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C-13 Methanol Far-Infrared Laser: Newly Discovered Lines, Predictions, and Assignments

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We report 25 new laser lines from $^{13}CH_3OH$ methanol when pumped by a cw CO_2 laser. The majority of the lines are pumped by the 10R (regular) and 10SR (sequence) bands of the CO_2 laser. Two are pumped by the 9HP(20) hot-band CO_2 line. We measured 22 laser frequencies in this molecule, 19 from new lines and three from previously reported lines. We also remeasured and corrected the frequency of the 9P(44) pumped line as 3 378 404.87 MHz (88.738 μm). We assigned two lines—10SR(17), 77.5758 cm^{-1} and 10R(50), 119.3020 cm^{-1}—and predicted other potential far-infrared laser lines with these two pumps.

1. INTRODUCTION

Methanol (CH_3OH) and 10 isotopomers have contributed over 2000 far-infrared (FIR) laser lines in the range 19.5 to 3030 μm (*1, 2*) when optically pumped with CO_2 lasers. The normal CH_3OH species alone contributes over 600 laser lines; it is the isotopic form that produces the greatest number of lines. $^{13}CH_3OH$ methanol, on the other hand, accounts for just 116 lines with a greater concentration in the 100-μm range, where there have been many applications to spectroscopic studies.

In this work we optically pumped the $^{13}CH_3OH$ methanol molecule with a cw CO_2 laser with an extended coverage in its emission range, and we have discovered 24 new FIR laser lines. The pump laser oscillates on regular-band laser lines, sequence-band, and hot-band laser lines. We performed measurements on the frequency, pump-offset, relative polarization, and relative intensity. Fourier-transform infrared (IR) and FIR spectroscopy were used for the identification of specific laser transitions. Assignments of two laser transitions and prediction of two further potential laser lines were possible.

2. EXPERIMENTAL

The pump laser was a cw CO_2 laser with extended coverage in its emission range what was possible with the use of several different high resolution gratings in its 1.5-m-long Fabry–Perot cavity. This allowed operation on 275 regular-band, sequence-band, and hot-band lines with power levels ranging from 10 to 40 W. For pumping with the CO_2 laser lines reported in this work, we used 171 line/mm gratings.

The FIR laser cavity used in this experiment was a metal-dielectric rectangular waveguide described in detail elsewhere (*3*). Essentially, the 2-m-long FIR cavity was closed by two flat end mirrors: one with a central coupling hole for the CO_2 laser in a longitudinal pumping scheme and the other, movable longitudinally, through attachment to a micrometer. A small 45° copper mirror near the pumping entrance coupled a fraction of the FIR radiation out through a Brewster-angle silicon window.

A metal-insulator-metal (MIM) diode was used to detect the laser radiation and also as a mixer for the frequency measurements. The movable mirror tunes the FIR cavity into resonance with the FIR laser modes. 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 10 wavelengths by translating the movable mirror and counting the FIR modes displayed on an oscilloscope screen. The length variation was measured with the micrometer attached to the mirror. This yields a wavelength determination accurate to about 0.05 μm, which leads to an estimated frequency that is then used to select the CO_2 frequencies for the precise heterodyne measurement.

To measure the FIR frequency, the FIR radiation is 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 from the equation

$$\nu_{\mathrm{FIR}} = n|\nu_1 - \nu_2| \pm m\nu_{\mu\mathrm{wave}} \pm \nu_{\mathrm{beat}}, \qquad [1]$$

where ν_1 and ν_2 are the stabilized CO_2 frequencies, $\nu_{\mu\mathrm{wave}}$

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TABLE 1
Far-Infrared Laser Lines from $^{13}CH_3OH$ Methanol

