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Investigation of $^{13}CH_3OH$ methanol: new laser lines and assignments

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Abstract. We have reinvestigated $^{13}CH_3OH$ as a source of far-infrared (FIR) laser emission using a CO_2 laser as a pumping source. Thirty new FIR laser lines in the range 36.5 μm to 202.6 μm were observed and characterized. Five of them have wavelengths between 36.5 and 75 μm and have sufficient intensity to be used in LMR spectroscopy. Using Fourier-transform spectroscopic data in the infrared (IR) and FIR regions we have determined the assignment for 10 FIR laser transitions and predict nine frequencies for laser lines which have yet to be observed.

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The technique of optically pumping polar molecules is the most efficient for far-infrared (FIR) laser generation. Moreover, it provides a versatile and powerful tool for molecular spectroscopy in this spectral region. As with regular methyl alcohol ($^{12}CH_3^{16}OH$), the $^{13}CH_3OH$ isotopomer is an excellent source of laser radiation when optically pumped with CO_2 lasers. Before this work there were 174 FIR laser lines [1–6] detected in $^{13}CH_3OH$, 86 of which have been assigned. In this work, we have used a CO_2 laser that lases on regular, hot, and sequence bands to reinvestigate $^{13}CH_3OH$ as a lasing molecule. There are two motivations to look for new FIR laser lines. The first one is to further understand the spectroscopy of the lasing molecule. The second is to find new, short-wavelength (from 25 to 75 μm) laser lines that can be used in LMR spectroscopy of low-lying bending vibrations. We performed wavelength measurements, determined the relative polarization, recorded the optimum pressure of operation, and measured the relative intensity for 30 new FIR laser emissions. We also present the assignments for 10 FIR laser lines and the prediction of nine additional potential laser transitions.

1 Experimental setup

The experimental apparatus consists of a 2-m long CO_2 pump laser and a Fabry–Perot FIR laser cavity. The CO_2 laser has a grating specially blazed to provide approximately 3% output coupling in the zeroth order from 9 to 11 μm. A total of 230 CO_2 laser lines from sequence, hot, and regular bands were available. A detailed description of this laser can be obtained from [7, 8].

The newly constructed FIR laser cavity used in this work is formed by two gold-coated-copper concave mirrors with a 1.9-m radius of curvature and separated by ~ 2 m. One of these mirrors is fixed while the other is moveable and coupled to a micrometer, allowing tuning of the cavity into resonance with the longitudinal modes of the FIR laser. A variable resistor biased at 1.5 V dc (output range 0 to 1.5 V dc) is coupled to the micrometer to provide output in the x direction to an $x-y$ plotter. For each wavelength measurement the cavity was scanned over several longitudinal modes and the intensity was plotted as a function of cavity length. This allowed us to determine the FIR laser wavelengths with an uncertainty of approximately ±0.5 μm. The FIR output power is coupled out by a 45° mirror (radially adjustable) and was detected using a pyroelectric detector. This new FIR laser cavity has a versatile configuration that allows us to change it to a V- [9], an X-, or an XV-type pumping geometry. We have used it in V-type configuration to perform this work. It will be completely described in a forthcoming paper.

2 Results and discussion

2.1 New FIR laser lines

Table 1 presents the data of the 30 new FIR laser lines observed, arranged according to the CO_2 pump lines. Information about the wavelength, the relative polarization, the operation pressure, and the relative intensity are given for each line. The intensity of each line was measured and calibrated against the intensity of the 118.8 μm line from $^{12}CH_3OH$ (8.5 mW, or 6 V on the pyroelectric detector). The wavelengths of the new lines ranged between 36.5 and 202.6 μm. Six lines have wavelengths in the region between 25 and 75 μm; five of them have sufficient intensity to be used in

