3</sub> OH	10R(08)	281.388	1 065 410.33( 5)	1 065 407.30( 70) <sup>8</sup>
CH <sub>2</sub> F <sub>2</sub>	9P(04)	289.500	1 035 552.89(20)	1 035 552.70( 50)

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