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Optically Pumped FIR Laser Lines from CH_3OH: New Laser Lines, Frequency Measurements, and Assignments

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We report the identification and characterization of eight new FIR laser lines from methanol (CH_3OH) in the range 48.4 to 453.7 μm pumped by sequence and hot bands of a cw CO_2 laser. Frequency measurements for most of the new FIR laser lines and from previously reported ones were obtained in the range 0.6–6.8 THz with a one-sigma reproducibility of two parts in 10^7. We propose an assignment of energy levels for two of the new laser lines and for five pumped by 10R(46) previously reported. The high frequency lines with absorption centers outside of the tuning range of the CO_2 laser pump showed doublets. These were used to evaluate the offsets of the CO_2 absorption transitions.

I. INTRODUCTION

This work reports eight new optically pumped FIR laser lines from methanol (CH_3OH) in the range 48.4–453.7 μm. The sequence and hot bands of a high-resolution CO_2 laser and a low-loss Fabry–Perot FIR cavity were used. The new lines were characterized in wavelength, pump-offset frequency, optimum pressure, relative polarization, and relative intensity. The frequency was also measured for most of the new lines and several previously reported lines with a one-sigma reproducibility of two parts in 10^7. The assignments of energy levels for two CO_2 laser-pumped sets will be discussed.

The generation of coherent radiation in all regions of the electromagnetic spectrum has been a field of great interest in physics. The far-infrared (FIR) region, between the microwave and the midinfrared regions, has been covered mainly by optically pumped polar molecules. The absence of a plasma in the laser cavity permits a good frequency reproducibility (a few parts in 10^7) and a stability (a few parts in 10^9) of the frequency of the optically pumped FIR laser lines. These characteristics permit the use of frequency-measured FIR laser lines in various research fields, for example, metrology (*1*), laser magnetic resonance (*2*), and active medium spectroscopy (*3*).

These applications have inspired the search for new laser lines in the FIR region. The recent development of a high-resolution CO_2 laser (*4*) and low-loss short-wavelength FIR Fabry–Perot cavity (*5*) have contributed to the generation of new FIR laser lines. Methanol (CH_3OH) is the most efficient active medium to generate optically pumped FIR laser lines. It has been used as an active medium in many experiments since its first use in 1970 (*6*) and more recently in 1995 (*7*) and 1996 (*3*). The complexity of the ro–vibrational spectrum of methanol is mainly due to the hindered internal rotation and the permanent electric dipole moment components. This, along with the good overlap of the absorption C–O stretch vibrational mode with the CO_2 laser lines, has made the assignment of FIR laser lines a challenging field of spectroscopy (*8*).

II. EXPERIMENTAL APPARATUS

To search for new FIR laser lines, a high-resolution CO_2 pump laser (*4*) and a low-loss Fabry–Perot cavity for high-frequency FIR lines (*5*) were used. These lasers were recently developed at the Time and Frequency Division, National Institute of Standards and Technology (NIST), Boulder, CO. Their main characteristics will be described in the following paragraphs.

The CO_2 pump laser has a 2.0-m long cavity formed by a Littrow-mounted diffraction grating, a five-ribbed tube, and a gold-coated 20-m radius-of-curvature mirror. The ribbed tube has an internal diameter of 18 mm with sharp ribs spaced every 50 cm. They dramatically increase the effective resolution of the grating by preventing wall-bounce (or waveguide) modes. A gas mixture of 10% CO_2, 12% N_2, and 78% He flowed through the laser tube at a total pressure of about 3.3 kPa (25 Torr). A specially blazed 150 line/mm grating provides 3% output coupling in the zeroth order. The electric discharge (12 kV, 50 mA) is obtained in each 100-cm half of the tube. This CO_2 system lases cw on more than 275 lines, including the regular band lines, many hotband lines, and many sequence-band lines. Typical output power was 25 W for regular band lines, 10 W for hotband lines, and 7 W for sequence band lines. Figure 1 shows the CO_2 laser output as the grating is rotated.

The FIR Fabry–Perot cavity has less than 0.5% diffraction loss at wavelengths below 150 μm. It uses a near-confocal geometry formed by a 36-mm diameter, 2-m long Pyrex tube.

