Appl. Phys. B 73, 257–260 (2001)
DOI: 10.1007/s003400100643

Applied Physics B
Lasers and Optics

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Laser frequency measurements and spectroscopic assignments of optically pumped $^{13}CH_3OH$

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Received: 31 May 2001 – © U.S. Government 2001/
Published online: 19 September 2001 • Springer-Verlag 2001

ABSTRACT A three-laser heterodyne system was used to measure the frequencies of twelve optically pumped laser emissions from $^{13}CH_3OH$ in the far-infrared (FIR) region. These emissions, ranging from 54 to 142 μm, are reported with fractional uncertainties up to $\pm 2 \times 10^{-7}$ along with their polarization relative to the CO_2 pump. Using the $9P32$ and $10R14$ CO_2 lines, complete spectroscopic assignments for two laser systems were confirmed.

PACS 42.60.By; 42.60.Da; 42.62.Fi

1 Introduction

Methanol and its isotopes are the most important lasing molecules in the far-infrared (FIR) region, producing over 2200 lines when optically pumped by CO_2 lasers [1–3]. Since FIR laser emissions were first reported from the ^{13}C methanol isotope by Henningsen and Petersen in 1978 [4], over 175 laser lines have been discovered in the wavelength range from 34.7 to 784.4 μm [5–10]. This actually represents a relatively low number of laser lines with respect to several other symmetric methanol isotopes. The primary reason for this is the lack of a convenient pump, since the crowded Q-branch of the $^{13}C-O$ stretch falls in the region from 1014 to 1018.5 cm^{-1}, where regular CO_2 laser lines are not present [11].

In this paper, we report the frequencies for twelve FIR laser lines of $^{13}CH_3OH$ optically pumped by eight different CO_2 lines. Frequencies were measured with the three-laser heterodyne technique, whereby the FIR laser emission was mixed with radiation from two stabilized CO_2 lasers and a microwave synthesizer [12]. Analysis of the Fourier transform (FT) $^{13}CH_3OH$ spectra [13, 14] and the systematic investigation of all possible closed transitions loops has confirmed the spectroscopic identification of two FIR laser systems [10, 15].

2 Experimental details

The experimental setup for the optically pumped molecular laser (OPML) system consists of two laser cavities. The CO_2 pump laser is 1.5 m long and includes a partially ribbed cavity surrounded by a water-cooled jacket and five equally spaced glass ribs. The laser uses the zeroth-order output coupling from a 133 line/mm grating with 3% output coupling in zero order. The radiation from the CO_2 laser is focused into the FIR cavity with a gold-coated concave mirror, having a 12 m radius of curvature, externally mounted on the far (fixed mirror) end of the cavity at approximately 2 m from the ZnSe window. A flat gold-coated mirror then reflects the CO_2 beam into the 2 m FIR cavity and to the X–V mirror system illustrated in Fig. 1 [16]. This X–V mirror geometry uses three copper mirrors, a gold-coated copper mirror with a 1 m radius of curvature, and one of the FIR cavity mirrors. The advantage to this system is that many of the longer-wavelength lines are suppressed, thereby allowing some of the shorter wavelengths to emerge [16].

The FIR laser radiation was coupled out of the cavity by a 45° mirror and detected by a metal–insulator–metal (MIM) point-contact diode. Preliminary measurements of the FIR laser wavelengths were made by tuning the Fabry–Perot cavity with the moveable end mirror and measuring the mirror displacement through 10 wavelengths of that laser mode. The value thus obtained is accurate to within ±0.5 μm. A set of absorbing filters calibrated with wavelength attenuates the CO_2 laser radiation and helps distinguish different FIR wavelengths. The relative polarizations of the laser lines were measured with a multi-Brewster-angle polarization selector.

The frequencies of optically pumped FIR laser lines were accurately measured by mixing the unknown FIR frequency with two CO_2 laser frequencies in a MIM diode. The frequency standards were synthesized from the difference between two CO_2 laser frequencies stabilized by locking each directly to a Lamb dip in the 4.3 μm CO_2 fluorescence signal from an external reference cell [12]. A microwave signal ($\nu_{\mu wave}$) from a synthesized signal generator (from 2 to 18 GHz) can also be mixed on the MIM diode if the CO_2 difference is outside the band of the spectrum analyzer (1.8 GHz). The resulting FIR laser frequency is given by

$$\nu_{FIR} = | n_1 \nu_{CO_2}(\mathrm{I}) - n_2 \nu_{CO_2}(\mathrm{II}) | \pm m \nu_{\mu wave} \pm \nu_{beat}, \qquad (1)$$

where n_1, n_2 and m are integers that correspond to the respective harmonics generated in the MIM diode, and ν_{beat} is the beat frequency. The ± sign used in the equation is determined

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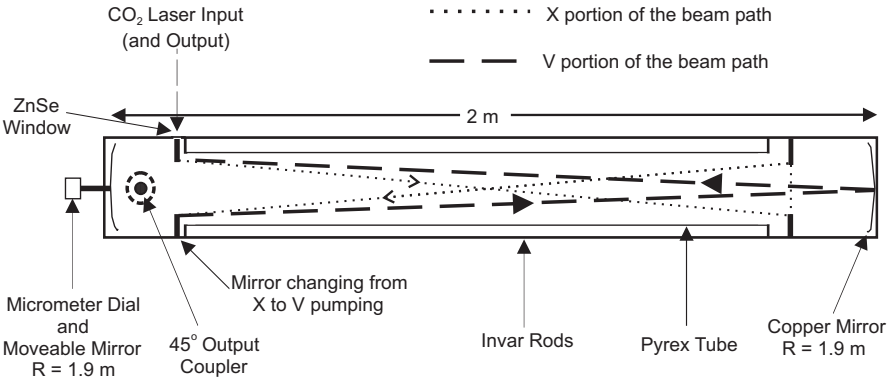