CO_2 Pump Line	Frequency[a] (MHz)	Wavelength[b] (μm)	Wavenumber[b] (cm^{-1})	Pressure (Pa)	Relative Intensity	Offset (MHz)	Rel. Polar.
9P(44)	3 378 404.87	88.73787	112.69146	13	W	-14	//
9HP(20)	1 301 177.7	230.40086	43.4026	20	M	9	//
9HP(20)	1 299 177.7	230.75554	43.3359	20	M	9	//
10R(54)	6 812 119.1	44.00869	227.22783	37	W		//
10R(52)	6 672 912.5	44.92678	222.58440	27	M	2	//
10R(50)	3 576 584.4	83.82088	119.30201	19	M	-45	//
10R(46)′	2 712 817.0	110.50965	90.48983	28	M		//
10R(46)″	1 862 786.3	160.93765	62.13586	43	VS	22	//
10R(46)″	1 862 788.4	160.93747	62.13593	43	VS	22	//
10R(44)	2 055 165.0	145.8727	68.55293	40	S	-20	⊥
10R(44)	1 474 976.3	203.25239	49.19991	53	VS	-20	//
10R(42)		125.9	79.43	53	M	-7	⊥
10R(40)	4 158 911.8	72.08435[c]	138.72637	35	VS	-24	//
10R(38)	2 044 805.1	146.61175	68.20736	21	M	-30	//
10R(36)		339.9[c]	29.42			38	//
10R(34)		49.1	203.67	31	M	8	//
10R(32)	891 144.1	336.413[c]	29.72537	27	W	47	//
10SR(21)	3 713 175.1	80.7375	123.85819	41	M	-9	//
10SR(19)		70.0	142.9	13	VW		//
10R(14)	955 817.9	313.65018	31.88265	31	W	21	//
10SR(17)′	6 388 391.4	46.92769	213.0938	47	W		//
10SR(17)″		112.5	88.89	40	W	24	//
10SR(17)‴		128.9	77.58	40	W	47	//
10R(12)	2 958 198.7	101.34291[c]	98.67489	51	M	8	//
10SR(15)	3 738 951.2	80.1809	124.71799	39	S	-38	//
10SR(11)	5 938 379.6	50.48388	198.08302	53	S	27	//
10R(06)′	4 178 156.9	71.75232	139.36831	40	W	-28	//
10R(06)″	3 668 292.2	81.72535	122.36106	51	M	-40	//
10R(06)‴		127.1	78.68	40	W		⊥
10R(06)′		240.1[c]	41.65			-30	//

Note. ′, ″, and ‴, indicate different CO_2 laser frequency offsets. SR stands for sequence-band line and HP stands for hot-band line. VS, S, M, W, and VW, stand for very strong, strong, medium, weak, and very weak, respectively. 1 Torr = 133.3 Pa.

[a] Estimated uncertainty in the reproducibility of the FIR laser frequency: $\Delta\nu/\nu = 2 \times 10^{-7}$.

[b] Calculated from the measured frequency with $c = 299\,792\,458$ m/s.

[c] Not a new line.

is the microwave frequency, ν_{beat} is the beat frequency, and n and m are the order of the harmonics generated by the MIM diode. The estimated uncertainty in the reproducibility of the FIR laser frequency is $\Delta\nu/\nu = 2 \times 10^{-7}$. The same principle is used to measure the pump offsets of the FIR laser lines. In this case, a frequency-stabilized CO_2 laser set to the same laser line as the pump is mixed in the diode with the pump frequency. The frequency of a microwave source is added to the mixture whenever the pump line is a sequence-band or a hot-band line to make up for the frequency difference.

3. RESULTS

3.1 FIR Laser Lines

Table 1 lists the 25 new FIR laser lines produced by $^{13}CH_3OH$, the 9P(44) pumped 88.738-μm line whose frequency was remeasured and corrected, plus five other previously reported laser lines for which we measured either the frequency or the pumping offset. The optimum pressure, relative polarization, pump offset, and relative intensity are also reported for most of the lines. The wavelengths range from 44.01 to 313.65 μm (6 812 119.1 to 955 817.9 MHz or 227.22783 to 31.88265 cm^{-1}), with half of the lines having wavelengths below 100 μm. The reported intensities are proportional to the rectified voltage on the MIM diode. Among the newly discovered lines there are a few with relative intensity levels considered to be very strong (VS). The optimum pressure for each line was measured by a pressure gauge and it was in the range 13–53 Pa (100–400 mTorr).