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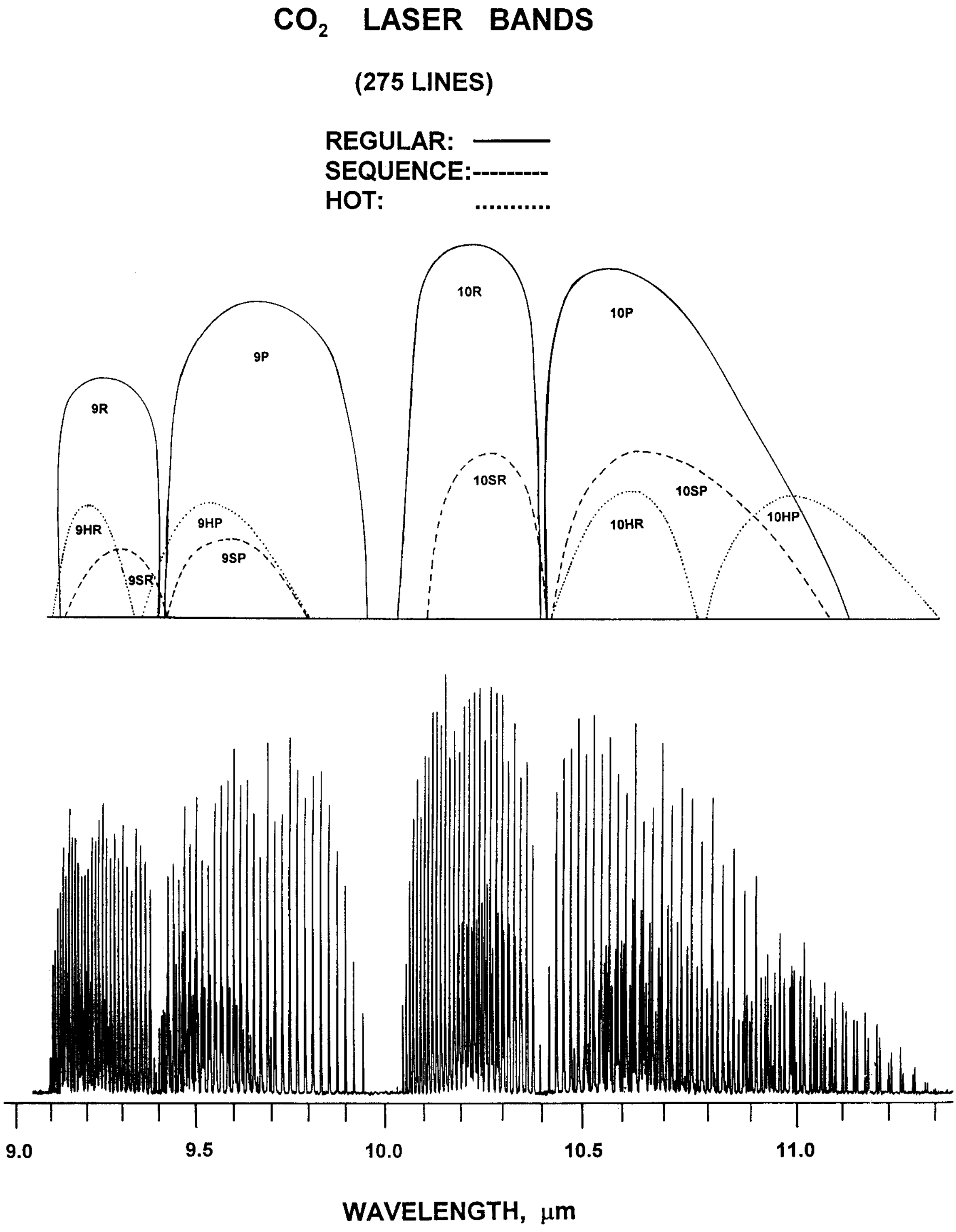

FIGURE 1

The ends were terminated with 1.9-m radius-of-curvature and gold-coated copper end mirrors; one is fixed, and the other is attached to a micrometer for scanning the length of the cavity. A microphone was placed inside the cavity in order to obtain Doppler-broadened optoacoustic signals indicating the CO_2 laser line absorptions in the active medium.

