New Frequency Measurements and Laser Lines of Optically Pumped $^{12}CH_3OH$

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Abstract—The frequencies of 70 optically pumped CW FIR $^{12}CH_3OH$ laser lines have been measured relative to stabilized CO_2 lasers. Fifteen new laser lines together with the relative output powers and polarizations for most of the 104 known lines pumped by laser lines in the normal 9 and 10 μm bands of $^{12}C^{16}O_2$ are also reported.

METHYL alcohol was one of the first molecules which was optically pumped by CO_2 lasers to produce CW FIR laser radiation [1]. Indeed, at the present time, over 100 FIR lines have been observed to lase when pumped by lines in the normal 9 and 10 μm bands of the $^{12}C^{16}O_2$ laser [1]-[6], and the list is increasing as the FIR lasers are refined. (Here, we exclude from consideration FIR lines produced by sequence band CO_2 lasers; e.g., see Weiss *et al.* [7].) The known lines span the wavelength spectrum from 38 μm to 1.2 mm with CW power outputs from less than 0.1 to over 100 mW, depending on the line and experimental conditions. The frequency stability of this optically pumped laser appears to be better than that of discharge pumped FIR lasers [8], and the uncertainty in the frequency reproducibility is of the order of a few parts in 10^7. As a result of these characteristics, the methyl alcohol laser has application in laser frequency synthesis [9], [10], laser magnetic resonance spectroscopy of molecules and free radicals [11], spectroscopy of methyl alcohol itself [6], FIR detector development and evaluation [18], etc. Generally, in the work in which new CH_3OH laser emission lines have been reported, wavelengths have been measured rather crudely—usually with fractional uncertainties of 10^{-2}-10^{-3}. These uncertainties are too large for frequency synthesis and are usually too large for spectroscopy since at 40 μm, e.g., an uncertainty of 10^{-2} corresponds to 2.5 cm^{-1}, which is three times the rotational constant in the vibrational ground state of methyl alcohol. As a result, frequency measurements have been made on a number of these lines [12]. We report here measurements on 70 additional lines, a number of which are strong and useful for metrology and spectroscopy. Over a thousandfold improvement in the accuracy of frequencies derived from wavelength measurements has been attained.

Methyl alcohol was optically pumped either by a 2 or 3 m $^{12}C^{16}O_2$ laser with an output power typically of the order of 20 W. Two FIR cavities were used. One was a 2 m long by 14 mm diameter copper waveguide with flat copper mirrors, one of which was movable for tuning purposes. Pump power was coupled into the waveguide through a 1 mm hole in the center of the fixed mirror. FIR power was coupled out of the cavity through a 3 mm hole located 5.5 mm from the center of the same mirror. Methyl alcohol pressures ranging from 4 to 80 Pa (1 torr = 133.3 Pa) were adjusted to maximize the FIR output power.

Since the bandpass of the frequency measurement system was only about 1500 MHz, reduction of the wavelength uncertainty was required in many cases (e.g., 1500 MHz at 40 μm implies $\Delta\lambda/\lambda = 2 \times 10^{-4}$). Because of the complicated mode structure in the waveguide cavity, it was difficult to make accurate wavelength measurements by varying the length of the cavity, particularly at wavelengths below 100 μm. Also, some of the longer wavelength lines, e.g., 1.2 mm, would not oscillate in this cavity. Therefore, a 1 m Fabry-Perot free-space cavity was constructed. Again, CO_2 power was coupled into the cavity through a 1 mm hole in one copper end mirror (2 m radius), and, for the first group of measurements, FIR power was coupled out through a 3 mm hole 5.5 mm from the center of the same mirror. Later, a variable coupler consisting of an elliptical mirror formed by cutting and polishing a 6 mm diameter copper cylinder at 45° was constructed. The mirror could be moved perpendicular to the cavity axis to optimize the output coupling at each wavelength. The reflected radiation was transmitted through a polyethylene window in the side of the vacuum chamber of the laser. A flat gold-coated pyrex mirror at the other end was adjusted by a calibrated micrometer to change the resonant frequency of the cavity. Higher order transverse modes and longer wavelength lines could be controlled by irises at each end of the resonator. CO_2 pump powers and methyl alcohol pressures were about the same as in the waveguide case. Total FIR output power was less, but fewer modes were oscillating and more accurate wavelength measurements were much easier to make.

