Discovery and Frequency Measurement of Short-Wavelength Far-Infrared Laser Emissions From Optically Pumped $^{13}CD_3OH$ and CHD_2OH

Gustav M. Borstad, Cathy Connell
Chris Uranga, Department of Chemistry, San Diego State University

Faculty Sponsors: M. Jackson and L. R. Zink, Department of Physics

ABSTRACT
A three-laser heterodyne system was used to measure the frequencies of twelve previously observed far-infrared laser emissions from the partially deuterated methanol isotopologues $^{13}CD_3OH$ and CHD_2OH. Two laser emissions, a 53.773 μm line from $^{13}CD_3OH$ and a 74.939 μm line from CHD_2OH, have also been discovered and frequency measured. The CO_2 pump laser offset frequency was measured with respect to its center frequency for twenty-four FIR laser emissions from CH_3OH, $^{13}CD_3OH$ and CHD_2OH.

INTRODUCTION
Methanol and its isotopic forms have proved effective in generating optically pumped far-infrared (FIR) laser emissions [1-3]. A review by Xu and Hurtmans in 1997 [4] compiles fifteen experimental investigations of $^{13}CD_3OH$ as an FIR laser medium that began in 1984 and includes the spectroscopic assignment of 100 FIR laser emissions. Combined with the discovery of four FIR laser emissions in 2003 [5], this molecule is capable of generating 193 laser emissions, ranging in wavelength from 32 to 2615 μm. CHD_2OH first generated FIR laser emissions in 1978 [6] and is known to produce 166 FIR laser emissions using both continuous-wave (cw) and pulsed CO_2 laser pump sources [6-12]. In this work, two new short-wavelength ($\lambda < 150$ μm) FIR laser emissions have been discovered and the frequencies of fourteen FIR laser emissions from optically pumped $^{13}CD_3OH$ and CHD_2OH have been measured. Also reported are the offset frequencies for twenty-four FIR laser emissions from optically pumped CH_3OH, $^{13}CD_3OH$ and CHD_2OH.

EXPERIMENTAL DETAILS
The optically pumped molecular laser and frequency measurement system is shown in Figure 1. The FIR laser generates short-wavelength FIR emissions using an X-V pumping geometry [13]. The 2 m long, cw CO_2 pump laser has a 135 line/mm grating that provides approximately 5% output coupling in zeroth order [14]. This CO_2 laser generates lines out to 9*R*54, 9*P*56, 10*R*54 and 10*P*56 with powers up to 30 W while emissions from the sequence and hot bands were observed with powers up to 10 W. The 2 m long FIR laser cavity utilizes a nearly confocal mirror system with one mirror mounted on a calibrated micrometer that tunes the cavity into resonance with the FIR laser radiation. Initial FIR laser wavelengths were estimated by measuring the micrometer movement between twenty adjacent longitudinal modes. The $^{13}CD_3OH$ (99% ^{13}C, 98% D) sample was obtained from Cambridge Isotope Laboratories and the CHD_2OH (98.6% D) sample was obtained from MSD Isotopes.

The frequencies for particular FIR laser emissions were measured using the three-laser heterodyne system [15, 16]. Reference frequencies from two cw CO_2 lasers were selected such that a harmonic of their difference frequency nearly equals that of the unknown FIR laser frequency. The CO_2 reference emissions were stabilized to the saturation dip in the 4.3 μm fluorescence signal of an external reference cell [17]. The reference frequencies and unknown FIR laser frequency were mixed in a metal-insulator-metal (MIM) point contact diode consisting of a sharpened tungsten whisker in contact with a polished nickel rod. Here, the unknown FIR laser emission and reference frequencies combine to create a beat frequency in the microwave region that was then amplified and measured on a spectrum analyzer.

