Far Infrared Laser Frequencies of $^{13}CD_3OH$

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***Abstract*—We have measured 30 far-infrared laser frequencies of optically pumped $^{13}CD_3OH$, 13 of which are new lines. The frequencies range from 0.5 to 4.9 THz with the majority between 0.75 and 1.5 THz. Two frequency stabilized CO_2 lasers were used as standards for the heterodyne measurements.**

I. Introduction

In this letter, we report frequency measurements for 30 far-infrared (FIR) $^{13}CD_3OH$ lines, including 13 new lasing transitions. The $^{13}CD_3OH$ isotope of methanol was first investigated as a lasing gas by Inguscio *et al.* [1]. They reported 36 optically pumped laser lines and measured the frequencies of 11 of these. Recently, Moraes *et al.* [2] discovered an additional 57 lines, and measured 13 laser frequencies.

II. Measurements

The FIR laser is a near-confocal, 0.85 m long Fabry–Perot cavity using nearly transverse (zig-zag) pumping in a 50 mm diameter copper tube. The $^{13}CD_3OH$ is pumped by a 40 W, CW CO_2 laser with 100 MHz free spectral range. The pump radiation enters the FIR cavity through an antireflection (AR)-coated Zn–Se window at an angle of 75° with respect to the FIR cavity axis. The pump beam is initially focused to the center of the tube by a section of a 100 mm diameter, polished copper tube and is refocused upon reflection from the 50 mm copper tube. The FIR radiation was coupled out by reflection from a 12.5 μm thick, polypropylene intracavity beamsplitter, which was rotated about Brewster's angle to maximize the FIR output.

The laser frequencies were measured by mixing the FIR radiation with radiation from two frequency stabilized CO_2 lasers and a microwave source on a metal–insulator–metal (MIM), point contact diode [3]. The MIM diode generates a beat note such that

$$\nu_{\text{beat}} = \nu_{\text{FIR}} - |\nu_1 - \nu_2| \pm \nu_{\mu\,\text{wave}}. \tag{1}$$

ν_1 and ν_2 (the CO_2 laser frequencies) and $\nu_{\mu\,\text{wave}}$ are chosen so that

$$0 < |\nu_{\text{beat}}| < 1.5\,\text{GHz}. \tag{2}$$

The beat note is amplified and displayed on a spectrum analyzer, using a peak-hold feature that records the beat note as the FIR is tuned. The center of this recording is then marked with an oscillator, whose frequency is counted.

TABLE I
Far Infrared Laser Frequencies of Optically Pumped $^{13}CD_3OH$

CO_2 Pump Line	Wavelength[a] (μm)	Pressure Pa (mTorr)	Rel. Intensity	Frequency[b] (MHz)	Ref.
9R(52)	317.556	7(50)	40	944 059.0	New
	542.748	7(50)	10	552 360.3	New
9R(30)	150.177	27(200)	150	1 996 261.6	[1], [2]
	227.368	15(110)	70	1 318 533.5	New
9R(28)	336.339	13(100)	30	891 339.3	[1], [2]
9R(22)	250.452	7(50)	50	1 197 005.1	New
	268.761	7(50)	30	1 115 461.4	New
9R(8)	221.052	7(50)	100	1 356 207.4	[1], [2]
	389.503	7(50)	20	769 680.0	[1], [2]
9P(10)	246.806	13(100)	20	1 214 686.4	New
	258.341	13(100)	18	1 160 451.9	New
9P(48)′	238.162	11(80)	80	1 258 774.6	New
	299.890	11(80)	75	999 676.2	New
9P(48)″	238.164	11(80)	70	1 258 766.4	New
	299.895	11(80)	65	999 657.8	New
10R(46)	157.679	10(75)	100	1 901 282.4	New
10R(24)	61.682	27(200)	300	4 860 288.7	[2]
10R(10)′	327.280	7(50)	8	916 011.1	2[c]
10R(10)″	71.682[d]	- - -	25	4 182 256.6	[6], [2]
10P(8)	175.10	13(100)	140	1 712 097.5	[8], [2]
	462.285	24(180)	350	648 501.6	[1], [2]
10P(12)	133.641[d]	11(80)	30	2 243 269.0	[7], [2]
	146.096	13(100)	15	2 052 029.8	[2]
10P(24)′	124.253	27(200)	175	2 412 757.4	[4], [1][e], [2][c]
	216.356	11(80)	350	1 385 645.4	[4], [2][c]
	290.909	16(120)	120	1 030 536.3	[1][e], [2]
10P(24)	118.650	20(150)	30	2 526 691.4	[2]
	203.641	27(200)	50	1 472 160.2	New
10P(42)	148.178	13(100)	80	2 023 188.3	[1], [2]
	187.036	9(70)	20	1 602 861.0	[2]