Table 1. New FIR laser lines from $^{13}CH_3OH$

Pump line	Wavelength / μm	Wavenumber / cm^{-1}	Rel. pol.	Pressure / mTorr	Relative intensity[a]
9R6	85.3	117.23	∥	140	0.5
9R8	89.9	111.23	∥	120	0.6
9P2	196.5	50.89	⊥	140	0.2
9HP16	85.4	117.10	∥	190	1.2
	89.4	111.86	∥	190	2.3
9HP24	54.1	184.84	∥	230	7.5
9P18	111.6	89.61	∥	140	0.1
	140.0	71.43		140	0.1
9P20	195.0	51.28	∥	200	2.0
9SP17	45.9	217.86	∥	130	1.3
	51.9	192.68	⊥	150	0.8
	108.0	92.59	∥	150	0.3
9HP31	51.5	194.17	⊥	170	1.7
	103.7	96.43	∥	140	3.3
9P36	37.5	266.67	∥	120	0.3
9P44	124.8	80.13	∥	210	1.2
9P46	120.4	83.06	∥	280	6.2
9P52	36.5	273.97	⊥	390	3.3
9P54	139.5	71.68	⊥	100	0.2
	133.6	74.85	∥	100	0.1
9P56	138.5	72.20	⊥	220	0.2
9P60	116.1	86.13	∥	160	2.2
	166.2	60.17	∥	150	4.2
	202.6	49.36	⊥	100	0.8
10R56	105.7	94.61	∥	190	0.7
10R38	97.2	102.88	⊥	340	1.4
10R36	70.4	142.04	⊥	300	4.7
10R26	116.2	86.06	∥	240	0.6
10SR25	71.3	140.25	∥	240	0.1
10R14	86.3	115.87	∥	170	2.3

[a] Relative to the 118.8 μm line of $^{12}CH_3OH$ (8.5 mW)

LMR spectroscopy. The 86.3 μm line pumped by 10R14 has been previously predicted by us [10] and the 89.4 μm line pumped by 9HP16 by Xu et al. [3].

2.2 Assignments

The laser-line assignments given in this paper were based on our systematic investigation of high-resolution Fourier-transform (FT) absorption spectra in the FIR and IR regions [10–12]. For this investigation, we utilized spectroscopic data from analyses of $^{13}CH_3OH$ spectra recorded at a resolution of 0.002 cm^{-1} from 900–1250 cm^{-1} for the C−O stretching and the CH_3-rocking bands. In the assignment procedure used in the systematic investigation, a simultaneous fit of all FIR and IR absorptions-assigned transitions automatically forms and checks all possible closed-transitions loops [10]. This method provides both very accurate energy-level values and a check of the reliability of the assignments.

The energy-level notation employed in the assignment lists of the present work is the same as used in our previous works [10, 12]. Five quantum numbers in the form $(n, K; J)^{\nu}\sigma$ are used to determine an energy level. The quantum number n denotes the torsional state, J is the total angular momentum, and K is its projection along the internal rotation axis. The quantum number ν labels the vibrational state. In this paper we represent the ground vibrational state by $\nu = \mathrm{gr}$, the excited C−O stretch state by $\nu = \mathrm{co}$, and the excited CH_3 in-plane rocking state by $\nu = \mathrm{ri}$. The label σ stands for the symmetry species, A or E, common to the upper and lower levels of the transition. The quantum number K has only non-negative values for A symmetry, while it can have positive, zero, or negative values for E symmetry. The σ and ν labels will be omitted whenever obvious from the context.

Table 2 reports our new assignments and (in brackets) our predicted new FIR laser transitions of $^{13}CH_3OH$, arranged according to the CO_2 pump line frequencies. Of the seven assigned transition systems, six involve pumping into the C−O stretch mode and only one into the CH_3-rocking mode. All the calculated wavenumbers for the pump and laser emission transitions are determined with an accuracy of 10^{-4} cm^{-1}. The agreement between the CO_2 and FTS pump wavenumbers is good in all cases. The relative polarizations and wavenumbers of the FIR laser transitions shown in brackets in Table 2 are predicted from our assignment work, but are not yet observed experimentally. For all cases the observed polarization agrees with that predicted by the rule for the relative polarization of the pump and emission radiation [13].