In cases where the wavelengths were poorly known, or unknown in the case of new lines, new measurements were made by counting the number of modes over a 5 mm scan by the movable end mirror. The micrometer scale was calibrated from the known wavelength of the 118.8 μm $^{12}CH_3OH$ line. For wavelengths greater than about 50 μm, measurements could be made with fractional uncertainties between 10^{-3} and 10^{-4}, which allowed frequency predictions within the 1500 MHz bandpass of the frequency measurement system. How-

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TABLE I
SUMMARY OF $^{12}CH_3OH$ LASER FREQUENCY MEASUREMENTS. VACUUM WAVENUMBERS WERE CALCULATED WITH c = 299 792 458 m/s.

$^{12}CH_3OH$ Laser Line λ(μm)	Measured Frequency (MHz) (Uncertainty: $\frac{\Delta\nu}{\nu} = \pm 5\times10^{-7}$)[a]	Vacuum Wavenumber (cm^{-1})	$^{12}CH_3OH$ Laser Press. Pa(mTorr)[b]	$^{12}C^{16}O_2$ Pump Line
37.9	7 919 660.2	264.171 428	24(180)	$P_{II}(32)$
39.9	7 509 036.2	250.474 487		$P_{II}(34)$
42.2	7 110 981.4	237.196 807	32(240)	$P_{II}(32)$
53.9	5 566 052.7	185.663 533	32(240)	R_{I} (36)
55.4	5 414 344.1	180.603 079	15(110)	$P_{II}(40)$
60.2	4 982 153.1	166.186 738	11(83)	$P_{II}(40)$
61.6	4 865 709.8	162.302 607	15(110)	$R_{II}(18)$
63.0	4 761 182.4	158.815 951	15(110)	R_{I} (16)
63.4	4 730 860.6	157.804 522	15(110)	$P_{II}(34)$
67.5	4 441 675.2	148.158 338	15(110)	$R_{II}(18)$
69.7	4 302 444.9	143.514 116	15(110)	R_{I} (16)
70.5[c,d,e]	4 251 674.0	141.820 579	7(50)	$P_{II}(34)$
73.3	4 089 579.6	136.413 691	21(160)	$P_{II}(40)$
77.4	3 873 005.1	129.189 543		R_{II}(8)
77.9	3 848 185.5	128.361 651	19(140)	R_{I} (16)
85.6	3 502 210.2	116.821 159	21(160)	$P_{II}(40)$
86.2	3 476 282.5	115.956 302		R_{II}(8)
92.5	3 239 461.6	108.056 807	10(75)	$P_{II}(24)$
92.7	3 235 253.6	107.916 443	10(75)	R_{I} (34)
96.5[c,d,f]	3 105 936.8	103.602 901	13(100)	$R_{II}(10)$
97.5	3 074 210.0	102.544 609	28(210)	R_{I} (40)
100.8	2 973 940.6	99.199 981	35(260)	$R_{II}(14)$
113.7	2 635 958.0	87.926 096	29(220)	R_{II}(8)
118.0[c]	2 541 485.6	84.774 833		$P_{II}(14)$
118.8[c,d,f,g]	2 522 781.6	84.150 935	7(50)	$P_{II}(36)$
129.5[c]	2 314 111.3	77.190 443		R_{I} (34)
133.1[c]	2 252 054.2	75.120 442		$P_{II}(24)$
151.3	1 982 050.6	66.114 090	23(170)	$R_{II}(26)$
159.7	1 877 508.5	62.626 943	23(170)	$R_{II}(26)$
163.0[c,d]	1 838 839.3	61.337 076	7(50)	R_{I} (38)
164.5[c]	1 822 362.7	60.787 476		$P_{II}(14)$
164.6	1 821 335.2	60.753 202	16(120)	$P_{II}(16)$
