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NEW FIR LASER LINES AND FREQUENCY MEASUREMENTS OF CD_3OD

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Abstract

The isotopomer of methanol, CD_3OD, was optically pumped by a cw CO_2 laser resulting in 53 new far-infrared (FIR) laser lines. The wavelengths are in the range 42.9 μm to 189.9 μm with the majority below 100 μm. Ten different CO_2 lines were used for the first time to pump CD_3OD yielding new FIR laser lines. Some of the CO_2 pump lines belong to the hot-bands and sequence-bands of CO_2 in the 10 μm region. The frequency was measured for 40 FIR laser lines in the range 1.5 THz to 6.9 THz, 32 of which were new laser lines.

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I- Introduction

CD_3OD has been recognized as an efficient lasing molecule in the far-infrared (FIR) region for many years. Since first reported by Kon et. al.[1], several works have been performed resulting in more than two hundred laser lines from this molecule [2,3,4]. As in other isotopomers of methanol, the large number of lines is mainly due to the components of the permanent electric dipole moment both parallel and perpendicular to the quasi-symmetrical molecular axis. This makes the selection rules less restrictive than in symmetrical molecules. Furthermore, the exchange of H by D does not shift appreciably the frequency center of the *C-O* stretch vibrational mode; it is 1033.5 cm^{-1} for the normal specie and 981.8 cm^{-1} for the fully deuterated specie [5]. Thus, the strong absorptions belonging to the *C-O* stretch mode still lies in the range of the CO_2 laser emission spectrum.

The purpose of this work is to reinvestigate CD_3OD as an active medium for FIR laser lines. For this, a highly efficient CO_2 laser and a Fabry-Perot cavity were used as a pump laser and a FIR laser cavity, respectively. The motivation is to discover new FIR laser lines at high frequency which increases the number the lines available for applications in other fields. Furthermore, the new data can be used in the spectroscopic analysis of CD_3OD itself.

II- Experiment Setup and Procedure

The experimental setup to discover new FIR laser lines consisted of a pump laser, a FIR laser, and detectors. A highly efficient cw CO_2 laser with 75 MHz free spectral range was used as a pump source. Its design follows that described elsewhere [6]. It lases on more than 275 lines from the regular, hot, and sequence bands with enough power for optical pumping of cw-lasing FIR transitions. Typical powers were 25 W for the regular band lines, 10 W for hot-band lines, and 7 W for sequence band lines.

The FIR laser was a nearly confocal Fabry-Perot cavity 2 m long formed by a Pyrex tube of 36 mm inside diameter. It was mechanical sustained by 3 invar bars and aluminum blocks at the ends. The mirrors were fastened on each block: one was fixed, and the other one was coupled to a micrometer for cavity tuning. The FIR laser line was coupled out using a 45°, 6 mm diameter mirror, radially adjustable. The output was detected by a metal-insulator-metal (MIM) point contact diode (W-Ni) or a pyroelectric detector. A quartz window was used as the output window to avoid the unwanted CO_2 pump radiation on the detector.

The CO_2 pump radiation was modulated with a mechanical chopper and it was focused into the FIR laser cavity with a 2 m radius-of-curvature concave mirror placed 1 m from the laser cavity. The CO_2 radiation enters through a 5 mm diameter hole in the fixed mirror 14.5 mm above the laser axis. The coupling hole is outside the mode diameter of the FIR beam for wavelengths below 100 μm. This forms a high Q cavity for short wavelengths. This coupling geometry has been successfully used in previous works [7].

A microphone was mounted inside the cavity in order to identify the absorption from the active medium at each CO_2 pump line. An optoacoustic signal is generated when the pump radiation is absorbed by CD_3OD.

The active medium was a sample 99% pure of fully deuterated methanol. It was flowed slowly through the laser cavity to avoid exchange with H from regular methanol and water on the walls of the FIR cavity. The *C-O* stretch vibrational mode for both CD_3OH and CD_3OD lie very close in energy to each other. The center of the *C-O* stretch mode is at 984.4 cm^{-1} for CD_3OH and at 981.8 cm^{-1} for CD_3OD [5]. To confirm the parent molecule, all new lines were checked with those from CD_3OH and CH_3OH.