The CO_2 pump radiation was focused into the FIR laser cavity with a 2-m radius-of-curvature concave mirror 1 m from

TABLE 1
New FIR Laser Lines from CH_3OH

CO_2 pump line	Wavelength (μm)	Offset (MHz)	Rel. Pol.	Pressure Pa(mTorr)	Intens. (μV)
10SR (23)	71.280	29	$\|\|$	16(120)	0.3
	75.616	29	$\perp$	19(140)	23
10SR (25)	118.117	31	$\|\|$	8(60)	12
10R (46)	49.2	48	$\perp$[a]	13(100)	<0.1
9SP (15)	48.4	-39	$\perp$	13(100)	80
9HP (29)	71.290	-24	$\|\|$	20(150)	1000
	77.394	-24	$\perp$	20(150)	300
9HP (18)	453.697	11	$\|\|$	8(60)	100
9HP (12)	52.0	0	$\perp$	20(150)	0.1

[a] From Ref. (*3*).

the FIR laser cavity. It enters through a 3-mm diameter hole in the fixed mirror, located 16.3 mm above the laser axis, at an angle so that it is aimed at the center of the opposite mirror. This yields a V-shaped pumping region. This coupling hole is outside the FIR Fabry–Perot mode for wavelengths below 150 μm, yielding a high Q FIR laser cavity.

The FIR laser line output coupling is from a 45° 6-mm diameter polished copper mirror that is radially adjustable. The FIR output was detected by a metal-insulator-metal (MIM) point contact diode (W–Ni) or a pyroelectric detector.

III. NEW FIR LASER LINES

The opto-acoustic signal was used as the first step to search for new IR absorptions. After a new absorption was detected, the FIR laser was scanned to search for new laser lines. As a result, eight new FIR laser lines were discovered. They ranged from 48 to 454 μm and were pumped by three hotband CO_2 laser lines, three sequence-band CO_2 laser lines, and one regular-band CO_2 laser line and are listed in Table 1, which summarizes the characteristics of the new FIR laser lines. The wavelengths in Table 1, which are reported to three decimal places, have been frequency measured and then calculated with $c = 299, 792, 458$ m/s.

The wavelength was determined by using the cavity itself as a scanning Fabry–Perot interferometer and tuning the movable mirror through at least 20 fringes. The value of λ obtained in this way has a one-sigma uncertainty of about 0.05 μm.

The pump offset frequency is defined as the rest frequency (ν_{abs}) of an absorption transition minus the center frequency (ν_{CO_2}) of the CO_2 pump laser. It is obtained by beating the CO_2 pump laser frequency, when the FIR laser power is maximized, with a stabilized CO_2 reference laser frequency in a MIM diode. For sequence and hotband measurements, a regular band line reference laser lying close in frequency was chosen. In this case, microwave radiation was added to observe the beat note within the bandwidth of the spectrum analyzer. The offset obtained has an estimated one-sigma uncertainty of 2 MHz. For absorption transitions which lie outside the tuning range of the CO_2 pump laser, the offset is determined by an indirect method that will be discussed later.

The relative polarization of the FIR laser line with respect to the pump line is measured with a multi-Brewster angle polarization selector and denoted by $\perp$ for perpendicular and $\|$ for parallel.

The intensity of a FIR laser line depends on the absorption coefficient of the IR pump radiation, the FIR transition moment, and the experimental conditions such as cavity design, pump power, pressure of the active medium, output coupling, and the antenna of the MIM diode. The rectified signal from the MIM diode is an estimate of the FIR linestrength. The strong 119-μm line pumped by 22 W from the 9P(36) CO_2 pump line, produced 16 mV of rectified signal.

IV. FREQUENCY MEASUREMENTS

The frequency measurements of optically pumped FIR laser lines play a fundamental role for their applications in spectroscopy. The frequencies were measured by mixing the unknown FIR frequency with two CO_2 laser frequency references in a MIM diode. The frequency standards were synthesized from the difference between two CO_2 laser frequencies, each stabilized by locking each directly to a saturation dip in the 4.3 μm CO_2 fluorescence signal from an external reference cell (*8*). The pair was chosen to be close to the unknown FIR frequency calculated from its wavelength measurement. A microwave signal from a synthesized signal generator can also be mixed on the MIM diode if the CO_2 difference is outside the band of the spectrum analyzer.

The signal from MIM diode is preamplified and then observed on a spectrum analyzer to determine the beat note (ν_{beat}) at the frequency given by the equation:

$$\nu_{FIR} = |n_1\nu_{CO_2}(\mathrm{I}) - n_2\nu_{CO_2}(\mathrm{II})| \pm m\nu_{\mu wave} \pm \nu_{beat}. \quad [1]$$

The integers n_1, n_2, and m correspond to their respective harmonics generated in the MIM diode. The (+) or (−) signs and the values of n_1, n_2, and m are determined experimentally by tuning the FIR laser frequency and the microwave frequency and observing the beat note shift on the spectrum analyzer.

