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NEW OPTICALLY PUMPED FIR LASER LINES AND FREQUENCY MEASUREMENTS FROM CH_3OD

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Abstract

This work reports the discovery of 45 new optically pumped far-infrared (FIR) laser lines from CH_3OD in the range 42.6 μm to 207.2 μm. A highly efficient CO_2 laser was used as the pump laser for an Optically-pumped Fabry-Perot FIR laser. The frequencies of most of the new lines were measured in the range 1.7 to 6.4 THz. Twenty-eight CO_2 lines were used as pump lines; nineteen of these had frequencies lower than those previously used to pump CH_3OD in a FIR laser. Sixteen of the new FIR lines had absorption transitions which belong to the OD bending vibrational mode.

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I- Introduction

The purpose of this work is to reinvestigate the isotopic species CH_3OD as a FIR lasing molecule. The main motivation is the overlap of the hot and sequence bands of the CO_2 laser lines near 11 μm (909 cm^{-1}) with part of the OD bending vibrational mode.[1] The hot and sequence bands are obtained using a new optical geometry for the CO_2 laser cavity. This resulted in the observation of forty-five new laser lines in CH_3OD.

Before we started this work, one hundred thirty-eight laser lines had been identified from CH_3OD [2,3]. In previous work, a regular band CO_2 laser was used as a pump source and several designs for FIR cavities were used to optimize the FIR cavities. The assignment of the pump and laser transitions were determined from other experiments, for example, infrared-infrared double resonance[4] and high resolution Fourier Transform spectroscopy in the region of C-O stretch band.[5]

Optical pumping of polar molecules is a very versatile technique for generating coherent radiation in far-infrared (FIR) region of the electromagnetic spectrum. In fact, using these techniques, more than 3000 FIR laser lines have been observed from almost 100 molecules.[6] The CO_2 laser is used as a pump source and methanol (CH_3OH), along with its isotopic species, are some of the best lasing molecules. The characteristics of FIR laser lines generated from normal methanol and its isotopic species were summarized in recent reviews.[7,8,9] The success of methanol as an active medium is due mainly to the strong overlap of the C-O stretch vibrational mode with the CO_2 laser lines and the permanent electric dipole moment with components both parallel and perpendicular to the quasi-symmetrical axis. As a consequence, the selection rules for methanol are less restrictive than for symmetrical molecules.

Furthermore, methanol has a torsional internal rotation of the hydroxyl group around the symmetry axis of the methyl group. The transitions from the internal rotational states yield lines with wavelengths shorter than 100 μm; this makes methanol almost unique for generating optically pumped laser lines below 100 μm.

II- Experiment

The experimental apparatus used to search for new FIR laser line is formed by the CO_2 pump laser, the FIR laser, and a detector. The CO_2 laser uses a new design recently reported in the literature.[10] This laser has a 2.0 m long cavity formed by a Littrow-mounted diffraction grating with

0-order output coupling, a ribbed tube, and a gold-coated 20 m radius-of-curvature end mirror. The ribbed tube has an internal diameter of 18 mm with five ribs spaced every 50 cm. A gas mixture (CO_2, N_2, He) flows through the laser tube at a total pressure of about 2.9 kPa (22 Torr). A specially blazed 150 lines/mm grating provides 3 % output coupling in the zeroth order from 9.2 to 11.4 μm. The electric discharge (12 kV, 50 mA) is obtained in two regions each approximately 100 cm long. This CO_2 laser oscillates on about 275 lines cw including the regular-bands, hot-bands, and sequence-bands. The laser has excellent selectivity of these lines by simply rotating the grating. Typical output powers are 25 W for regular-band lines, 10 W for hot-band lines, and 7 W for sequence-band lines.

The FIR laser has a low-loss Fabry-Perot cavity with a design similar to that recently reported,[11] but it now has a nearly confocal geometry and is more efficient. It is formed with a 36 mm inside diameter 2 m long Pyrex tube with two 1.9 radius-of-curvature gold-coated concave mirrors at each end. One mirror is fixed while the other is coupled to a micrometer for scanning the cavity length. A microphone is placed inside the cavity to detect Doppler broadened acousto-optic signals in order to find coincidences of the pump line with the absorption transition of the active medium.

The CO_2 pump radiation was focused into the FIR laser cavity with a 4 m radius-of-curvature concave mirror placed 2 m from the laser end mirror. The CO_2 radiation enters through a 3 mm diameter hole in the fixed mirror located 16.5 mm above the laser axis. The coupling hole is outside the mode radius of the FIR beam at wavelengths below 150 μm, thus producing a high Q cavity.

