Discovery and Frequency Measurement of Far-Infrared Laser Emissions Generated by Optically Pumped CH_2DOH

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ABSTRACT
A recently improved three-laser heterodyne system was used to frequency measure ten previously observed optically pumped far-infrared (FIR) laser emissions from the partially deuterated methanol isotopologue CH_2DOH. Also, a 64.0 μm FIR emission generated by the 9*P*32 line of the carbon dioxide (CO_2) laser was discovered and frequency measured. These newly measured frequencies have fractional uncertainties on the order of $\pm 2 \times 10^{-7}$ and correspond to laser wavelengths ranging from 42.6 to 152.7 μm. The offset frequency for the CO_2 pump laser was measured for twenty-two CH_2DOH FIR laser emissions.

INTRODUCTION
The CH_2DOH isotopic species of methanol has emerged as an effective medium for generating optically pumped far-infrared (FIR) laser emissions. Along with the first observation of FIR laser action from this molecule in 1978 [1], subsequent investigations have detailed the discovery and frequency measurement of CH_2DOH FIR laser emissions [2-6]. Currently, there are over eighty known FIR laser emissions having wavelengths that range from 42.6 to 762.5 μm. Of these, twenty-three lines are in the short-wavelength (25 μm < λ < 150 μm) portion of the FIR region and fifty have been frequency measured. Utilizing improvements recently made to the three-laser heterodyne system [7, 8], the frequencies of ten previously discovered FIR laser emissions have been measured for the first time. Along with the discovery and frequency measurement of a new short-wavelength FIR laser emission, twenty-two CO_2 offset frequencies for FIR laser lines are reported.

EXPERIMENTAL DETAILS
The optically pumped molecular laser used to generate FIR emissions consisted of a tunable Fabry-Perot cavity that was pumped in a X-V geometry with infrared radiation from a 2-m-long CO_2 laser, discussed in detail in Ref. [9]. The FIR cavity utilizes a nearly confocal mirror system with one mirror mounted on a calibrated micrometer used to tune the cavity into resonance with the FIR laser radiation. Initial FIR laser wavelengths were determined by measuring the micrometer movement between twenty adjacent longitudinal modes, corresponding to ten full wavelengths. The CH_2DOH, 98% D enriched, sample was obtained from Cambridge Isotope Laboratories.

The frequencies of the FIR laser emissions were measured using the three-laser heterodyne technique [7, 8, 10, 11]. Here, reference frequencies were used from two continuous-wave CO_2 lasers, selected such that their difference frequency was in the FIR region, close to that of the unknown laser frequency. The CO_2 reference emissions were stabilized by locking each laser to the saturation dip in the 4.3 μm fluorescence signal from an external reference cell [12]. These signals, along with the unknown FIR laser emission, were then combined in a metal-insulator-metal (MIM) point contact diode consisting of a sharpened tungsten whisker in contact with a polished nickel rod. The unknown FIR laser emission and the difference frequency created from the two CO_2 reference emissions produced a beat frequency in the microwave region that was amplified (using one of two amplifiers) and observed on a spectrum analyzer. The amplifiers used in this work were either an Avantek amplifier (operating between 0.1 and 1200 MHz) or a Miteq AFS44 amplifier (operating between 0.1 to 26.5 GHz). Once the beat was observed, it was measured by placing standardized frequency markers at half the maximum amplitude, symmetrically about the center of the peak. The average of these frequencies was taken as the center of the beat frequency. A typical display on the spectrum analyzer can be seen in Fig. 1. Due to the increased spectral range (up to 25 GHz) and sensitivity (up to a factor of 30) of the heterodyne system [8], several previously observed FIR emissions, such as the 49.0 μm FIR emission shown in Fig. 1, were able to be frequency measured.

