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OPTICALLY PUMPED cw CH_2DOH FIR LASER: NEW LINES AND FREQUENCY MEASUREMENTS

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We have measured the output powers and relative polarizations of 66 cw FIR laser lines from CH_2DOH (including 50 not previously reported), which were optically pumped by a CO_2 laser. The frequencies of 43 of these lines were measured relative to stabilized CO_2 lasers.

Key words: CH_2DOH, CO_2 laser, FIR laser, laser frequency measurement, new laser lines, relative intensity, relative polarization.

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Optically pumped FIR lasers have been successfully used in several interesting applications, including the spectroscopy of paramagnetic molecules and ions, chemical kinetics, frequency metrology, heterodyne radiometry, plasma diagnostics, and solid state spectroscopy (1-4). In the cw regime, these lasers can be tuned only over a narrow frequency range, typically 1-10 MHz, which restricts their application in spectroscopy to the cases where there is a close coincidence between the laser frequency and the absorption of the sample. At present, there are about 1000 lines available in the region of 5-250 cm^{-1}, and less than 100 of them have power in the mW range (5). It is therefore important to find more powerful lines to fill the gaps in the FIR spectrum.

Methyl alcohol, CH_3OH, is the best known FIR laser molecule with wide spectral coverage; over 100 lines in the 37-1200 µm region can be obtained when pumped by the normal CO_2 laser lines (6). The CO_2 infrared radiation excites the C-O vibrational mode of methanol. The exchange of H by D in the molecule does not shift this absorption appreciably. The center of the C-O band for regular methanol and all of its deuterated species falls in the 900-1100 cm^{-1} region of the CO_2 laser spectrum (7); so in principle, all are good FIR laser candidates. The symmetrically deuterated species CD_3OH (8), CH_3OD (9), and CD_3OD (10) give many strong lines when pumped by the CO_2 laser. The species obtained by substituting H for D in the methyl group CH_3 of methanol have the internal symmetry broken and should yield even more FIR lines than the symmetrical species. CH_2DOH and CHD_2OH have been observed to emit FIR lines when pumped by the CO_2 laser (11), but the number of lines found was significantly less than with the symmetric species. We have searched for new FIR lines in CH_2DOH by pumping over a wide range of methanol pressure with CO_2 laser lines from approximately J=4 to 46 in both the 9 and 10 µm bands. The results are presented in this paper.

The experimental setup consists of a 30 W CO_2 laser and a FIR cavity. The CO_2 laser is 2.2 m long with a 100 lines/mm diffraction grating on one end for line selection and a partially transmitting IR mirror on the other end. This mirror can be moved by a PZT translator for fine tuning of the laser over the gain curve. A 105 cm long FIR Fabry-Perot resonator is formed by two 12.5

cm diameter concave mirrors, one stationary and the other moveable, with radii of curvature R=200 cm. The input pump radiation is focused by a R=200 cm mirror through a 1 mm diameter hole at the center of the stationary copper mirror. The hole is sealed by a ZnSe window. A gold coated pyrex mirror on a mechanical translator at the other end permits tuning the FIR cavity to resonance with the rotational transition of the active gas. Power from the FIR laser is coupled out by an adjustable mirror formed by cutting and polishing a 6 mm diameter copper cylinder at 45°. This mirror can be positioned at various distances from the laser axis to couple radiation from the outer edge of the mode. The radiation exits the laser through a polyethylene window opposite to this mirror. Irises in front of both end mirrors provide excellent discrimination against longer wavelengths.

The measured FIR laser lines are listed in Table I. The approximate wavelengths were determined by counting the number of modes over a 5 mm scan of the FIR cavity length which was calibrated from the known wavelength of the 118.8 µm line of CH_3OH. With this technique, an accuracy of ±0.1 µm is obtained. This wavelength value is then used as an initial guess for direct frequency determination. Lines on which frequency measurements were performed are noted in Table I and listed separately in Table II.