Two of the laser systems detailed in Table 2 will now be discussed. Two new FIR laser lines were observed pumped off-center by the 9HP16 line of the CO_2 laser. Although we have experimentally observed them oscillating together, the assignment indicates that these two FIR laser emissions are associated with different but very close IR-absorption transitions. The separation between the centers of the two absorption lines would be on the order of 3 MHz. The 111.86 cm^{-1} line was predicted by Xu et al. [3] as pumped by the $(0, 9; 30)^{\mathrm{gr}} \rightarrow (0, 9; 31)^{\mathrm{co}}A$ absorption transition. For the 117.10 cm^{-1} line we propose an assignment where it and the known 208.2700 μm (48.0146 cm^{-1}) line [3] would be pumped by the same IR-absorption transition. To be certain about this assignment, it would be necessary to perform a frequency measurement of the 117.10 cm^{-1} line, which has not been done.

The 9P60 laser system is a good example to show the accuracy of our assignments. Figure 1 shows the diagram of the energy levels and the transitions of the laser system excited by the 9P60 line. The dashed traces represent the IR- (from A to G) and FIR- (from a to g) absorption transitions observed in our FT spectrum and assigned by our systematic investigation. The wavenumbers of all transitions shown in the diagram are given in the figure caption. The absorption transition occurring between $(0, 7; 8)^{\mathrm{gr}}$ and $(0, 7; 7)^{\mathrm{co}}$ levels is in good coincidence with the 9P60 CO_2 laser line. The FIR laser lines are represented by continuous traces. The wavenumbers of these two laser transitions can be determined, for instance, as follows:

$$L_a = f + G - E = a + b + f + G - A = 49.4280\,\mathrm{cm}^{-1}\,,$$

$$L_b = a + b + f + G - B = e + G - D = 60.3080\,\mathrm{cm}^{-1}\,.$$

The large number of independent combination loops lead to the same wavenumbers for these two FIR laser lines. The assignments for L_a and L_b would be definitely confirmed by frequency measurements, but the good agreement between observed and predicted polarizations and the difference between observed and calculated wavenumbers within the experimental error indicate the consistency of our assignments.

Table 2. New assignments of $^{13}CH_3OH$ FIR laser transitions

Pump line	CO_2 pump / cm^{-1}	Pump assign. $(n'', K''; J'')^{\nu''}\sigma$	FTS pump / cm^{-1}	$\Delta\nu^a$ / $\times 10^{-4} cm^{-1}$	Emiss. assign. $(n', K'; J')^{\nu'} \rightarrow (n'', K''; J'')^{\nu''}$	Rel. pol.	ν_{obs} / cm^{-1}	ν_{calc} / cm^{-1}	Obs.
9HP16	1058.1717	$(0, 9; 30)^{gr}$A	1058.1702	+0.5	$(0, 9; 31)^{co} \rightarrow (0, 9; 30)^{co}$	$\parallel$	48.0146	48.0146	[3]
					$\rightarrow (0, 8; 30)^{co}$	$\parallel$	111.86	111.8256	new
		$(0, -11; 30)^{gr}$E	1058.1702	+1.4	$(0, -11; 31)^{co} \rightarrow (0, -11; 30)^{co}$	$\parallel$	48.0146	48.0146	new
					$\rightarrow (0,-10; 31)^{co}$	$[\perp]$		[72.0821]	predicted
					$\rightarrow (0, -10; 30)^{co}$	$\parallel$	117.10	120.0783	new
9P46	1021.0569	$(0, 7; 26)^{gr}$E	1021.0510	−2.0	$(0, 7; 25)^{ri} \rightarrow (0, 7; 24)^{ri}$	$[\parallel]$		[39.0976]	predicted
					$\rightarrow (0, 6; 25)^{ri}$	$[\perp]$		[43.9826]	predicted
					$\rightarrow (0, 6; 24)^{ri}$	$\parallel$	83.06	83.1028	new
9P54	1012.2918	$(1, -1; 9)^{gr}$E	1012.2901	−1.0	$(1, -1; 9)^{co} \rightarrow (1, -1; 8)^{co}$	$[\perp]$		[14.0180]	predicted
					$\rightarrow (1, 0; 9)^{co}$	$\parallel$	74.85	74.8590	new
					$\rightarrow (1, 0; 8)^{co}$	$[\perp]$		[88.8165]	predicted
		$(0, 4; 25)^{gr}$E	1012.2901	−4.0	$(0, 4; 25)^{co} \rightarrow (0, 3; 24)^{co}$	$\perp$	71.68	71.8437	new
					$\rightarrow (0, 3; 25)^{co}$	$\parallel$		[32.9595]	predicted
					$\rightarrow (0, 4; 24)^{co}$	$[\perp]$		[38.8037]	predicted
9P60	1005.4775	$(0, 7; 8)^{gr}$E	1005.4782	+0.3	$(0, 7; 7)^{co} \rightarrow (0, 6; 7)^{co}$	$\perp$	49.36	49.4281	new
					$\rightarrow (0, 6; 6)^{co}$	$\parallel$	60.17	60.3081	new
					$\rightarrow (3, 6; 6)^{gr}$	$\parallel$	86.13	84.9807	new
10R56	995.0766	$(0, -10; 14)^{gr}$E	995.0742	+0.4	$(0, -10; 13)^{co} \rightarrow (0, -9; 12)^{co}$	$\parallel$	94.61	94.7867	new
					$\rightarrow (0, -10; 12)^{co}$	$[\parallel]$		[20.1946]	predicted
					$\rightarrow (0, -9; 13)^{co}$	$[\perp]$		[74.5723]	predicted