For each new line, a scan of the FIR cavity length was recorded as a function of the FIR laser power. The scans were recorded using an x-y plotter. A 10-turn potentiometer biased at 1.5 volts was coupled to the micrometer. The y signal came from a lock-in amplifier. These scans are also useful to identify other laser lines that may be oscillating from the same absorption. In addition, this procedure used on the FIR laser cavity permits wavelength measurements of the FIR laser lines.

III- New FIR laser lines

Observing an opto-acoustic signal from CD_3OD near each CO_2 pump absorption is the initial step in the discovery of new FIR laser lines. The strong absorptions identified were carefully studied as candidates to yield laser lines.

The new laser lines discovered in this work are summarized in Table 1 ordered by increasing pump frequency. Columns 1 and 2 give the

CO_2 pump line and its frequency, respectively. Column 3 lists the wavelength with an estimated accuracy of ±0.05 μm, which was measured by scanning the laser cavity through at least 20 longitudinal modes (10λ). Column 4 gives the relative polarization of the FIR lasing line relative to that of the pump. It was measured by inserting a multi-Brewster angle polarization selector in the FIR beam before the detector. It is denoted by // for parallel and by ⊥ for perpendicular. Column 5 gives the optimum working pressure of the lasing medium, and the column 6 gives the intensity. The intensity is the rectified voltage from the MIM diode. It depends on the experimental conditions (cavity design, coupling, and detection) and then it is an estimate of the intensity because its amplitude also depends on the antenna in the MIM diode. For comparison, the 119 μm line from CH_3OH yielded a rectified voltage of 20 mV for 22 W of the 9P(36) CO_2 pump line.

IV- Frequency measurements

The frequency measurement plays an important role in the use of the FIR laser lines for spectroscopic sources. Furthermore, frequency measurements are necessary for the spectroscopic assignments of the lasing transitions. The laser frequencies of 32 new laser lines and 8 previously reported lines, were directly measured.

The unknown frequency (ν_{FIR}) was tuned to the center of it's gain curve and then mixed with two frequency stabilized CO_2 lasers (ν_{CO2}) on a MIM diode. The beat note signal (ν_{beat}) from the MIM was amplified and displayed on a spectrum analyzer. If the beat note frequency was larger than 1.5 GHz (the bandwidth of the preamplifier and the spectrum analyzer), microwave radiation ($\nu_{\mu MW}$) from a synthesized signal generator was also mixed on the MIM diode. The unknown frequency is determined using the beat note frequency measured from the expression:

$$\nu_{FIR} = \left| n_1 \nu_{CO_2}(I) - n \nu_{CO_2}(II) \right| \pm m \nu_{MW} \pm \nu_{BEAT} \qquad (1).$$

The numbers n_1, n_2 and m are integers corresponding to the harmonic generated in the MIM diode. Generally, they are usually one, in order to obtain the beat note signal with good intensity. However, for higher FIR frequencies is it necessary to use higher harmonics. For example, for frequencies larger than 5 THz, $n_1 = n_2 = 2$ is used. The (+) or (-) signal and m in expression (1) were determined experimentally by tuning the FIR laser frequency and microwave radiation, respectively, and observing the beat note shift on the spectrum analyzer.

The 1σ uncertainty of frequency measurements is estimated to be about $\Delta\nu/\nu = 2\times10^{-7}$. This is due mainly to the uncertainty in the setting of the FIR laser cavity to the center of its gain curve. For minimizing this uncertainty, we tuned the FIR laser across its gain curve and observed the change in the beat note on the spectrum analyzer using a peak hold feature. The final beat note frequency was the average from at least 10 different measurements.