The FIR laser line intensities were measured with a diamond window Golay cell with a 0.24 mm thick crystal quartz filter to stop 10 µm radiation. Other calibrated attenuators were used when necessary to prevent saturation of the Golay detector. The signal was modulated at 80 Hz by a chopper in front of the CO_2 laser beam, and the output of the Golay cell was measured with an oscilloscope or detected synchronously with a lock-in amplifier and then displayed on an X-Y recorder as a function of the length of the laser cavity. The Golay detector was calibrated with the 118.8 µm line of CH_3OH by comparing its output with the power as measured with a calibrated cone calorimeter (1). Table I lists the output power for each FIR laser line as measured with the Golay cell. This Fabry-Perot cavity has a very high Q and is excellent for observing the maximum number of lines over the whole FIR region. The output of the strong lines should be appreciably higher with a cavity designed for maximum output at a given laser wavelength as, e.g., in Hodges et al (12).

The CH_2DOH pressure was measured by a thermocouple gauge calibrated with a capacitance manometer or directly with the capacitance manometer. Isotopic purity of the sample gas was 98%. The pressures in Table I are those for which maximum output signal was obtained. The polarization of each FIR line was measured relative to the pump laser by a metal mesh polarizer. The shorter the wavelength, the better defined was the polarization.

We have directly measured the frequency of 43 of the CH_2DOH laser lines. Most of the weak ones were omitted because of the difficulty of measurement and because their power is too small for most practical uses even though an accurate determination of their frequencies might be important in the assignment of the transitions in the CH_2DOH molecule. Two CO_2 lasers and an X-band klystron were used to synthesize the FIR frequencies, and the radiations were mixed in a W-Ni point contact diode. The details of the experimental procedure are given elsewhere (13). The results of the frequency measurements are presented in Table II. Vacuum wavenumbers are derived from the frequency measurements with c = 299 792 458 m/s (14). Each line is labeled by the approximate wavelength and the CO_2 laser pump line.

In a careful investigation of the CH_2DOH FIR laser, 50 new laser lines were found. All but three of the lines reported by Ziegler and Durr (11) were also observed. Since these three lines have the same CO_2 pump and identical wavelengths but with greater output power for CHD_2OH, it is suggested that their origin in the CH_2DOH experiment arose from contamination of the sample gas by CHD_2OH. The 43 lines whose frequencies were measured constitute a considerable addition to the available lines for spectroscopy. Also, the determination of the relative intensities and polarization will help in the assignment of the transitions in CH_2DOH which in turn will permit the prediction of new lines when pumped by other lasers like N_2O or the sequence bands of CO_2.

Table I. *Summary of observed submillimeter laser lines obtained from* $^{12}CH_2D^{16}OH$ pumped by the normal laser bands of $^{12}C^{16}O_2$. FIR laser output powers for the listed methanol pressures, CO_2 pump powers, and the 1 m, variable output coupling, Fabry-Perot resonator were measured with a Golay detector. Response is assumed to be independent of the wavelength and intensity level over the ranges used. Primed and double-primed pump line entries in the table refer to different CO_2 pump offset frequencies.

CO_2 Pump Line	CH_2DOH Laser Line λ(μm)	Relative Polarization	FIR Output Power (mW)	CH_2DOH Laser Press. Pa(mTorr)	CO_2 Pump Power (W)	Reference
$R_{II}(24)'$	152.7	$\parallel$	0.20	13(100)	31	New
$R_{II}(24)''$	219.1[a]	$\parallel$	0.13	13(100)	30	New
	272.3[a]	$\parallel$	0.90	13(100)	30	11
	682.6	$\perp$	0.030	13(100)	30	New
$R_{II}(22)$	182.1	$\parallel$	0.063	9(70)	30	New
	171.8	$\parallel$	0.008	5(40)	30	New
	218.0	$\parallel$	0.025	6(45)	30	New
$R_{II}(16)$	216.8	$\parallel$	0.050	15(110)	29	New
$R_{II}(8)$	135.8[a]	$\perp$	0.038	11(80)	26	New
	164.7[a]	$\parallel$	0.050	9(70)	26	New
	422.2[a]	$\perp$	0.015	8(60)	26	New
$P_{II}(6)$	273.0[a]	$\parallel$	0.025	11(80)	20	New
$P_{II}(10)$	183.6[a]	$\parallel$	1.0	21(160)	24	New
	295.4[a]	$\parallel$	0.55	17(130)	24	11
$P_{II}(12)$	108.8[a]	$\parallel$	0.50	24(180)	24	11
	112.5[a,b]	$\parallel$	0.80	24(180)	24	New
	172.8[a,b]	$\perp$	0.20	13(100)	24	11
	322.5[a,b]	$\parallel$	0.50	18(135)	24	11
$P_{II}(14)$	206.7[a]	$\parallel$	0.68	13(100)	27	11
	308.0[a]	$\parallel$	0.50	15(110)	27	11
$P_{II}(16)$	102.0[a]	$\perp$	0.088	11(80)	30	New
$P_{II}(18)'$	87.1	$\perp$	0.20	19(145)	32	New
	100.0	$\parallel$	0.25	21(160)	32	New
	762.5	$\parallel$	0.063	17(130)	32	New
$P_{II}(18)''$	167.5[a]	$\parallel$	0.63	9(70)	27	11
	396.0	$\parallel$	0.15	9(70)	27	11