3.2 FIR Laser Assignments

For the identification of the specific transition and energy level systems giving rise to the optically pumped FIR-laser lines, Fourier-transform IR and FIR spectroscopy have proven to be powerful techniques, and numerous assignments have been determined for $^{13}CH_3OH$ in recent years (*5*, *6*). These assignments have generally employed the spectroscopic data to form closed frequency–combination loops containing the FIR laser transitions. The requirement that the frequency closure condition be satisfied for a combination loop within the experimental uncertainty gives a stringent test of any proposed assignment scheme. In this way, we have identified the transition systems for two of the new $^{13}CH_3OH$ FIR laser lines observed in the present work.

The first assigned transition is the 128.9-μm FIR laser line pumped by the 10SR(17) CO_2 sequence-band line. A strong feature at 971.4513 cm^{-1} in the IR spectrum consists of the P(26) member of the $(n\tau K) = (016)^{CO}$ A CO-stretching subband (*5*) blended with the weaker P(25) member of the $(133)^{CO}$ E_1 torsionally excited subband (*6*), and we identify the former as the IR pump transition for the 128.9-μm laser line. Here we use the customary Dennison $(n\tau K, J)^{v}$ energy level notation in which n is the torsional state, τ is an index defining the A, E_1 or E_2 torsional symmetry, and K is the component along the molecular a-axis of the rotational angular momentum J. The v superscript labels the vibrational state as $v = 0$ for the ground state and $v =$ CO for the excited CO-stretching mode.

The energy level and transition diagram for the 10SR(17) system is shown in Fig. 1 with the IR pump represented as a bold arrow and the observed and predicted FIR laser lines as thin arrows. Sample transitions among the IR and FIR spectral data available to form combination loops are shown as dashed arrows along with their spectroscopic wavenumbers. The observed 128.9-μm FIR laser line is denoted as Lc, and two further transitions which might potentially yield FIR laser emission are labeled in brackets as [La] and [Lb]. The wavenumber of the assigned line

Lc can be determined by the combination difference relations for two independent loops:

$$\begin{aligned} \text{Lc} &= (016, 25)^{\text{CO}} \leftarrow (016, 26)^{0} \leftarrow (025, 25)^{0} \leftarrow (025, 24)^{\text{CO}} \\ &= 971.4513 + 79.6345 - 973.5098 \qquad [2] \\ &= 77.5760\ \text{cm}^{-1}, \end{aligned}$$

and

$$\begin{aligned} \text{Lc} &= (016, 25)^{\text{CO}} \leftarrow (016, 24)^{0} \leftarrow (025, 23)^{0} \leftarrow (025, 24)^{\text{CO}} \\ &= 1051.4975 + 76.5588 - 1050.4807 \qquad [3] \\ &= 77.5756\ \text{cm}^{-1}. \end{aligned}$$

The two values are consistent to well within the estimated net measurement uncertainty of ± 0.001 cm^{-1} for each loop, giving useful support for the IR and FIR assignments. The mean wavenumber of 77.5758 cm^{-1} agrees with the value of 77.58 cm^{-1} determined from the 128.9-μm wavelength for this line, which was not measured in frequency.

The two further potential laser wavenumbers [La] and [Lb] can also be accurately predicted from combination loops in Fig. 1. The $\Delta J = -1$ transition [La] would have polarization parallel to the $\Delta J = -1$ P-branch pump, while