The frequency measurements are showed in the Table 2. Columns 1 and 2 give the CO_2 pump line and its frequency, respectively. Column 3 gives the wavelength calculated from frequency measured using c = 299 792 458 m/s. Column 4 gives the wavenumber, and the last column gives the measured frequency.

The FIR laser line at 136.552 μm pumped by 10 R46 was considered a new line because the frequency measurement was about 6.5 GHz different from a previous value [8].

V- Conclusion

A cw CO_2 laser was used as source to pump CD_3OD. This resulted in 53 new laser lines in the range 42.9 μm to 189.9 μm. They were characterized by wavelength, relative polarization, optimum pressure, and intensity. The majority of them had wavelengths below 100 μm. Ten lines from our CO_2 laser were used for the first time to pump CD_3OD; seven of which belong to the hot-band and sequence-band lines in the 10 μm region. The frequencies of 40 FIR laser lines were also measured, 32 of which were new lines in the range 1.5 THz to 6.9 THz with a reproducibility of two parts in 10^7. These new data will aid in the theoretical analysis of CD_3OD. Furthermore, the new laser lines can be used as highly accurate radiation sources for molecular spectroscopy.

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Table 1 : New FIR laser lines of CD_3OD.

CO₂ pump		FIR laser line			
Line	Frequency (cm^{-1})	Wavelength[a] (μm)	Rel. Pol.	Pressure (mTorr)	Int. (mV)
10 HP14	915.6277[b]	77.719	//	27(200)	0.20
10 P48	916.5818	52.80	//	9(70)	0.10
10 P46	918.7183	119.542	//	23(170)	2.0
10 SP39	923.8970[b]	59.692	⊥	25(190)	0.10
		87.6	//	27(200)	<0.01
10 P38	927.0083	65.5	//	21(160)	0.20
		87.729	⊥	21(160)	0.10
		96.197	//	21(160)	0.20
10 P30	934.8945	74.9	⊥	24(180)	0.04
10 P16	947.7420	62.687	//	20(150)	0.10
		77.436	⊥	20(150)	0.20
10 HR34	950.5447[b]	170.642	//	12(90)	0.01
10 P12	951.1923[b]	87.9	⊥	23(170)	<0.01
10 P 4	957.8005	69.569	⊥	13(100)	0.25
10 R2	963.2631	53.562	//	13(100)	0.50
		66.188	//	15(110)	0.20
10 R4	964.7690	49.539	//	17(130)	0.20
		109.8	//	16(120)	0.30
		140.4	//	16(120)	0.90
10 R6	966.2504	97.730	⊥	29(220)	0.05
10 R8	967.7072	69.269	⊥	17(130)	0.10
		86.802	//	25(190)	0.30
10 R12	970.5472	115.035	⊥	27(200)	1.5
10 SR17	971.4480[b]	56.634	⊥	15(110)	0.40
10 SR21	974.0482[b]	84.614	⊥	12(90)	0.10
		101.316	//	15(110)	0.10
10 R22	977.2139	147.6	⊥	16(120)	0.10

10 SR27	977.7632[b]	189.863	$\perp$	12(90)	0.40
10 SR29	978.9517[b]	72.0	$\perp$	11(80)	<0.01
10 R42	988.6466	86.620	//	24(180)	0.20
10 R46	990.6196	120.850	$\perp$	20(150)	0.30
		136.552	//	20(150)	0.20
10 R48	991.5658	107.658	//	12(90)	0.10
9 P52	1014.5179	118.548	//	15(110)	0.10
		140.885	$\perp$	15(110)	0.04
9 P42	1025.2979	71.3	//	12(90)	0.06
		83.0	$\perp$	12(90)	0.03
9 P28	1039.3693	68.1	$\perp$	13(100)	0.04
9 P14	1052.1955	96.7	//	12(90)	0.30
		120.2	$\perp$	12(90)	<0.01
9 P12	1053.9235	138.1	//	12(90)	<0.01
9 R6	1069.0141	62.272	$\perp$	15(110)	0.10
		79.470	$\perp$	12(90)	0.25
9 R16	1075.9878	48.3	//	11(80)	0.01
		85.489	//	11(80)	0.20
9 R18	1077.3025	109.120	$\perp$	15(110)	0.10
9 R22	1079.8522	72.8	//	8(60)	0.10
		78.4	$\perp$	8(60)	0.02
9 R32	1085.7654	75.0	//	12(90)	0.06
		88.354	$\perp$	12(90)	0.15
9 R42	1091.0302	42.983	$\perp$	17(130)	0.20
9 R52	1095.6636[b]	108.6	//	20(150)	0.05
9 R54	1096.5163[b]	109.4	$\perp$	13(100)	0.15

