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OPTICALLY PUMPED FAR-INFRARED LASER LINES OF METHANOL ISOTOPOMERS: $^{12}CD_3OH$, $^{12}CH_3OD$, AND $^{12}CH_2DOH$

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ABSTRACT

Twenty-seven new FIR, far-infrared, laser lines from the isotopomers of methanol: $^{12}CD_3OH$, $^{12}CH_3OD$, and $^{12}CH_2DOH$, were obtained by optically pumping the molecules with an efficient cw CO_2 laser. The CO_2 laser provided pumping from regular, sequence, and hot-band CO_2 laser transitions. The 2 m long far-infrared cavity was a metal-dielectric waveguide closed by two, flat end mirrors. Several short-wavelength (below 100 µm) lines were observed. The frequencies of 28 laser lines observed in this cavity (including new lines and already known lines) were measured with a fractional uncertainty limited by the fractional resetability of the far-infrared laser cavity, of 2 parts in 10^7.

Key Words: $^{12}CD_3OH$, $^{12}CH_3OD$, $^{12}CH_2DOH$, new far-infrared laser lines, optically pumped far-infrared laser, laser frequencies, relative intensity, relative polarization, pump-frequency offset.

INTRODUCTION

Methanol has many isotopomers obtained by exchanging D for H, ^{13}C for ^{12}C, and ^{18}O for ^{16}O. Several forms have already been studied as far-

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infrared (FIR) laser media: $^{12}CH_3OH$, $^{13}CH_3OH$, $^{12}CD_3OH$, $^{13}CD_3OH$, $^{12}CD_3OD$, $^{13}CD_3OD$, $^{12}CH_3OD$, $^{12}CH_3{}^{18}OH$, $^{12}CH_2DOH$, $^{12}CH_2DOD$ and $^{12}CHD_2OH$, with about 2200 laser lines generated by optically pumping the molecules, mainly with CO_2 lasers.[1, 2] In the present work, 27 new laser lines were obtained by optically pumping the following isotopomers of methanol: $^{12}CD_3OH$, $^{12}CH_3OD$, and $^{12}CH_2DOH$, pumped with an efficient cw CO_2 laser lasing on regular bands to high J as well as sequence and hot-band CO_2 transitions. The 2 m long far-infrared cavity was a metal-dielectric waveguide closed by two, flat end mirrors. Several short-wavelength (below 100 μm) lines were observed. The frequency measurement of these lines is important for assigning the lines in methanol and for their eventual use in laser spectroscopy.

EXPERIMENTAL

The pump laser was a cw-CO_2 laser operating on 250 lines including regular, sequence, and hot-band CO_2 transitions with power levels from 10 to 30 W. This was accomplished with the use of several different high resolution gratings in a Fabry-Perot cavity 1.5 m long. The most recent version of this laser uses only one grating which provides output power up to 40 W on 275 lines in a 2 m cavity.

The 2 m long FIR laser cavity used in this experiment is described in detail elsewhere.[3] Essentially it is a metal-dielectric rectangular waveguide closed at its ends by two flat mirrors. Its glass sides are 6 mm tall and the metal side is 35 mm wide. One mirror has a 1 mm diameter hole in the center for coupling the CO_2 laser into the FIR cavity for longitudinal pumping. The other, attached to a micrometer, is movable longitudinally providing for the adjustment of the cavity length into resonance with the FIR laser modes. A small, moveable, 45° copper mirror near the pumping entrance couples a fraction of the FIR radiation out through a Brewster angle silicon window perpendicular to the laser axis.

A metal-insulator-metal (MIM) diode was used to detect the laser radiation, and also as a mixer for the frequency measurements. Once a new laser line is detected by the MIM we estimate the FIR wavelength of the radiation by varying the cavity length of the FIR laser over about ten wavelengths, by translating the movable mirror and counting the FIR modes displayed on an oscilloscope. The length variation was measured with the micrometer attached to the mirror, yielding a wavelength determination accurate to about 0.05 μm. This wavelength then was used to select the CO_2 frequencies for the precise heterodyne frequency measurement.

To measure the FIR laser frequency, the FIR radiation was mixed with radiation from two frequency-stabilized CO_2 lasers and from a microwave source,[4] generating a beat note in the diode. The precise FIR frequency is obtained by the equation:

$$\nu_{FIR} = n \left| \nu_1 - \nu_2 \right| \pm m\nu_{\mu wave} \pm \nu_{beat} \qquad (1)$$

where ν_1 and ν_2 are the stabilized CO_2 frequencies, $\nu_{\mu wave}$ is the microwave frequency, ν_{beat} is the beat frequency, and n and m are the orders of the harmonics generated by the MIM diode. The coefficients n and m are determined experimentally by changing the associated frequencies slightly. The estimated uncertainty in the reproducibility of the FIR laser frequency is $\Delta\nu/\nu = 2x10^{-7}$. When measuring the pump offsets of the FIR laser lines a frequency-stabilized CO_2 laser is set to the same laser line as the pump laser and mixed in the diode with the pump laser frequency.

When the pump line is a sequence-band or a hot-band line, the frequency of a microwave source is added to the mixture in order to make up for the frequency difference between the regular line and the sequence or hot band line.

RESULTS AND COMMENTS

The methanol isotopomer $^{12}CD_3OH$ is reported with 387 far-infrared laser lines when pumped with CO_2 lasers,[1,2] the highest percentage (≈ 29%) of the lines having wavelengths between 21.7 and 100 μm. However, just 40 of these lines had their frequencies measured. In the present work we discovered 15 new laser lines with wavelengths in the range 46.6 to 482.8 μm, and measured 12 of their frequencies.