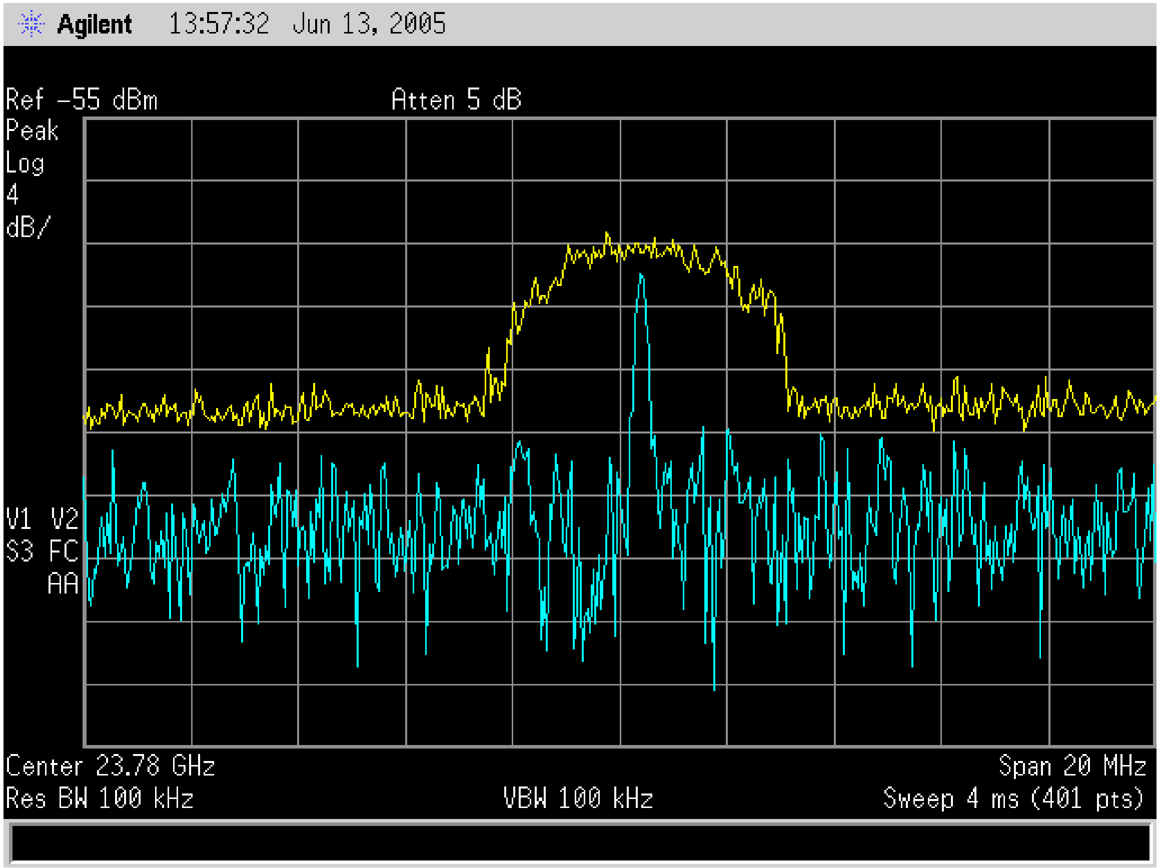

Figure 1. Observed beat frequency at –23782.5 MHz between the 49.0 μm FIR emission of CH_2DOH (generated by the 10*P*46 pump line) and the 9*R*40 and 10*R*40 CO_2 reference emissions.

To calculate the unknown FIR laser frequency, ν_{FIR}, the relation

$$\nu_{FIR} = |n_1 \nu_{CO2(I)} - n_2 \nu_{CO2(II)}| \pm \nu_{beat} \quad \text{Eq. 1}$$

was used, where $|n_1 \nu_{CO2(I)} - n_2 \nu_{CO2(II)}|$ is the difference frequency synthesized by the two CO_2 reference lasers and ν_{beat} is the measured beat frequency. The integers n_1 and n_2 correspond to the respective harmonics used to generate the difference frequency.

The one-sigma fractional uncertainty, $\Delta\nu/\nu$, of the FIR laser frequency measurements in this work was $\pm 2 \times 10^{-7}$. This uncertainty was derived mainly from the broadened gain curve of the observed FIR laser emission and the reproducibility of the measurements. To minimize this uncertainty, the FIR cavity was tuned across the gain curve and the center frequency was measured using a peak hold feature. Irises internal to the laser cavity were used to eliminate higher-order modes and help shape the gain curve to a symmetric pattern. In all cases, two or more sets of CO_2 reference lines were used and at least fifteen sets of measurements were recorded and averaged to obtain the FIR laser frequencies. In general, the fundamentals ($n_1 = 1$, $n_2 = 1$) and first harmonics ($n_1 = 2$, $n_2 = 2$) were used to generate the beat frequency; however, for wavelengths shorter than 60.0 μm, only the first harmonics could be used.