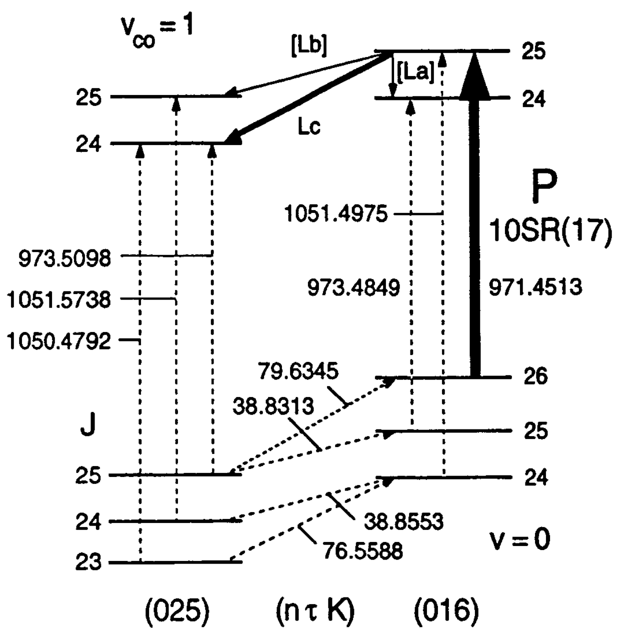

FIG. 1. Energy level and transition diagram for the FIR laser system of ^{13}CH$_3$OH optically pumped by the 10SR(17) sequence-band CO_2 laser line. The IR pump is the P(016,26)^{co} *A* transition of the CO-stretching band of C-13 methanol, and the FIR laser line Lc has an observed wavelength of 128.9 μm. Lines [La] and [Lb] are predicted. The wavenumbers are given in cm^{-1} for the IR and FIR spectroscopic transitions shown as dashed arrows.

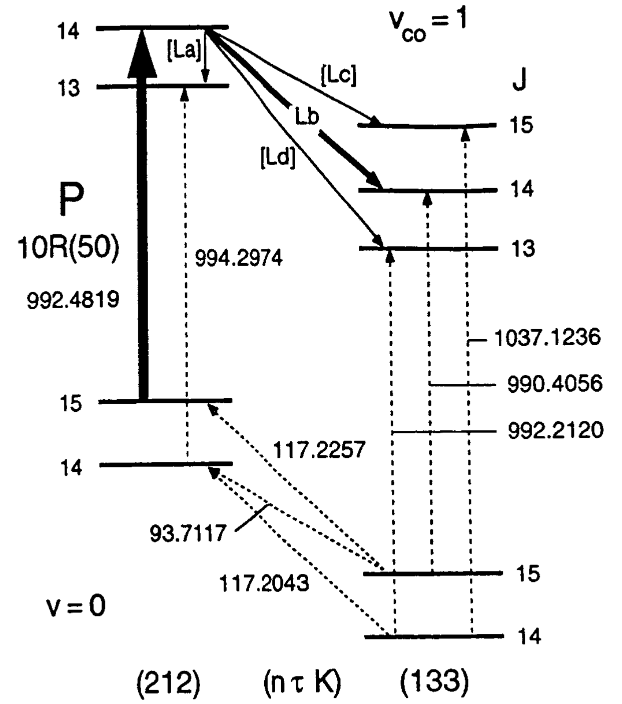

FIG. 2. FIR laser system of ^{13}CH$_3$OH optically pumped by the 10R(50) CO_2 laser line. The IR pump is the P(212,15)$^{\text{CO}}$ E_1 torsionally excited transition of the CO-stretching band. The observed FIR laser line Lb has an experimental wavenumber of 119.30201 cm^{-1}; lines [La], [Lc], and [Ld] are predicted. Wavenumbers are given in cm^{-1} for the IR and FIR spectroscopic transitions shown as dashed arrows.

that for the $\Delta J = 0$ Q-branch transition [Lb] would be perpendicular. The wavenumbers are given from the following combination relations:

$$\begin{aligned} [\text{La}] = {} & (016, 25)^{\text{CO}} \leftarrow (016, 26)^{0} \leftarrow (025, 25)^{0} \leftarrow \\ & (016, 25)^{0} \leftarrow (016, 24)^{\text{CO}} = 971.4513 + 79.6345 \qquad [4] \\ & - 38.8313 - 973.4849 = 38.7696\ \text{cm}^{-1}, \end{aligned}$$

and

$$\begin{aligned} [\text{Lb}] = {} & (016, 25)^{\text{CO}} \leftarrow (016, 24)^{0} \leftarrow (025, 24)^{0} \leftarrow \\ & (025, 25)^{\text{CO}} = 1051.4975 + 38.8553 \qquad [5] \\ & - 1051.5738 = 38.7790\ \text{cm}^{-1}. \end{aligned}$$