164.7	1 820 261.5	60.717 388	9(70)	$P_{II}(24)$
164.8[c]	1 819 314.0	60.685 781		$R_{II}(10)$
167.6	1 788 876.6	59.670 502	28(210)	R_{I} (40)
170.6[c,d,g]	1 757 526.3	58.624 765	7(50)	$P_{II}(36)$
179.7	1 668 035.0	55.639 660	15(110)	R_{I} (4)
180.7	1 659 278.6	55.347 575	8(60)	$P_{II}(34)$
185.5	1 616 128.4	53.908 241	9(70)	$P_{II}(34)$
186.0	1 611 421.9	53.751 247	16(120)	$R_{II}(18)$
186.3	1 609 026.7	53.671 355	7(55)	$P_{II}(34)$
190.7	1 571 849.7	52.431 263	11(80)	$P_{II}(34)$
191.6	1 564 518.7	52.186 726	21(160)	R_{I} (10)
193.1	1 552 190.1	51.775 487	11(80)	$P_{II}(38)$
194.1	1 544 818.7	51.529 607	21(160)	$R_{II}(14)$
198.7	1 509 040.2	50.336 162	11(80)	$P_{II}(38)$
206.8	1 449 778.0	48.359 388	4(30)	$P_{II}(12)$
209.9	1 428 057.6	47.634 874	21(160)	$R_{II}(14)$
211.26	1 419 049.3	47.334 389	15(110)	R_{I} (4)
211.31	1 418 701.0	47.322 770	4(30)	$P_{II}(12)$
213.5	1 404 427.0	46.846 644	10(75)	$P_{II}(22)$
225.5	1 329 362.9	44.342 773		R_{II}(8)
232.8	1 287 832.2	42.957 458	21(160)	$R_{II}(22)$
232.9[c,d,f]	1 286 999.5	42.929 683	15(110)	$R_{II}(10)$
242.5[c]	1 236 396.8	41.241 758		R_{I} (34)
250.8[c,d]	1 195 433.9	39.875 383	12(90)	R_{I} (34)
251.1[c,d]	1 193 727.3	39.818 455	15(110)	R_{I} (38)
251.4	1 192 338.3	39.772 124	11(80)	$R_{II}(18)$
253.6	1 182 366.2	39.439 490	9(70)	$P_{II}(34)$
254.0	1 180 092.5	39.363 649	7(55)	$P_{II}(34)$
263.7	1 136 942.0	37.924 304	7(55)	$P_{II}(34)$
264.5	1 133 277.0	37.802 053	8(60)	$P_{II}(34)$
267.4[c]	1 120 957.7	37.391 122		R_{I} (34)
278.8	1 075 277.1	35.867 385	13(100)	$P_{II}(38)$
280.9	1 067 127.2	35.595 533	23(170)	$R_{II}(18)$
292.1	1 026 189.3	34.229 989	11(80)	$P_{II}(38)$
293.8	1 020 321.1	34.034 249	15(110)	R_{I} (10)
302.0[c]	992 708.9	33.113 206		$P_{II}(14)$
346.5	865 233.1	28.861 069	12(90)	$P_{II}(22)$
369.1[c,d]	812 195.4	27.091 924	7(50)	$P_{II}(16)$
386.3	775 982.4	25.883 986	11(80)	$P_{II}(14)$
392.1[c,d]	764 642.6	25.505 733	11(80)	$P_{II}(36)$
416.5[c]	719 751.1	24.008 311		$P_{II}(14)$
418.1[c]	717 065.0	23.918 714		$P_{II}(36)$
469.0[c,d]	639 184.6	21.320 902	17(130)	R_{I} (38)
570.6[c,d,f,h]	525 427.5	17.526 375	11(80)	$P_{II}(16)$
602.5	497 591.6	16.597 869	10(75)	$P_{II}(24)$
614.3	488 034.7	16.279 084	10(75)	$P_{II}(24)$
624.6	480 105.7	16.014 602	7(50)	$P_{II}(38)$
694.2	431 859.8	14.405 294	9(70)	$P_{II}(24)$
695.3	431 139.0	14.381 248	17(130)	R_{I} (16)
699.4[c,d,f]	428 628.5	14.297 508	7(50)	$P_{II}(34)$
1 223.7	244 996.6	8.172 206		$P_{II}(16)$