The reported offset was the difference measured between the CH_2DOH absorption frequency and the center frequency of the CO_2 pump emission. The CO_2 pump line was set to obtain optimal FIR power and was then mixed (in the MIM diode) with the same CO_2 emission, generated by the CO_2 reference laser, locked to its center frequency. As with FIR laser frequency measurements, the difference between these laser emissions creates a beat frequency in the microwave region. The beat was observed and measured on the spectrum analyzer with an uncertainty of either ± 10, ± 15 or ± 20 MHz. This uncertainty was mainly derived from the reproducibility of these measurements. A typical offset measurement using the 10*R*34 CO_2 pump line is shown in Fig. 2.

RESULTS

The measured FIR laser frequencies and their offsets, along with new offset measurements for previously measured FIR laser frequencies, are listed in Tables 1 and 2 respectively, arranged in order of the CO_2 pump line. All new frequency measurements are reported with their corresponding wavelength and wavenumber, calculated from the average frequency using 1 cm^{-1} = 29 979.2458 MHz, as well as with their offset and respective reference. All FIR laser frequencies were measured under optimal operating conditions.

Table I

Measured FIR Laser Frequencies Generated by Optically Pumped CH_2DOH

CO_2 Pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Offset (MHz)	Ref.
9*R*24	152.738	1 962 784.8 ± 0.6[a]	65.4715	–32 ± 10	2
9*P*18	87.156	3 439 707.5 ± 0.7[a]	114.7363	+19 ± 10	2
	100.092	2 995 176.4 ± 0.6[a]	99.9083	+19 ± 10	2
9*P*30	44.870	6 681 301.8 ± 1.4[a]	222.8642	+25 ± 10	2
9*P*32	56.041	5 349 477.7 ± 1.1[b]	178.4394	+23 ± 10	6
	64.000	4 684 228.9 ± 1.0[c]	156.2491	+23 ± 10	New[d]
9*P*38	42.556	7 044 642.6 ± 1.5[c]	234.9840	+20 ± 10	2
9*P*40	86.520	3 465 008.5 ± 0.7[a]	115.5802	–19 ± 10	6
10*P*30	90.219	3 322 932.6 ± 0.7[a]	110.8411	–4 ± 20	2
10*P*46	49.014	6 116 458.0 ± 1.3[a]	204.0231	–21 ± 15	6
	56.853	5 273 139.0 ± 1.1[c]	175.8930	–21 ± 15	6

[a] Measured with four sets of reference lasers.
[b] Measured with two sets of reference lasers.
[c] Measured with three sets of reference lasers.
[d] Observed in the parallel polarization at 13 Pa as a weak (0.01 to 0.001 mW) line.