This system has the interesting quirk that the predicted [La] and [Lb] wavenumbers are virtually identical, showing that the upper state (016, 24)$^{\text{CO}}$ and (025, 25)$^{\text{CO}}$ *A* levels are almost exactly degenerate. Thus, one would expect two FIR laser lines with very close frequencies, but different polarizations, which could be rather perplexing to interpret experimentally without knowing the situation in advance.

The additional 47.0- and 112.5-μm FIR laser lines pumped by the 10SR(17) CO_2 line do not appear to belong to the energy level system of Fig. 1. We do not have any plausible identifications for these lines at this time.

The second assigned system involving the 10R(50) CO_2 pump is particularly interesting from a spectroscopic point of view since the pumping is to a torsionally excited $n = 2$ level of the CO-stretching mode followed by FIR lasing down to an $n = 1$ torsional level. Spectroscopic data are still sparse for $n = 2$ CO-stretching states (*6*); hence the backup for the IR assignments given by the FIR laser identification represents important support for the IR analysis. The energy level and transition diagram is shown in Fig. 2 with representative IR and FIR spectral data. The wavenumber of the assigned FIR laser line Lb is determined from the following loop:

$$\text{Lb} = (212, 14)^{CO} \leftarrow (212, 15)^{0} \leftarrow (133, 15)^{0} \leftarrow (133, 14)^{CO} = 992.4819 + 117.2257 - 990.4056 = 119.3020 \text{ cm}^{-1}. \quad [6]$$

This result is in exact agreement with the value derived from the measured frequency of line Lb. Loops can also be formed for the other potential FIR laser lines [La], [Lc], and [Ld] that might be observable for this system to give the predicted wavenumbers below:

$$[\text{La}] = (212, 14)^{CO} \leftarrow (212, 15)^{0} \leftarrow (133, 15)^{0} \leftarrow (212, 14)^{0} \leftarrow (212, 13)^{CO}$$
$$= 992.4819 + 117.2257 - 93.7117 - 994.2974 = 21.6985 \text{ cm}^{-1}, \quad [7]$$

$$[\text{Lc}] = (212, 14)^{CO} \leftarrow (212, 15)^{0} \leftarrow (133, 15)^{0} \leftarrow (212, 14)^{0} \leftarrow (133, 14)^{0} \leftarrow (133, 15)^{CO}$$
$$= 992.4819 + 117.2257 - 93.7117 + 117.2043 - 1037.1236 = 96.0766 \text{ cm}^{-1}, \quad [8]$$

and

$$[\text{Ld}] = (212, 14)^{CO} \leftarrow (212, 15)^{0} \leftarrow (133, 15)^{0} \leftarrow (212, 14)^{0} \leftarrow (133, 14)^{0} \leftarrow (133, 13)^{CO}$$
$$= 992.4819 + 117.2257 - 93.7117 + 117.2043 - 992.2120 = 140.9882 \text{ cm}^{-1}. \quad [9]$$

4. CONCLUSIONS

In conclusion, we have obtained 25 new FIR laser lines from $^{13}CH_3OH$ and measured the frequencies for 22 of them as well as the relative polarization, relative intensity, pump offset, and optimum pressure of operation. The lines were pumped by regular-band, sequence-band, and hot-band lines, mainly from the 10-μm branch of a CO_2 laser. We also remeasured and corrected the frequency of the 9P(44) pumped line as 3 378 404.87 MHz (88.738 μm). Assignment of two lines—10SR(17), 77.5758 cm^{-1} and 10R(50), 119.3020 cm^{-1}—and predictions for other five potential FIR laser lines with these two pumps are also included in this work. We have not as yet tried to look for the predicted laser lines.

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