The estimated one-sigma uncertainty of frequency measurements is $\Delta\nu/\nu = 2 \times 10^{-7}$. It is due mainly to the uncertainty in the setting of the FIR laser cavity to the center its gain curve. For minimizing this uncertainty, we tuned the FIR laser across its gain curve and observed the change to the beat note on the spectrum analyzer using a peak hold feature. The value of this frequency is calculated from the average of at least 10 different measurements.

TABLE 2
Frequency Measurements of FIR Laser Lines from CH_3OH

CO_2 laser		FIR laser line					
Line	Wavenumber (cm^{-1})	Offset (MHz)	Frequency (MHz)	λ (μm)	Wavenumber (cm^{-1})	Rel. Pol.	obs.
10R (36)	985.4883	21[a]	6 847 473.2	43.781	228.40712	//	
9P (16)	1050.4413	67	6 775 783.5	44.245	226.01581	⊥	*
9P (10)	1055.6250	68	6 493 911.5	46.165	216.61357	//	*
9SP (21)	1042.7762	7	5 211 045.0	57.530	173.82175	//	
9SP (15)	1048.1410	-39	4 877 208.2	61.468	162.68615	⊥	*
9SP (15)	1048.1410	-39	4 418 342.9	67.852	147.38006	//	*
10SR (23)	975.3114	30	4 205 855.0	71.280	140.29222	//	
9HP (29)	1046.3433	-24	4 205 264.2	71.290	140.27251	//	
10SR (23)	975.3114	30	3 964 647.7	75.616	132.24641	⊥	
9HP (29)	1046.3433	-24	3 873 593.1	77.394	129.20916	⊥	
9SP (21)	1042.7762	7	3 710 218.5	80.801	123.75957	⊥	
9HP (14)	1059.9401	-5	3 526 633.5	85.008	117.63583	⊥	
9HP (14)	1059.9401	-5	2 760 123.5	108.616	92.06781	//	
10SR (25)	976.5497	31	2 538 096.6	118.117	84.66179	//	
9HP (18)	1056.3758	11	1 900 601.4	157.736	63.39724	//	
9HP (18)	1056.3758	11	1 341 904.1	223.409	44.76110	//	
9HP (18)	1056.3758	11	660 777.3	453.697	22.04116	//	

* doublet, see text.
[a] Ref. (*9*).

Table 2 summarizes all frequency measurements of FIR laser lines from CH_3OH performed in this work, ordered by increasing wavelength. Columns 1 and 2 give the CO_2 pump line; column 3 gives offset frequency measurement of the absorption transition as previously defined (±2 MHz); column 4 gives the frequency measurement. Column 5 gives the wavelength calculated from the measured frequency with $c = 299,792,458$ m/s; column 6 gives the wavenumber; column 7 gives the relative polarization; and column 8 gives comments about the measurement.

The frequency measurement for the FIR laser line pumped by 10R(36) from CO_2 laser is of special interest because it was recently used in a laser magnetic resonance (LMR) experiment to study the bending FIR spectra of the FeD_2 molecule (*10*).

V. DOUBLET PEAKS

The FIR laser lines denoted by an asterisk in Table 2 displayed doublet peaks on the beat note signal. This characteristic is usually observed for longitudinally pumped laser lines, the absorption center of which lies outside the tuning range of the pump laser. The frequency and offset were also measured for those lines by using an indirect method which will now be described.

An optically pumped FIR laser can be considered a coupled three-level system with both pump and FIR transitions Doppler-broadened. The active medium in the resonator interacts with the pump beam and excites molecules to a rotational level in an excited vibrational level. If the pump frequency is tuned to an absorption center, it excites the molecules with zero velocity in the pump direction. Then, the laser oscillation will occur at a single frequency ν_0. However, if the pump frequency is detuned from the absorption center line, it excites molecules with a finite velocity in the pump direction. In this case, the laser oscillation will occur at two different frequencies (a doublet peak) given by

$$\nu_\pm = \nu_0 \pm \frac{\nu_0}{\nu_p}|\Delta \nu_p|, \qquad [2]$$

where ν_0 is the rest frequency of the lasing transition, ν_p is the pump frequency, and $\Delta \nu_p = \nu_{abs} - \nu_p$ is the rest frequency of the absorption transition (ν_{abs}) minus the pump frequency (ν_p).

The doublet structure is easily observed by observing two beat notes while frequency measuring FIR laser lines. It is useful in the study of the anisotropic gain of an optically pumped FIR laser (*11*, *12*) and tuning of the FIR laser line (*13*).