[a]Estimated uncertainty in the reproducibility of the FIR laser frequency.
[b]Pressure was measured with a capacitance manometer in torr (1 torr = 133.322 Pa) or with a thermocouple gauge which was calibrated for methyl alcohol with the capacitance manometer. Pressure was adjusted to produce maximum power out for the CO_2 pump power and FIR cavity loss condition. FIR laser frequency measurement was made at this pressure.
[c]These FIR laser lines were from the optically pumped 2-m wave guide cavity. All others were from the optically pumped 1-m Fabry-Perot cavity.
[d]Petersen *et al.* [12].
[e]Frequency for this line reflects a better determination of line center. Under certain pumping conditions this line has an asymmetric splitting. Apparently, in the previous measurement (4 251 668.7 MHz), the FIR laser frequency was set to the center of the low frequency side lobe of the gain curve.
[f]These lines were reproduced with a Fabry-Perot cavity (versus waveguide cavity in previous measurement), and their frequencies were remeasured. Average difference was 0.3 MHz; maximum difference was 0.7 MHz.
[g]Fetterman *et al.*, 118.8 μm, 2522.78(1) GHz; 170.6 μm, 1757.526(6) GHz [18].
[h]Krammer and Weiss, 525 428.3(3) MHz [19].

ever, for shorter wavelengths, errors were often made in counting the number of modes in the 5 mm scan. Therefore, these shorter wavelengths were measured with 0.8 m Ebert-Fastie scanning monochromator equipped with a 30 line/mm grating and 200 μm slits. These measurements allowed frequency predictions well within the bandpass of the system.

The FIR power was focused onto a long wire (~3 mm) W-Ni point-contact diode with a 3 cm focal length polyethylene lens.

The angle between the beam and the wire was adjusted to maximize the coupling. The FIR frequencies were synthesized by two $^{12}C^{16}O_2$ lasers and an X-band klystron as described previously [12]. Each CO_2 laser was stabilized to the standing-wave saturation resonance in a low pressure (5.3 Pa) intracavity CO_2 absorption cell [13], [14]. The X-band klystron was stabilized to a quartz crystal, and its frequency was counted. As a result, uncertainty in the synthesized frequency was less than 100 kHz. The beat signal was amplified (25 dB) and measured on a 1500 MHz spectrum analyzer with a marker oscillator and frequency counter.

The new frequency measurements, along with previous results (13 lines) [12], are presented in Table I. Vacuum wavenumbers are derived from the frequency measurements with $c = 299\,792\,458$ m/s [15]. Each line is labeled by the approximate wavelength and the $^{12}C^{16}O_2$ pump line. In most cases, the $^{12}CH_3OH$ pressure at which each frequency measurement was made is also given. The pressure was adjusted to maximize the FIR output power for the given CO_2 pump power and FIR cavity loss conditions.

The estimated fractional uncertainty in the reproducibility of each FIR frequency of about $\pm 5 \times 10^{-7}$ results from several factors. Many of the FIR lines have a splitting which may result from the Stark effect, from an offset between the CO_2 pump frequency and the alcohol absorption frequency, or from both [16, [17]. Sometimes this splitting, which may be of the order of 10 MHz, is very asymmetric with one of the peaks very weak in relation to the other. (An extreme pumping situation can exist where only one of the peaks is above threshold.) In all of the measurements, the CO_2 pump frequency was first adjusted to minimize the splitting and asymmetry of the FIR laser gain curve. The FIR laser frequency was then set midway between the extinction points on the gain curve and measured. The estimated error in part reflects the uncertainty in this procedure. No corrections have been applied for Stark shifts, which may be of the order of several MHz depending on the frequency and pump power, or for pressure shifts, which are estimated to be considerably smaller. The remainder of the estimated error covers variations in these frequency shifts arising because of different CO_2 pump power and CH_3OH pressure conditions.

Two preliminary investigations were made to test the frequency reproducibility of the methyl alcohol laser under different pump power and CH_3OH pressure conditions. The early frequency measurements (24 lines) were done with the optically pumped waveguide laser. To determine if there was a measurable frequency difference between the waveguide and Fabry-Perot lasers, five of the early measurements were repeated with the Fabry-Perot cavity (see Table I). The new values agreed with the old ones to within the error limits. Since there is some variation in the optimum pressure for a given FIR CH_3OH laser line, depending on pumping and coupling conditions, type of cavity, cavity loss, etc., an attempt was made to measure the pressure shift of the 96.5 μm line which oscillates over a pressure range from 8 to 80 Pa. Other effects, such as pulling by the pump laser, tended to obscure the pressure shift. However, a preliminary result indicates a shift of about + 8(8) kHz/Pa (80 percent confidence interval). Thus, these variations appear to be within the estimated uncertainty. The estimated error, then, does not include any of the systematic frequency shifts from the unperturbed molecular frequency. It represents only an estimate of the reproducibility of the FIR laser frequencies in an optically pumped Fabry-Perot or waveguide cavity.