The FIR power was coupled out of the cavity using a 45°, 6 mm diameter mirror radially adjustable inside the FIR laser cavity. Either a metal-insulator-metal (MIM) point contact diode (W-NiO-Ni) or a pyroelectric detector detected the FIR output. A 75 μm polypropylene window was used as an output window; then, a crystal quartz filter or a thin piece of paper was added to avoid unwanted CO_2 pump radiation on the detectors.

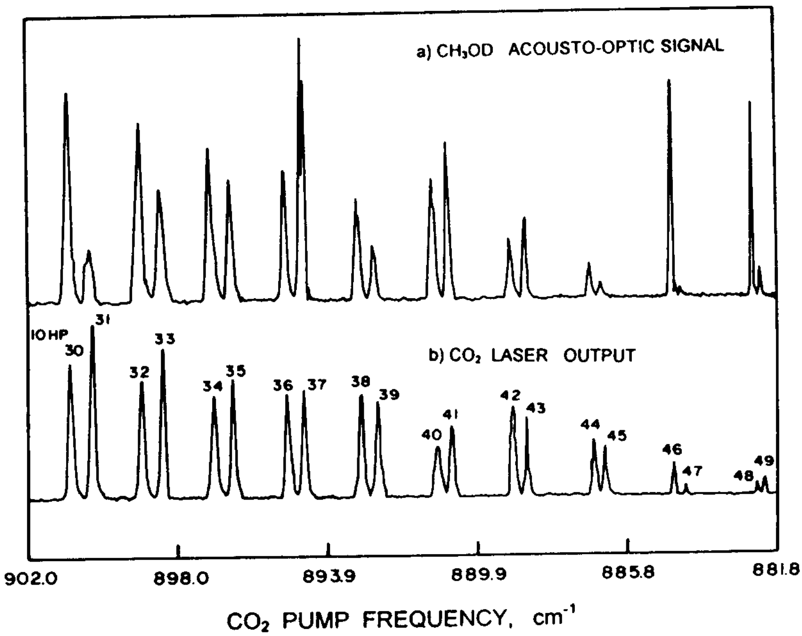
The CH_3OD sample had an isotopic purity of 99%. A small flux of the sample was flowed through the laser cavity to avoid laser lines from the normal species which is created by the exchange reaction of residual OH species on the walls. All new lines were also identified as belonging to CH_3OD by checking with those from the normal isotopic species.

III- Results and Comments

The efficiency of the pump CO_2 laser and FIR laser cavity permitted the discovery of 45 new laser lines. The acousto-optic signals generated when the pump radiation is in resonance with the sample is used to identify new absorptions. The FIR laser cavity was used as an acousto-optic cell with multiple passes for the pump radiation. The sample flow was maintained through the laser cavity during the measurements. First, the CO_2 laser was tuned to each of the approximately 275 lines (by rotating the grating) from 10 HP49 to 9 R56 (11.3 μm to 9.1μm; 882 cm^{-1} to 1097 cm^{-1}). Then, the strongest absorptions were tested to determine if they generated FIR laser lines.

Figure 1 shows part of the acousto-optic spectrum obtained in the range from 882 cm^{-1} to 902 cm^{-1}. This region coincides with absorptions which belong to the OD bending vibrational mode centered [12] at 864 cm^{-1} and ending [5] at about 980 cm^{-1}. The opto-acoustic spectrum from CH_3OH was also obtained in the same region for comparison with

Figure 1: Acousto-Optic Spectrum from CH3OD in the region of the OD bending vibrational mode.



that from this isotopomer. Thus, the absorption lines observed were definitely from CH_3OD and the purity of the sample was assured.

Table 1 summaries the new FIR laser lines. Columns 1 and 2 give the pump CO_2 laser line and its frequency, respectively. Column 3 gives the wavelengths of the FIR laser lines with an uncertainty of about 0.5 μm. The wavelength was measured using the laser cavity as an interferometer, and the movable end mirror on the micrometer was scanned at least twenty half-wavelengths for each line identified. Column 4 gives the relative polarization of the FIR laser line to that of the pump line and is labeled by $\perp$ for perpendicular and by $||$ for parallel. Column 5 gives the optimum working pressure, and column 6 gives the intensity of each FIR laser line. The intensity recorded is the rectified voltage on the MIM diode. For the strong 119 μm line from CH_3OH, the rectified voltage was 20 mV pumped with 22 W from the 9P(36) CO_2 pump line. The weakest lines had relative intensities smaller than 0.01 mV.