TABLE 3
Frequency Measurements of FIR Doublet Laser Lines from CH_3OH

CO_2 Pump (cm^{-1})	FIR laser line λ (μm)	ν_0 (MHz)	$\Delta\nu_p$ $\nu_p-\nu_{CO2}$ (MHz)	$\nu_{abs}-\nu_p$ (MHz)	Absorption transition Offset $\nu_{abs}-\nu_{CO2}$ (MHz)	ν_{abs} Offset - ν_{CO2} (cm^{-1})	ν (cm^{-1})
9SP (15)	67.852	4 418 342.9	-22	-17	-39	1048.1397	1048.1394[a]
1048.1410	61.468	4 877 208.2	-22	-17	-39		
9P (16) 1050.4413	44.245	6 775 783.5	27	41	68	1050.4435	1050.4435[a]
9P (10) 1055.6251	46.165	6 493 911.5	29	39	68	1055.6274	1055.6272[b]

[a] Ref. (*14*).
[b] Ref. (*15*).

In this work, the doublet peak was carefully used for precise determination of the rest frequency of the FIR laser line and the offset frequency. In fact, the rest frequency ν_0 can be determined from Eq. [2], resulting in the average of the two peak frequencies measured. From this value and ν_p, measured by beating the pump CO_2 laser with a reference CO_2 laser, the difference $\Delta\nu_p$ is determined using Eq. [2]. Table 3 summarizes the measurements performed, the rest frequencies of FIR laser lines, the offset frequencies ($\nu_{abs} - \nu_{CO_2}$), and the absorption frequencies (offset + ν_{CO_2}). The last column gives the absorption frequency (ν) from different methods.

The absorption frequency in Ref. (*14*) was obtained from the Fourier Transform (FT) spectra, and in Ref. (*15*), from heterodyne techniques by tuning the absorption transition with an electric field (the Stark effect). There is good agreement between the values obtained in this work and those from different methods.

VI. ASSIGNMENT OF THE NEW FIR LASER LINES

A. The 9HP(29) CO_2 Laser Line

From the two new FIR laser lines shown in Table 1, the absorption frequency measured for the 9HP(29) CO_2 laser line, and data available from Fourier transform (FT) spectrum for CH_3OH, we have been able to propose the assignment of the energy levels of transitions in this laser cycle. In fact, the absorption frequency measured (1046.3425 cm^{-1}) is in agreement with that obtained from FT spectrum (1046.3425 cm^{-1}) (*14*). From the FT spectrum, the absorption transition was assigned as symmetry A from $(20^+, 6)^0$ to $(20^+, 7)^{CO}$ in the usual notation (nK, J), where n is the torsional quantum number, K is the projection of the overall rotation angular momentum J along the near-symmetric a axis and represents the vibrational quantum number labeled by $\nu = 0$ for the ground vibrational state, and by $\nu = co$ for the C–O stretch. The additional superscript (+) or (−) to K for transition of A symmetry are used to label the components of the doublets split by molecular assymmetry.

The relative polarization of the two FIR laser lines, the energies of which will be denoted by L_a and L_b, gives important information to their assignment. It is associated with the changes of the J number in the pump and FIR laser transitions according to the rules (*16*)

$$\Delta J_{\text{pump}} + \Delta J_{\text{FIR}} = \text{even} \rightarrow \text{FIR lines is parallel} \quad [3]$$

$$\Delta J_{\text{pump}} + \Delta J_{\text{FIR}} = \text{odd} \rightarrow \text{FIR line is perpendicular.} \quad [4]$$

From the assignment proposed using the FT spectrum data, the absorption transition had $\Delta J_{\text{pump}} = 1$. Then, according to the rules for relative polarization, the parallel FIR line must have $\Delta J_{\text{FIR}} = 1$, while the perpendicular FIR line must have $\Delta J_{\text{FIR}} = 0$. Furthermore, considering the two new FIR lines as pertaining to a triad of emissions satisfying the energy relation $L_a - L_b \approx L_c$, relative polarization, and selection rules of methanol transitions, the third missing line (L_c) can be predicted to be at 11.0635 cm^{-1}, parallel, $\Delta J = -1$, and $\Delta K = 0$. From the energy predicted, the upper level J quantum number gives approximately 7, in agreement with the value of J obtained from FT spectrum data, using the relation $J_{\text{upper}} \approx L_c/2B$. In this case, 0.7855 cm^{-1} was used for the B value of the C–O