Table II is a summary of all known CW FIR laser lines in CH_3OH pumped by the $^{12}C^{16}O_2$ laser. This table contains a total of 104 lines. The relative powers, pressure for maximum power, and polarization for most of the 93 lines which oscillate in the 1 m long, variable output coupling, Fabry-Perot FIR laser cavity were measured. Additional lines are reported in the literature, and Table II contains 11 of these that do not oscillate in this laser but which have been clearly identified by wavelength and pump line. The references in Table II correspond to the first citation of the line in the literature, and, when there is doubt, more than one reference is given. The relative powers were measured with a diamond window Golay cell with a 0.24 mm thick crystal quartz filter to remove 10 μm radiation. Calibrated attenuators were used to prevent saturation of the Golay detector. The relative powers were not normalized for line-to-line variations in CO_2 pump powers or for any other effects which could cause variations from one pump line to another. The relative powers are, therefore, most useful for comparing intensities of FIR lines produced by a given CO_2 pump line under optimum coupling conditions for the Fabry-Perot type laser described here. The Golay detector, calibrated with a commercial power meter, had an approximate calibration factor of 0.017 mW/relative power unit.

Methyl alcohol is still one of the best FIR laser molecules with many strong lines over a wide spectral range. The only comparable optically pumped laser molecule is difluormethane, CH_2F_2, which has fewer but very strong lines [24]. The new data presented in this paper should make $^{12}CH_3OH$ an even more useful submillimeter laser molecule for applications where broad spectral coverage and accurate line frequency values are needed.

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TABLE II
SUMMARY OF KNOWN SUBMILLIMETER LASER LINES OBTAINED FROM $^{12}CH_3OH$ PUMPED BY $^{12}C^{16}O_2$. RELATIVE OUTPUT POWERS, UNNORMALIZED FOR PUMP POWER AND CAVITY LOSS VARIATIONS, ARE GIVEN FOR THE 1 m, VARIABLE OUTPUT COUPLING, FABRY-PEROT LASER. THE METHYL ALCOHOL PRESSURE WAS ADJUSTED TO MAXIMIZE THE FIR OUTPUT POWER. PRIMED AND DOUBLE PRIMED CO_2 LINES DENOTE DIFFERENT PUMP FREQUENCIES.