Previous to this work, the 10 HP30 (901 cm^{-1}) was the lowest pump frequency used to produce FIR laser lines.[13] Figure 1 shows that nineteen new pump lines were used with frequencies lower than 10 HP30; and five of these generated new FIR laser lines. As shown in Table 1, the

Table 1: New FIR laser lines from CH_3OD.

CO_2 pump line	FIR laser line Frequency (cm^{-1})	Wavelength[a] (μm)	Rel. Pol.	Pressure Pa(mTorr)	Int. (mV)
10 HP46	884.6304	173.754	||	11(80)	2.50
10 HP41	890.5330	204.6	||	17(130)	0.50
10 HP38	892.9926	92.2	||	13(100)	0.04
10 HP37	894.5231	173.785	||	11(80)	4.00
10 HP35	896.4841	46.7	(b)	12(90)	<0.01
10 P60	903.2118	58.9	||	16(120)	<0.01
10 HP27	904.1021	76.381	⊥	31(230)	0.05
10 HP26	904.7660	53.3	(b)	11(80)	<0.01
10 P58	905.5066	87.222	||	32(240)	1.50
10 HP22	908.4874	42.6	||	17(130)	0.10
		141.3	||	24(180)	0.40
10 HP21	909.5791	126.208	||	21(160)	2.00
10 P54	910.0159	207.179	||	24(180)	3.00
10 HP16	913.8804	106.857	||	25(190)	0.60
10 SP31	931.7559	152.366	||	11(80)	0.30
10 HR25	945.4668	125.842	||	11(80)	0.15
10 P4	957.8005	51.4	⊥	13(100)	0.04
0 R26	979.7054	88.8	||	20(150)	0.06
10 R28	980.9132	50.2	||	37(280)	<0.01
0 R34	984.3832	53.219	||	35(260)	0.10
0 R36	985.4883	48.775	||	59(440)	0.04
		60.622	⊥	51(380)	0.04
0 R38	986.5674	95.341	⊥	27(200)	0.60
		68.865	||	40(300)	0.25
0 R48	991.5658	118.1	||	13(95)	0.10

10 R52	993.3764	101.378	||	17(130)	0.40
10R54	994.2404	69.6	||	17(130)	0.01
9 P50	1016.7209	62.133	||	31(230)	0.10
		73.691	||	31(230)	0.20
9 P38	1029.4421	62.544	||	20(150)	0.10
		51.9	⊥	37(280)	0.02
9 P36	1031.4774	65.3	||	11(80)	<0.01
9 SP17	1046.3796	58.3	⊥	9(70)	0.04
9 SP15	1048.1410	70.142	||	13(100)	0.20
		77.442	⊥	11(80)	0.04
9 SP13	1049.8754	61.674	||	23(170)	0.20
9 HP22	1052.7017	85.760	||	11(80)	0.20
		117.4	⊥	12(90)	0.10
		148.5	||	21(160)	0.10
9 P10	1055.6250	112.912	||	20(150)	1.00
9 P8	1057.3002	85.2	⊥	13(100)	<0.01
9 HP14	1059.9401	55.3	||	12(90)	<0.01
9 R6	1069.0141	92.738	||	20(150)	0.30
9 R14	1074.6465	54.8	⊥	33(250)	0.40
9 R28	1083.4788	108.4	||	53(400)	0.20

[a] The lines with wavelengths reported with just one decimal place have not been frequency measured. The lines belonging to the same pump were at the same offset frequency.

[b] The relative polarizations of these lines could not be determined because of the low intensity of these lines.

strongest new laser lines had absorption transitions at the low frequency OD bending vibrational mode. In this region, of course, the output power of the CO_2 laser is smaller than at the center of the bands. It decreases from 8 W for the 10 P54 line to 2.5 W for 10 HP46. As a consequence, the strongest new FIR lines are actually very efficient laser lines.

The frequencies of the twenty-four new laser lines and four previously reported ones were also measured directly. For this, the unknown frequency and two stabilized CO_2 laser frequencies were mixed on a (W-NiO-Ni)[14] metal-insulator-metal (MIM) point contact diode. The CO_2 laser frequencies were stabilized by locking the two CO_2 lasers directly to a saturation dip in the 4.3 μm CO_2 fluorescence signal from an external reference cell. The difference ($|I\nu_{CO2} - II\nu_{CO2}|$) between the two stabilized CO_2 laser frequencies was chosen to be nearly equal to the calculated FIR frequency from the wavelength measurement. Thus an RF beat note signal in the frequency operation range of the spectrum analyzer and preamplifier of 1.5 GHz was obtained. When necessary, microwave radiation ($\nu_{\mu MW}$) from a synthesized signal generator was also used on the MIM diode to obtain a beat-note less than 1.5 GHz.