TABLE 4
Assignment of FIR Laser Lines from CH_3OH Pumped by the 9HP(29) Line of the CO_2 Laser

CO_2 Pump (cm^{-1})	IR absorption (cm^{-1})	FIR laser transitions $(n' K', J') \Rightarrow (n'' K'', J'')$	λ (μm)	ν_{obs} (cm^{-1})	ν_{cal}[a] (cm^{-1})	Rel. Pol.
9 HP 29	$R(2\,0^+, 6)^{co}$	$(2\,0^+, 7)^{co} \Rightarrow (1\,1^+, 7)^{co}$	77.394	129.20916	129.2093	⊥
1046.3433	1046.3425	$\Rightarrow (1\,1^-, 6)^{co}$	71.290	140.27251	140.2725	//
		$\Rightarrow [(2\,0^+, 6)^{co}]$	[900.38]	-	[11.1064]	[//]
		$\Rightarrow [(1\,1^-, 8)^{co}]$	[85.91]	-	[116.4011]	[//]

[a] From Ref. (*17*).

stretch level (*14*). Table 4 summarizes the assignment discussed. The data in brackets are predicted.

The assignment proposed was confirmed by using the Ritz program (*17*), which predicted an additional FIR laser line at the same absorption frequency with a calculated wavenumber of 116.4011 cm^{-1}.

B. The 10R(46) CO_2 Laser Line

The 10R(46) pump line was studied recently to assign the FIR laser lines at +48 and +15 MHz (*3*) offsets. In fact, the frequency measurements performed there confirmed the assignment of energy levels for the FIR lines at +48 MHz. The assignment predicted an additional FIR line at 49.18 μm (203.3523 cm^{-1}), with relative perpendicular polarization. In this work, it was identified with a wavelength measured at 49.2 μm (203.25 cm^{-1}) and a perpendicular relative polarization, in agreement with the characteristics predicted. Table 5 summarizes the assignment of energy levels for the FIR lines at +48 MHz pumped by the 10R(46) CO_2 line.

C. The 9HP(18) CO_2 Laser Line

For the 9HP(18) pump, the assignment of transitions was proposed in Ref. (*18*) as tentative, since IR spectroscopic data are not available for the methyl-rocking band of CH_3OH. The new FIR laser line identified in this work (22.0411 cm^{-1}) disagrees with the theoretical value proposed (22.5063 cm^{-1}). Actually, the new FIR laser line will help the future analysis of the methyl-rocking band of CH_3OH.

VII. CONCLUSION

We reported eight new optically pumped FIR laser lines from methanol in the range 48.4–453.7 μm. Most of them were pumped by sequence and hotbands from the highly efficient CO_2 laser. The offset frequency, relative polarization, optimum pressure, and relative intensity were obtained for all new lines. Furthermore, frequency measurements for most of them and several previously reported ones were also performed in the range 0.6–6.8 THz. An assignment of energy levels for new FIR laser lines pumped by the 9HP29 CO_2 line was proposed. The new FIR laser line at 49.2 μm pumped by 10R(46) had been previously predicted. It was also possible to measure the offset frequency and the frequency of the FIR lines of absorption transitions outside the tuning range of the CO_2 pump laser. The good agreement of the absorption frequency

TABLE 5
Assignment of FIR Laser Lines from CH_3OH Pumped by 10R(46) CO_2 Line at +48 MHz (3)

CO_2 Pump (cm^{-1})	IR absorption (cm^{-1})	FIR laser transitions $(n' K', J') \Rightarrow (n'' K'', J'')$	λ (μm)	ν_{obs} (cm^{-1})	ν_{calc}[b] (cm^{-1})	Rel. Pol.
10R(46)	$P(123, 24)^{co}$	$(123, 23)^{co} \Rightarrow (032, 23)^{co}$	49.2	203.25[a]	203.3523	⊥
990.61963	990.62123	$\Rightarrow (032, 22)^{co}$	41.630	240.21218	240.2123	//
		$\Rightarrow (014, 24)^{co}$	80.747	123.84435	123.8450	//
		$\Rightarrow (014, 23)^{co}$	61.819	161.76189	161.7618	//
		$\Rightarrow (014, 22)^{co}$	50.389	198.45711	198.4575	[//][c]

[a] Predicted in Ref. (*3*) and identified in this work.
[b] From Ref. (*3*).
[c] It was not observed in this work.

obtained in this work and those from direct FT data confirms our use of Eq. [1].

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