$P_{II}(20)$	140.3	⊥	0.025	12(90)	28	New
$P_{II}(26)$	468.2[a]	∥	0.55	11(80)	31	11
	616.3[a]	∥	0.75	11(80)	31	11
$P_{II}(30)$	44	∥	0.075	24(180)	30	New
$P_{II}(32)'$	108.9[a]	⊥	0.050	17(130)	28	New
	117.1[a]	⊥	0.063	17(130)	28	New
$P_{II}(32)''$	167.4[a]	∥	0.50	20(150)	29	New
	266.7[a]	∥	0.14	13(95)	29	New
	451.5[a]	⊥	0.075	11(85)	29	New
$P_{II}(36)$	195.5[a]	∥	0.43	11(85)	27	New
	336.2[a]	∥	0.40	11(85)	27	New
$P_{II}(38)$	42.5	⊥	0.025	28(210)	21	New
	200	⊥	0.015	9(70)	21	New
$P_{II}(40)'$	87.9	⊥	0.11	23(170)	19	New
$P_{II}(40)''$	387.6[a]	∥	0.20	11(80)	20	New
	523.1[a]	∥	0.25	10(75)	20	New
$P_{II}(46)$	226.3[a]	⊥	0.38	13(100)	15	New
	452.4	⊥	0.40	11(80)	15	New
$R_{I}(34)$	150.8[a]	∥	2.0	21(160)	34	11
	159.2[a]	∥	0.80	19(140)	34	New
	295.6[a]	∥	0.60	16(120)	34	11
$R_{I}(32)$	135.1718[a,c]	∥	0.13	17(130)	29	New
	135.1726[a,c]	∥	0.18	17(130)	29	New
	149.6[a]	∥	0.063	20(150)	29	New
	340.4[a]	∥	1.00	22(165)	29	New
$R_{I}(16)$	212.5	∥		11(80)		New
	300	∥	0.010	9(70)	33	11
$P_{I}(26)$	150.6[a]	⊥	0.31	15(110)	31	New
	188.4[a]	∥	0.70	15(110)	31	New
$P_{I}(28)$	189.3	∥	0.018	16(120)	31	New
	196.1	∥	0.025	16(120)	31	New
$P_{I}(30)$	90.4	∥	0.25	28(210)	34	New
	162.7	⊥	0.003	9(70)	34	New

$P_I(34)$	124.4[a]	$\parallel$	1.88	21(160)	24	11
	248.1[a]	$\perp$	0.75	15(115)	24	New
	249.7[a]	$\parallel$	0.43	15(115)	24	11
$P_I(36)$	149.4[a]	$\parallel$	0.020	13(100)	24	New
	224.2[a]	$\parallel$	0.050	13(100)	24	New
	427.2	$\perp$	0.004	20(150)	24	New
$P_I(46)$	374.1[a]	$\parallel$	0.045	12(90)	6	11

[a] Frequency measured and listed in Table II.

[b] These three lines probably arise from the following type transitions: 112.5 μm, J,K → J-1, K-1; 172.8 μm, J,K → J, K-1; and 322.5 μm, J,K → J-1,K.

[c] Experimental evidence for the existence of two lines is not conclusive. If there is one line, however, it appears to be split by 13.4 MHz with a width above lasing threshold of 20 MHz and no lasing between the two peaks. A typical width above lasing threshold for other lines of comparable wavelength and power is 10 MHz or less.

Table II. Summary of $^{12}CH_2D^{16}OH$ frequency measurements. Vacuum wavenumbers were calculated with c = 299 792 458 m/s (14).