The beat note (ν_{beat}) signal from MIM diode was amplified by a preamplifier and displayed on a spectrum analyzer. The unknown frequency (ν_{FIR}) is determined from the expression:

$$\nu_{FIR} = |n_1 \nu_{CO_2}(I) - n_2 \nu_{CO_2}(II)| \pm m\,\nu_{\mu MW} \pm \nu_{beat} .$$

The integers n_1, n_2, and m correspond to the respective harmonic generated in the MIM diode. The (+) or (-) signs and m were determined experimentally by tuning the FIR laser frequency and microwave radiation, and observing the direction and size of the beat note shift on the spectrum analyzer.

The 1σ uncertainty of frequency measurements is $\Delta\nu/\nu = 2\text{x}10^{-7}$. This uncertainty is due mainly to the uncertainty in the setting of the FIR laser cavity at the center its gain curve. To minimize this uncertainty, we tuned the FIR laser across its gain curve and observed the frequency and amplitude in the beat note on the spectrum analyzer using a peak-hold feature. The final value of the beat-note frequency was the average of at least ten different measurements. Table 2 summarizes the frequency measurements ordered by increasing pump frequency.

Table 2: Frequency measured FIR laser lines of CH_3OD.

CO_2 pump line	Frequency (cm^{-1})	FIR laser line Wavelength (μm)	Wavenumber[a] (cm^{-1})	Frequency (MHz)
10 HP46	884.6304	173.754	57.55264	1 725 384.7
10 HP37	894.5231	173.785	57.54237	1 725 077.0
10 HP27	904.1021	76.381	130.92338	3 924 984.2
10 P58	905.5066	87.222	114.65021	3 437 126.7
10 HP25	905.9503	227.610[b]	43.93474	1 317 130.5
10 HP21	909.5791	126.208	79.23450	2 375 390.7
10 P54	910.0159	207.179	48.26748	1 447 022.5
10 HP16	913.8804	106.856	93.58347	2 805 561.9
10 SP31	931.7559	152.366	65.63148	1 967 582.3
10 HR25	945.4668	125.842	79.46481	2 382 295.0
10 R34	984.3832	53.219	187.90185	5 633 155.6
10 R36	985.4885	60.622	164.95653	4 945 272.3
		48.775	205.02137	6 146 386.1
10 R38	986.5674	95.341	104.88716	3 144 437.9
		68.865	145.21244	4 353 359.5
10 R52	993.3764	101.378	98.64102	2 957 183.4
9 P50	1016.7209	73.691	135.70265	4 068 263.0
		62.133	160.94559	4 825 027.3
9 P38	1029.4421	62.544	159.88836	4 793 332.4
9 P32	1035.4736	108.884[b]	91.84087	2 753 320.0
9 P10	1055.6250	112.912	88.56485	2 655 107.5
9 HP22	1052.7017	85.760	116.60389	3 495 696.7
9 SP15	1048.1410	70.142	142.56849	4 274 095.8
		77.442	129.12962	3 871 208.5
9 SP13	1049.8754	61.674	162.14304	4 860 926.1
9 R6	1069.0141	92.738	107.83080	3 232 686.2
		69.539[b]	143.80330	4 311 114.4

9 R8	1070.4623	46.793[b]	213.70761	6 406 792.9

[a] Calculated from frequency with 1 cm^{-1} = 29 979.2458 MHz.
[b] Lines previously reported

IV- Conclusion

Using a highly efficient CO_2 laser as a pump source and a nearly confocal Fabry-Perot cavity as the FIR laser, we have discovered and characterized 45 new FIR laser lines from CH_3OD. Thirty of these had wavelengths below 100 μm. The frequencies for most of the new lines and the previously reported ones were measured with a reproducibility of a few parts in 10^7.

Twenty-eight CO_2 pump lines were used for the first time, and nineteen of these had frequencies lower than those previously reported. The absorption transitions belonging to the OD bending vibrational mode at about 900 cm^{-1} generated sixteen new FIR lines, three of which were the strongest lines identified in this work.

These new data are important for future assignments of transitions from CH_3OD and the determination of the molecular parameters for the excited vibrational state. The new FIR laser lines can be applied in other experiments, such as in laser magnetic resonance (LMR) spectroscopy, as radiation sources for spectroscopy.

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