Far-infrared laser lines of $^{12}CH_3OD$ have been reported when the molecule was pumped with regular-band lines of $^{12}CO_2$ and $^{13}CO_2$ lasers, regular, hot and sequence-band lines of an $C^{18}O_2$ laser, and with one pump line of an N_2O laser.[1,2] The 131 reported lines have wavelengths ranging from 46.6 to 1671 μm. Just 22 lines had their frequencies measured. This work adds seven new laser lines and frequency measurements of 5 of these and 5 previously reported lines. The newly discovered lines have wavelengths in the range from 65.5 to 249.1 μm

$^{12}CH_2DOH$ is reported as having 67 laser lines in the wavelength range 42.5 to 762.5 μm, obtained by optically pumping the molecule with CO_2 lasers.[1,2] Frequencies for 45 of these lines have been measured. In this work we discovered five new lines in the wavelength range from 139 to 379.2 μm and measured their frequencies.

The measurements are summarized in Table 1.

Table 1. Far-infrared laser lines from methanol isotopomers by CO_2 pump line.

CO_2 Pump Line	Frequency [a] MHz	Wavelength [b] μm	Wavenumber [b] cm^{-1}	Pressure Pa(mTorr)	Rel. Int.	Rel. Pol.	Offset MHz	Ref.
$^{12}CD_3OH$								
9R(54)		245.5	40.43	27(200)	M	//		New
9R(52)		61.0	163.93	33(250)	M	//		New
9R(52)		77.0	129.87	33(250)	W	//		New
9R(50)		53.4	187.27	47(350)				New
9R(50)	1 220 173.1	245.697	40.7006	24(180)	S	//	-27	New
9R(46)	2 097 054.2	142.959	69.9502	27(200)	S	//	-23	New
9R(46)	1 333 625.1	224.795[d]	44.4849	33(250)	M	//		1,2
9R(34)	4 988 091.2	60.102[d]	166.3848	33(250)	VS	//	-9	1,2
9R(28)	7 035 829.9	46.609	234.69	53(400)	M	//	+5	New
9R(6)	6 153 279.0	48.721[d]	205.251	29(220)		//	-15	1,2
9R(6)	850 839.5	352.349[d]	28.3810	20(150)	M	//	-27	1,2
9P(56)		129.2	77.40	27(200)	M	//		New
9P(60)?		482.8	20.71	24(180)	M	//		New
10R(56)		51.6	193.80	16(120)	W	//		New
10R(54)		92.9	107.64	20(150)	M	//		New
10R(48)		106.1	94.25	13(100)	W	//		New
10R(34)		42.4[d]	235.82			⊥		1,2
10R(20)	5 921 370.4	50.6289						1,2
10R(20)	5 697 191.3	52.6211						1,2
10R(20)	5 413 019.5	55.3836						1,2
10HP(29)	1 238 183.9	242.123	41.3014	13(100)	M	//		New
10HP(29)		356.0	28.09	13(100)	W	//		New
10HP?		350.6	28.52	13(100)	W	//		New
10P(56)	3 475 080.1	86.269[d]	115.9162	20(150)	M	//		1,2

CO_2 Pump Line	Frequency[a] MHz	Wavelength[b] µm	Wavenumber[b] cm^{-1}	Pressure Pa(mTorr)	Rel. Int.	Rel. Pol.	Offset MHz	Ref.
$^{12}CH_3OD$								
9R(16)	4 259 119.5	70.388[d]	142.0689	27(200)	M	//	-42	1,2
9R(16)	2 912 479.4	102.934	97.1499	13(100)	M	//	-42	New
9R(16)	1 295 296.5	231.447	43.2064	13(100)	M	//		New
9P(2)	766 163.0	391.291[d]	25.5556	13(100)	M	//	+10	1,2
9P(10)	2 239 654.5	133.857[d]	74.7068	33(250)	S	//	+11	1,2
9HP(18)	1 299 414.1	230.714	43.3438	20(150)	S	//	+20	New
9P(32)	2 650 697.4	113.099[d]	88.4177	27(200)	M	//	-42	1,2
9P(42)	1 372 741.7	218.39	45.7897	20(150)	M	//	-45	New
9P(46)	4 575 770.3	65.517	152.6313	33(250)	M	//	+40	New
9P(52)	6 406 792.8	46.793[d]	213.7076	27(200)	S	//	-34	1,2
10R(40)		141.2	70.82	47(350)	S	//		New
10R(40)		249.1	40.14	52(390)	W	//		New
$^{12}CH_2DOH$								
9R(38)	790 583.6	379.204	26.3710	13(100)	M	//	-28	New
9R(6)	1 727 869.6	173.504	57.6355	33(250)	M	//	+31	New
9R(4)	1 334 777.6	224.601	44.5234	13(100)	W	//	-23	New
9SR(5)	1 303 499.5	229.990	43.4801	13(100)	W	//	-5	
9P(2)	2 156 425.8	139.023	71.9306	20(150)	M	//	+16	New

[a] estimated uncertainty in the reproducibility of the FIR laser frequency: $\Delta\nu/\nu = 2x\ 10^{-7}$
[b] calculated from the measure frequency with c = 299 792 458 m/s.
[c] VS: 1 - 10 mW, S: .1 - 1.0 mW, M: 10 – 100 µW, W: 1 – 10 µW
[d] not a new line.
[e] // and ⊥ stand for parallel and perpendicular.

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