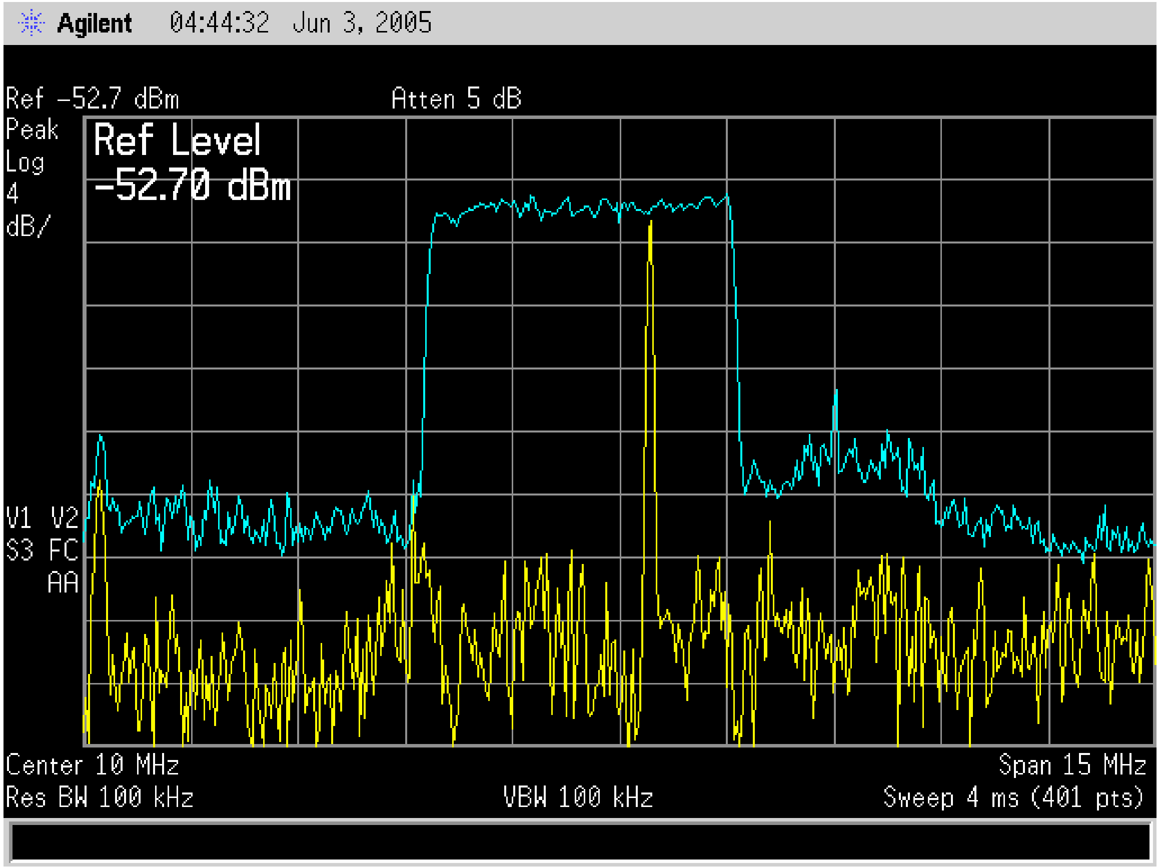

Figure 2. Observed beat frequency used for the offset measurement between the 10*R*34 CO_2 reference frequency and the 10*R*34 CO_2 pump frequency used to generate the 150.816 μm CH_2DOH FIR laser emission.

Table II

New offset measurements for previously measured FIR laser frequencies generated by optically pumped CH_2DOH

CO_2 Pump	Wavelength (μm)	Frequency [a] (MHz)	Wavenumber (cm^{-1})	Offset (MHz)
9*R*8	135.834	2 207 058.3 ± 1.1	73.6195	–10 ± 15
9*P*12	108.818	2 754 995.7 ± 1.4	91.8968	–17 ± 15
	112.532	2 664 058.3 ± 1.3	88.8634	–17 ± 15
9*P*16	102.023	2 938 465.1 ± 1.5	98.0166	–29 ± 10
9*P*32	108.941	2 751 872.9 ± 1.4	91.7926	–4 ± 15
	117.085	2 560 467.0 ± 1.3	85.4080	–4 ± 15
10*R*34	150.816	1 987 798.9 ± 1.0	66.3058	–12 ± 10
	159.218	1 882 906.3 ± 1.0	62.8070	–12 ± 10
10*R*32	135.172	2 217 863.3 ± 1.1	73.9800	–17 ± 10
	135.173	2 217 849.9 ± 1.1	73.9795	–17 ± 10
10*P*34	124.432	2 409 293.3 ± 1.2	80.3654	–26 ± 10

[a] All FIR laser frequencies were previously reported in Ref. [2].

CONCLUSIONS

This work reports the discovery of the 64.0 m FIR laser line from CH_2DOH when optically pumped by the 9*P*32 CO_2 emission. The frequency of this line, along with the frequencies of ten previously observed FIR laser emissions generated by optically pumped CH_2DOH, have been measured with fractional uncertainties on the order of $\pm 2 \times 10^{-7}$. In addition, the offset frequencies for twenty-two CH_2DOH laser emissions have been measured. These measurements will be useful for future assignments of FIR laser emissions by calculation of combination loops from high-resolution Fourier transform data [13]. Not only will this data be helpful in the theoretical modeling of CH_2DOH, these emissions can serve as sources of coherent radiation for a variety of spectroscopic investigations, including laser magnetic resonance spectroscopy.

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