a Calculated from the frequency using $c = 299\ 792\ 458$ m/s (speed of light in vacuum).
b Relative accuracy is $2 \cdot 10^{-7}$.
c Frequency measured in [2].
d May be from a different isotope of methanol; see text for discussion.
e Pump line previously listed as 10P(22).

III. Results

The measured $^{13}CD_3OH$ laser frequencies are given in Table I along with our optimum pressures and relative powers;

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polarization relative to the pump laser polarization was not measured. The majority of the lines are 200–400 μm in wavelength; only two are shorter than 100 μm. Thirteen new lines are reported; seven of these are pumped by high $J (J \geq 46)$ CO_2 lines, yet the other new lines are pumped by lower J CO_2 lines, which have been well researched. Several of the stronger, shorter wavelength lines could be useful for laser magnetic resonance studies. We did not observe some of the lines reported by Inguscio *et al.* [1] and Moraes *et al.* [2] because of differences in FIR laser cavity, CO_2 laser tuning, and detector sensitivity.

The intensities listed in Table I are proportional to the rectified voltage detected on our MIM diode. Because our FIR cavity, coupling, and detection are unique, these should be used only as a rough guide to the line's strength. For comparison, the very strong 118.8 μm line of CH_3OH and the 127 μm line of $^{13}CD_3OH$ [1] had relative strengths of 4200 and 3000.

IV. Discussion

The frequencies of four lines in Table I were previously measured by Moraes *et al.* [2]. The measurements agree within their uncertainty, but ours are 3.5× more accurate. Two lines pumped by 10P(24) were previously misassigned as pumped by 10P(22) in [1]. The 124 and 216 μm lines pumped by 10P(24) reported in Table I were previously observed and frequency measured as $^{13}CD_3OD$ lines [4]. Both of these lines are fairly strong in this work and have also been assigned from the Fourier transform spectra [5] as belonging to $^{13}CD_3OH$. In addition, the 9R(14) pumped 118.55 μm line assigned to $^{13}CD_3OD$ in [4] and remeasured as a $^{13}CD_3OH$ line in [2] was observed and remeasured in the course of this work. We think the earlier assignment is correct. Also, the 71.7 μm line pumped by 10P(10) was previously assigned as a CD_3OH line [6] and the 133.64 μm line pumped by 10P(12) was assigned as a $^{13}CH_3OH$ line [7]. Because of difficulties in isotope purity and D:H exchange on the walls (particularly on the methyl group), it is difficult to definitively assign these lines to one isotope or the other.

Seven of the measured frequencies have recently been assigned by the Fourier transform spectra of $^{13}CD_3OH$ by Xu *et al.* [5]. Although several of the measured frequencies disagree with the predicted frequency of [5] by more than the 30 MHz uncertainty in the calculated values, the overall agreement is very good. The present frequency measurements are much better than the previous wavelength measurements and confirm the assignments. Xu *et al.* [5] also predict many new laser lines; none of these correspond to our 13 new lines. Four of the new lines pumped by 9P(48) are two pairs of twins; two lines separated by less than 20 MHz. The paired lines have optimum power at slightly different CO_2 pump laser frequencies and practically the same intensity and optimum pressure.

V. Conclusion

We have measured and tabulated 30 FIR laser frequencies of $^{13}CD_3OH$, 13 of which are new lines. This more than doubles the measured frequencies for this molecule. Four of the lines were previously assigned to other isotopes of methanol; two of the assignments have been clarified, and the other two are still nebulous.

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