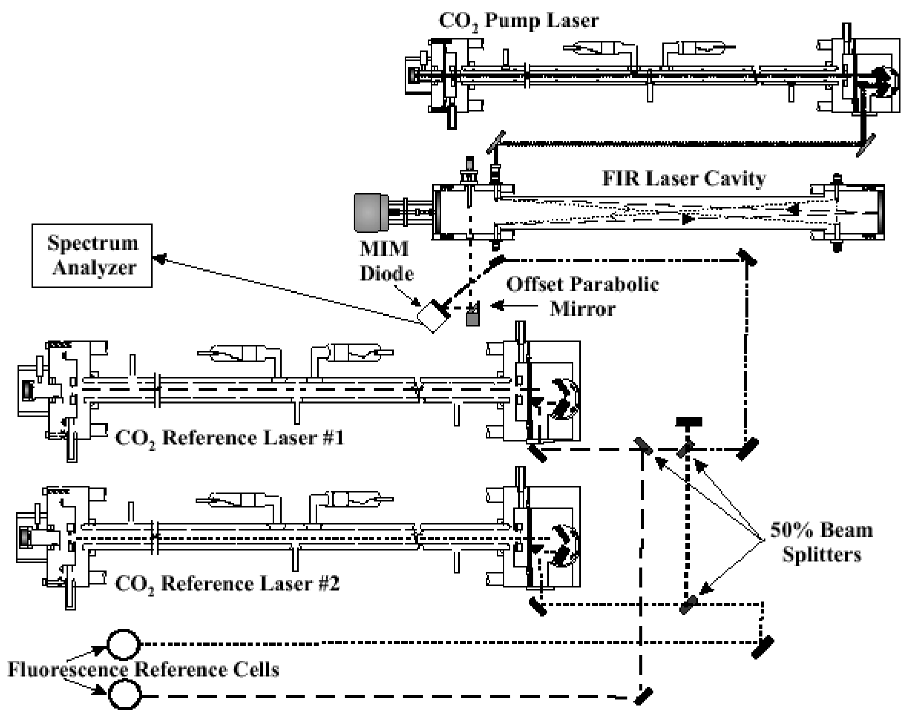

Figure 1. The three-laser heterodyne system.

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

$$\nu_{FIR} = n\left|\nu_{CO2(I)} - \nu_{CO2(II)}\right| \pm \nu_{beat},$$

was used, where $\left|\nu_{C02(I)} - \nu_{C02(II)}\right|$ is the difference frequency synthesized by the two CO_2 reference lasers and ν_{beat} is the measured beat frequency. The integer n is the respective harmonic of the CO_2 reference frequencies. The fundamental (or first harmonic, n = 1) and second harmonic (n = 2) were used to generate the beat frequency in this work.

The one-sigma fractional uncertainty, $\Delta\nu/\nu$, of the FIR laser frequency measurements is $\pm 2 \times 10^{-7}$. 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 laser gain curve and the center frequency was measured using a peak hold feature. Irises internal to the laser cavity eliminate higher-order modes and help shape the gain curve to a symmetric pattern. In most cases, at least two sets of CO_2 reference lines and at least fifteen sets of measurements were recorded for each FIR laser frequency.

The reported offset is the difference measured between the absorption frequency of the FIR laser medium and the center frequency of the CO_2 pump line. The absolute FIR absorption frequency can be calculated by adding the offset to the CO_2 reference frequency. The CO_2 pump line was set for optimal FIR power and was then mixed in the MIM diode with a known, stabilized CO_2 reference 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 uncertainties of ± 10, ± 15, or ± 20 MHz. The first two uncertainties were mainly derived from the reproducibility of the measurements. The ± 20 MHz uncertainty was reported when the CO_2 reference laser could not be stabilized to its center frequency or when the CO_2 pump laser could vary over 10 MHz while producing the FIR laser emission.

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 and arranged by molecule 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.

The 62.499 μm line of $^{13}CD_3OH$ generated with the 10*R*8 CO_2 pump was observed over a wide range of offset frequencies, from – 8 to 23 MHz. At various offset frequencies, this FIR laser emission was observed as either a singlet or doublet whose frequencies ranged from 4 796 751 to 4 796 761 MHz. Therefore the average frequency of this emission was observed to be 4 796 756 ± 6 MHz. Although consistent with the prior measurement [22], this particular laser emission might not be useful for spectroscopic applications due to the large frequency range over which it can operate. For CHD_2OH, the offset frequencies for the FIR laser emissions generated with the 10*HP*16 hot band emission were calculated from measurements made with respect to the unstabilized 10*P*50 CO_2 laser emission [25, 26]. The 164.924 μm laser emission (9*P*18 pump) appeared as a doublet due to its position at the edge of the CO_2 pump laser's gain curve and is reported with a larger uncertainty.