CH_2DOH Laser Line λ(μm)	Measured Frequency (MHz) (Uncertainty: $\frac{\Delta\nu}{\nu} = \pm 5 \times 10^{-7}$)[a]	Vacuum Wavenumber (cm^{-1})	CH_2DOH Laser Press. Pa(mTorr)[b]	CO_2 Pump Line
102.0	2 938 465.1	98.016 646	11(80)	$P_{II}(16)$
108.8	2 754 995.7	91.896 764	24(180)	$P_{II}(12)$
108.9	2 751 872.9	91.792 598	15(110)	$P_{II}(32)'$
112.5	2 664 058.3	88.863 420	28(210)	$P_{II}(12)$
117.1	2 560 467.0	85.407 984	15(110)	$P_{II}(32)'$
124.4	2 409 293.3	80.365 373	21(160)	P_{I} (34)
135.1718	2 217 863.3	73.979 955	13(100)	R_{I} (32)
135.1726	2 217 849.9	73.979 509	13(100)	R_{I} (32)
135.8	2 207 058.3	73.619 541	12(90)	R_{II}(8)
149.4	2 006 805.2	66.939 816	25(190)	P_{I} (36)
149.6	2 003 788.3	66.839 182	25(190)	R_{I} (32)
150.6	1 991 028.3	66.413 555	15(110)	P_{I} (26)
150.8	1 987 798.9	66.305 835	17(130)	R_{I} (34)
159.2	1 882 906.3	62.806 993	19(140)	R_{I} (34)
164.7	1 819 720.3	60.699 335	11(80)	R_{II}(8)
167.4	1 791 384.9	59.754 168	21(160)	$P_{II}(32)''$
167.5	1 789 365.9	59.686 822	12(90)	$P_{II}(18)''$
172.8	1 734 446.4	57.854 903	11(80)	$P_{II}(12)$
183.6	1 632 666.9	54.459 905	15(110)	$P_{II}(10)$
188.4	1 591 161.2	53.075 426	13(100)	P_{I} (26)
195.5	1 533 499.9	51.152 051	15(110)	$P_{II}(36)$
206.7	1 450 463.1	48.382 240	12(90)	$P_{II}(14)$
219.1	1 368 315.4	45.642 089	13(100)	$R_{II}(24)''$
224.2	1 337 012.5	44.597 937	21(160)	P_{I} (36)
226.3	1 324 771.9	44.189 633	15(110)	$P_{II}(46)$
248.1	1 208 246.0	40.302 748	19(140)	P_{I} (34)
249.7	1 200 512.7	40.044 794	21(160)	P_{I} (34)
266.7	1 123 932.7	37.490 360	17(130)	$P_{II}(32)''$
272.3	1 101 159.4	36.730 724	13(100)	$R_{II}(24)''$
273.0	1 098 125.9	36.629 537	15(110)	P_{II}(6)
295.4	1 014 881.0	33.852 786	15(110)	$P_{II}(10)$
295.6	1 014 047.7	33.824 991	12(90)	R_{I} (34)

308.0	973 224.3	32.463 270	17(130)	$P_{II}(14)$
322.5	929 726.8	31.012 348	11(80)	$P_{II}(12)$
336.2	891 586.3	29.740 116	12(90)	$P_{II}(36)$
340.4	880 818.6	29.380 946	17(130)	R_{I} (32)
374.1	801 399.6	26.731 813	12(90)	P_{I} (46)
387.6	773 539.9	25.802 513	15(110)	$P_{II}(40)$"
422.2	710 154.3	23.688 198	7(50)	R_{II}(8)
451.5	664 028.4	22.149 603	15(110)	$P_{II}(32)$"
468.2	640 259.5	21.356 758	7(50)	$P_{II}(26)$
523.1	573 116.8	19.117 119	11(80)	$P_{II}(40)$"
616.3	486 411.5	16.224 940	28(210)	$P_{II}(26)$

a Estimated uncertainty in the reproducibility of the FIR laser frequency. For a discussion of problems related to the laser frequency reproducibility, see Petersen et al (6).

b Pressure at which each frequency was measured. Pressure was adjusted to produce maximum power out under the pumping and output coupling conditions for the 1 m Fabry-Perot resonator at the time of measurement. Measurements were done with a capacitance manometer calibrated in Torr (1 Torr = 133.3 Pa) or with a thermocouple gauge calibrated for CH_2DOH with the capacitance manometer.

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