$^{12}C^{16}O_2$ Pump Line	$^{12}CH_3OH$ Laser Line λ(μm)	Relative Power	$^{12}CH_3OH$ Laser Press. Pa(mTorr)	Relative Polariz.	Reference
$R_{II}(26)$	151.3	9	23(170)	∥	3,4
	159.7	7	23(170)	∥	4
$R_{II}(22)$	232.8	1	16(120)	∥	4,6
$R_{II}(18)$	61.6	3	41(310)	⊥	New
	67.5	0.5	33(250)	⊥	New
	186.0	10	41(310)	∥	3,4
	251.4	4	33(250)	∥	4,6
	280.9	2	23(170)	∥	4,6
$R_{II}(14)$	100.8	9	28(210)	∥	New
	194.1	3.6	27(200)	⊥	6
	209.9	3.8	27(200)	∥	4,6
$R_{II}(10)$	96.5	20	80(600)	∥	3,4,12
	164.8	27	73(550)	⊥	4,20
	232.9	20	73(550)	∥	4,12
$R_{II}(8)$	77.4	5	60(450)	∥	New
	86.2	1	60(450)	∥	4
	113.7	1.5	40(300)	⊥	New
	225.5	0.5	40(300)	∥	4
$P_{II}(10)$	45.6[a]	0.2	27(200)		New
	214.3[a,b]	0.1	4(30)	∥	6
	218.2[a,b]	0.1	4(30)	∥	6
$P_{II}(12)$	206.8	0.3	4(30)	∥	6
	211.3	1	4(30)	∥	6
	290.6[a,b]			⊥	6
$P_{II}(14)$	37[a]	0.1	5(40)		New
	118.0	10	23(170)	∥	6
	164.5	12	13(100)	⊥	22
	302.0	4	13(100)	⊥	6
	386.3	2	13(100)	∥	6
	416.5	5	15(110)	∥	22
$P_{II}(16)'$	570.6	50	13(100)	∥	1
	1 223.7	0.3	7(65)	∥	21
$P_{II}(16)''$	44[a]	2.5	11(80)	⊥	New
	164.6	8	11(80)	⊥	1
	223.5[a]			∥	1
	369.1	15	20(150)	∥	1
$P_{II}(22)$	213.5	0.9	15(110)	∥	4
	346.5	1.8	15(110)	∥	4
$P_{II}(24)$	92.5	5	17(130)	∥	6
	133.1	12.5	20(150)	∥	4
	164.7	7.5	13(100)	⊥	4
	311.2[a,b]			⊥	4
	602.5	2	13(100)	∥	4
	614.3	1.5	13(100)	∥	6
	694.2	2	13(100)	∥	6
$P_{II}(32)$	37.9	15	33(250)		2
	42.2	10	53(400)	∥	2
$P_{II}(34)$	39.9	10	17(125)	⊥	2
	43.4[a,b]				2
	63.4	33	10(75)	∥	2
	70.5	45	13(95)	⊥	1
	80.3[a,b]				2
	180.7		8(60)	⊥	4
	185.5	10	9(65)	⊥	1
	186.3		7(55)	⊥	New
	190.7	7	9(65)	⊥	1
	237.6[a,b]			∥	1
	253.6	6	9(65)	∥	1
	254.0		7(55)	∥	1
	263.7		7(55)	∥	1
	264.5	4	9(65)	∥	1
	292.5[a,b]			⊥	1
	699.4	27	15(110)	⊥	1
$P_{II}(36)$	118.8	160	17(130)	⊥	1
	170.6	58	8(60)	∥	1
	202.4[a,b]			∥	1
	392.1	35	19(140)	⊥	1
	418.1	0.8	9(70)	⊥	1
$P_{II}(38)$	193.1	2.2	11(80)	⊥	1
	198.7	2.4	11(80)	⊥	1
	278.8	2.4	11(80)	∥	1
	292.1	2	11(80)	∥	1
	624.6	0.6	7(50)	⊥	New
$P_{II}(40)$	55.4	1	15(110)	⊥	6
	60.2	0.7	9(65)	∥	6
	73.3	0.1	20(150)	∥	6
	85.6	0.1	20(150)	∥	6
$R_I(48)$	286[a,b]				22
$R_I(46)$	274[a]	0.5	11(80)		22
$R_I(44)$	121[a]	0.5	13(100)		22
	251[a]	0.4	13(100)		22
$R_I(40)$	97.5	14	37(280)	⊥	22
	167.6	7	27(200)	∥	New
$R_I(38)$	163.0	30	13(100)	∥	23
	251.1	4	13(100)	∥	23
	469.0	50	13(100)	⊥	23
$R_I(36)$	43.8[a]	2.7	20(150)	∥	New
	53.9	7	32(240)	⊥	New
$R_I(34)$	43.4[a,b]			∥	6
	92.7	1	13(100)	∥	6
	129.5	5	13(100)	∥	20
	242.5	10	17(130)	∥	22
	250.8	11	13(100)	∥	5
	267.4	7	15(110)	⊥	6
$R_I(32)$	242.8[a]	0.1	5(40)		3
$R_I(16)$	63.0	10	16(120)	∥	New
	69.7	6.4	20(150)	⊥	6
	77.9	10	25(190)	∥	22
	695.3	1	17(130)	∥	22
$R_I(10)$	191.6	50	23(170)	∥	3
	293.8	5	27(200)	∥	5
$R_I(4)$	179.7	11	20(150)	∥	New
	211.3	16	35(260)	∥	22
	495[a]	0.5	20(150)	⊥	22

[a]No frequency measurements were done on these lines. [b]These lines did not oscillate in the 1 m Fabry-Perot laser.

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