[a] The lines with wavelength reported just one decimal place have not been measured in frequency. The lines belonging to same pump line were at same offset.
[b] Pump line used for the first time.

Table 2: New frequency measurements of CD_3OD.

CO_2 pump		FIR laser line		
Line	Frequency (cm^{-1})	Wavelength (μm)	Wavenumber[a] (cm^{-1})	Frequency (MHz)
10 P14	915.6277	77.719	128.66893	3 857 397.5
10 P46	918.7183	105.584[b]	94.71111	2 839 367.7
10 P46	918.7183	119.542	83.65247	2 507 838.0
10 SP39	923.8970	59.692	167.52693	5 022 331.1
10 P38	927.0083	76.970[b]	129.91996	3 894 902.4
10 P38	927.0083	96.197	103.95314	3 116 436.6
10 P38	927.0083	87.729	113.98765	3 417 263.9
10 P16	947.7420	62.687	159.52273	4 782 371.2
10 P16	947.7420	77.436	129.13773	3 871 451.8
10 HR34	950.5447	170.642	58.60201	1 756 844.1
10 P4	957.8005	69.569	143.74291	4 309 304.0
10 P4	957.8005	60.374[b]	165.63364	4 965 571.6
10 R2	963.2631	66.188	151.08495	4 529 413.0
10 R2	963.2631	53.562	186.69842	5 597 077.7
10 R4	964.7690	49.539	201.86253	6 051 686.3
10 R6	966.2504	97.730	102.32224	3 067 543.7
10 R8	967.2631	69.269	144.36453	4 327 939.7
10 R8	967.2631	86.802	115.20455	3 453 745.4
10 R12	970.5472	115.035	86.92987	2 606 091.9
10 R12	970.5472	103.447[b]	96.66801	2 898 034.0
10 SR17	971.4480	56.634	176.57204	5 293 496.6
10 SR21	974.0481	84.614	118.18360	3 543 055.2
10 SR21	974.0481	101.316	98.70049	2 958 966.3
10 SR27	977.7632	189.863	52.66949	1 578 991.5
10 R42	988.6466	79.401[b]	125.94379	3 775 699.8
10 R42	988.6466	86.620	115.44743	3 461 026.8

10 R44	989.6465	87.294[b]	114.55501	3 434 272.8
10 R46	990.6196	120.850	82.74724	2 480 699.9
10 R46	990.6196	136.552	73.23205	2 195 441.5
10 R48	991.5658	107.658	92.88708	2 784 684.7
9 P52	1017.5179	135.666[b]	73.71037	2 209 781.4
9 P52'	1017.5179	118.548	88.35440	2 528 881.4
9 P52'	1017.5179	140.885	70.97976	2 127 919.8
9 R6	1069.0141	62.272	160.58618	4 814 252.5
9 R6	1069.0141	79.470	125.83429	3 772 417.2
9 R16	1075.9878	85.489	116.97403	3 506 793.2
9 R18	1077.3025	109.120	91.642245	2 747 371.4
9 R32	1085.7654	88.354	113.18088	3 393 077.5
9 R38	1089.0011	64.395[b]	155.29042	4 655 489.8
9 R42	1091.0302	42.983	232.65005	6 974 673.0

[a] Calculated using the factor 1 cm^{-1} = 29 979.2458 MHz.
[b] Line previously reported.

(') Indicates different offset frequency from CO_2 pump laser.