Table 1. Measured frequencies for FIR laser lines generated by optically pumped $^{13}CD_3OH$ and CHD_2OH

CO_2 Pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Offset (MHz)	Ref.
$^{13}CD_3OH$					
9*R*14	53.773	5 575 144.3 ± 1.2	185.9668	25 ± 10	New[a]
10*P*22	46.151	6 495 898.3 ± 1.3	216.6798	–5 ± 10	4
CHD_2OH					
9*R*50	54.625	5 488 147.7 ± 1.1	183.0649	2 ± 10	7
9*P*6	34.224	8 759 838.4 ± 1.8	292.1968	–2 ± 10	7
9*P*18	164.924	1 817 762.5 ± 2.0	60.6340	31 ± 15	7
9*P*50	59.776	5 015 279.6 ± 1.0	167.2917	0 ± 10	7
	74.939	4 000 499.1 ± 0.8	133.4423	0 ± 15	New[b]
	158.322	1 893 556.2 ± 0.4	63.1622	3 ± 10	7
10*R*40	102.517	2 924 322.0 ± 0.6	97.5449	–19 ± 15	8[c]
10*R*26	32.743	9 155 955.4 ± 1.9	305.4098	–32 ± 10	8
10*SR*11	52.520	5 708 118.2 ± 1.2	190.4023	–19 ± 10	7
10*P*18	46.739	6 414 178.6 ± 1.3	213.9540	–3 ± 20	7
10*HP*16	142.944	2 097 269.1 ± 0.5	69.9574	–10 ± 20	7, 12[d]
	150.292	1 994 739.0 ± 0.4	66.5373	–10 ± 20	7

[a] Observed as a W laser line (1 mW ≤ Power ≤ 10 mW) in the perpendicular polarization at 23 Pa.
[b] Observed as a VW laser line (Power ≤ 1 mW) in the parallel polarization at 23 Pa.
[c] Observed in the parallel polarization.
[d] Offset previously reported as 0 MHz [12].

Table 2. New offset measurements for previously measured FIR laser frequencies generated by optically pumped CH_3OH, $^{13}CD_3OH$, and CHD_2OH

CO_2 Pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Offset (MHz)	Ref.
CH_3OH					
9*R*18	61.613	4 865 709.8 ± 2.5	162.3026	–10 ± 10	18
$^{13}CD_3OH$					
9*R*30	150.177	1 996 261.6 ± 0.4	66.5881	–20 ± 10	19, 20
9*P*10	72.858	4 114 772.2 ± 0.9	137.2540	29 ± 10	5, 19
10*R*24	81.717	3 668 687.3 ± 1.5	122.3742	28 ± 10	5, 21
10*SR*27	66.667	4 496 880.8 ± 0.9	149.9998	31 ± 10	22
10*R*22	108.891	2 753 148.1 ± 0.6	91.8351	–33 ± 10	5
10*R*8	97.625	3 070 869.7 ± 0.7	102.4332	22 ± 10	5, 22
10*P*10	53.389	5 615 302.4 ± 1.2	187.3063	25 ± 10[a]	5, 23
CHD_2OH					
9*R*30	120.895	2 479 771.1 ± 0.6	82.7163	21 ± 10	24
10*R*18	127.386	2 353 414.0 ± 0.7	78.5014	17 ± 10	24

[a] Offset previously reported as 56 MHz [23].

CONCLUSIONS

This work reports the discovery of the 53.773 μm line from $^{13}CD_3OH$ and the 74.939 μm line from CHD_2OH when optically pumped by the 9*R*14 and 9*P*50 CO_2 laser emissions, respectively. The frequencies of these FIR laser emissions along with twelve previously observed FIR laser lines have been measured with fractional uncertainties on the order of $\pm 2 \times 10^{-7}$. The offset frequencies for twenty-four FIR laser emissions from CH_3OH, $^{13}CD_3OH$ and CHD_2OH are also reported. These measurements will be useful for future assignments of FIR laser emissions and can serve as sources of coherent radiation for a variety of spectroscopic applications, including laser magnetic resonance spectroscopy [27].

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