[a] $\Delta\nu = \nu_{FT\ abs} - \nu_{calc}$

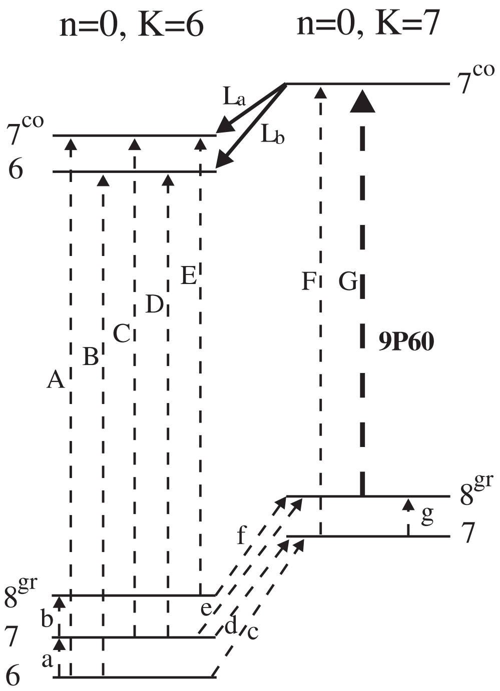

Fig. 1. Laser system pumped by CO_2 pump line 9P60. The experimental FIR laser wavenumbers are $L_a = 49.36$ and $L_b = 60.17\,cm^{-1}$. The IR (*capital letters*) and FIR (*small letters*) FT absorption transition wavenumbers (in cm^{-1}) are: $A = 1029.2435$, $B = 1018.3635$, $C = 1018.2282$, $D = 1007.3479$, $E = 1005.6394$, $F = 1018.0653$, $G = 1005.4781$, $a = 11.0156$, $b = 12.5885$, $c = 60.6065$, $d = 49.5907$, $e = 62.1778$, $f = 49.5893$, and $g = 12.5872$

The 86.13 cm^{-1} FIR laser line is not represented in the diagram. We are proposing this as a transition occurring between $(0, 7; 7)^{co}$ and $(3, 6; 6)^{gr}$ levels. In this case, the difference between experimental and calculated wavenumbers is bigger than the experimental error. Thus, this assignment will be confirmed only after frequency measurements are performed.

For the other laser systems only one non-frequency-measured laser emission is known, so its respective assignments will be definitely confirmed either after frequency measurements or after the detection of one or more of the predicted FIR laser lines.

3 Conclusions

We report the wavelength, relative polarization, and working pressure of 30 new FIR laser lines of the $^{13}CH_3OH$ isotopomer. To observe them we used the regular-, sequence-, and hot-band lasing lines, mainly in the 9 μm branch of an efficient CO_2 laser. The data of new lines have been compared to an analysis of a high-resolution FT absorption spectrum of $^{13}CH_3OH$. This allowed us to assign 10 FIR laser lines and to predict nine possible new FIR laser emissions. The assignments for most of the laser systems will be definitely confirmed after the observation of one or more of the predicted FIR laser lines, or after precise frequency measurements of their laser emission.

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