FIGURE 1 Side view of the X–V mirror geometry used in the optically pumped molecular laser system

experimentally by slightly tuning the FIR laser or microwave signal and observing the change in the beat note. For an accurate measurement of ν_{beat}, the FIR laser is tuned over its gain curve and the signal profile is stored on the spectrum analyzer; then the center of the profile is located using a frequency marker derived from an accurate rf signal generator. In an effort to improve the accuracy of ν_{beat}, ten independent measurements were taken, with at least two different sets of CO_2 pump lines. The relative reproducibility of the FIR laser frequency measurements is $\Delta\nu/\nu = 2 \times 10^{-7}$.

3 Results

The measured FIR laser frequencies from optically pumped $^{13}CH_3OH$ are listed in Table 1, arranged in order of the CO_2 pump line. Ten of the lines have been previously observed with measured wavelengths, but no frequencies were measured. The 75 μm line pumped by $9P16$ was the only new line observed. The wavelength, frequency and wavenumber are listed for each emission along with their respective reference. Except for the 97.7 μm line ($10R38$ pump), the polarization of each FIR emission was observed to be parallel with respect to the CO_2 pump.

In addition to the new measurements, we also reinvestigated the 123.2 μm line using the $10P16$ CO_2 pump. The frequency of this line had been measured as 2 433 639.5 ± 1.9 MHz and 2 433 640.2 ± 1.8 MHz [7]. The large uncertainty in this measurement was due principally to its low power [4]. With the new X–V pumping geometry, we observed this emission as a medium strength (M) line, approximately one hundred times stronger than prior observations. As a result, the frequency of this emission has been remeasured as 2 433 638.6 ± 0.3 MHz.

Pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Reference
$9P16$	54.087	5 542 754.1 ± 0.4	184.8864	[7]
$9P16$	75.002	3 997 130.4 ± 0.2	133.3299	New[a]
$9P32$	71.233	4 208 625.8 ± 0.2	140.3846	[17][b]
$9P32$	95.459	3 140 541.4 ± 0.2	104.7572	[17][b]
$9P32$	142.280	2 107 052.9 ± 0.2	70.2837	[15]
$9P44$	124.235	2 413 101.5 ± 0.3	80.4924	[10]
$9P46$	120.144	2 495 277.3 ± 0.3	83.2335	[10]
$10R40$	106.679	2 810 226.5 ± 0.3	93.7391	[7]
$10R38$	97.682	3 069 068.0 ± 0.3	102.3731	[10][c]
$10R14$	64.589	4 641 523.8 ± 0.2	154.8246	[15]
$10R14$	86.171	3 479 033.7 ± 0.2	116.0481	[10]
$10P16$	123.187	2 433 638.6 ± 0.3	81.1774	[4][d]

[a] Observed at 385 mTorr in the parallel polarization
[b] Previously observed only in waveguide mode
[c] Only line observed in the perpendicular polarization
[d] Previously measured with a ±1.8 MHz uncertainty [7]

TABLE 1 Frequency measurements for optically pumped $^{13}CH_3OH$

Recently, the assignments for eight laser systems were proposed by Moraes and co-workers [15]. Two of these systems can be considered as definitive because they include at least one frequency-measured FIR laser line. With the new FIR laser spectroscopic data presented in Table 1, it was possible to confirm the assignment for two other laser systems. The first involves the FIR laser transitions $(2, 1^+; 11)^{\text{co}} \rightarrow (2, 0; 12)^{\text{co}}A$ and $(2, 1^+; 11)^{\text{co}} \rightarrow (2, 0; 10)^{\text{co}}A$ pumped by the $9P32$ CO_2 line. This CO_2 line was found to be in agreement with the IR absorption transition $(2, 1^+; 10)^0 \rightarrow (2, 1^+; 11)^{\text{co}}A$. The customary $(n, K; J)^{\nu}\sigma$ energy-level notation [15, 18, 19], in which n is the quantum number associated with the torsional state, J is the total angular momentum and K is its projection along the internal rotation axis, is used here. The quantum number ν labels the vibrational state as $\nu = 0$ for the ground state and $\nu = \text{co}$ for the excited CO-stretch state. The label σ stands for the symmetry species, A or E, common to the upper and lower level of the transition. Figure 2 shows the energy level and transition diagram for the $9P32$ system. The dashed lines represent the IR (upper-case letter) and FIR (lower-case letter) absorption transitions observed in the Fourier transform spectrum and assigned by the Ritz program [14]. The bold dashed transition (**P**) is in good coincidence with the $9P32$ CO_2 laser. The observed 95.459 and 71.233 μm laser lines, listed in Table 1, are denoted as L_b and L_c, respectively. L_a (17.0087 cm^{-1}) is one further transition that may potentially yield FIR laser emissions. The wavenumbers of the L_b and L_c laser transitions can be determined, for instance, as follows:

$$L_b = d + E - B = 104.7565\,\text{cm}^{-1}$$

and

$$L_c = a + \mathbf{P} - F = 140.3843\,\text{cm}^{-1}.$$

Independent combination loops automatically formed by the Ritz program led to the average values of 104.7572 and 140.3846 cm^{-1}, which are in agreement with the frequencies measured. Furthermore, the new polarization measurement

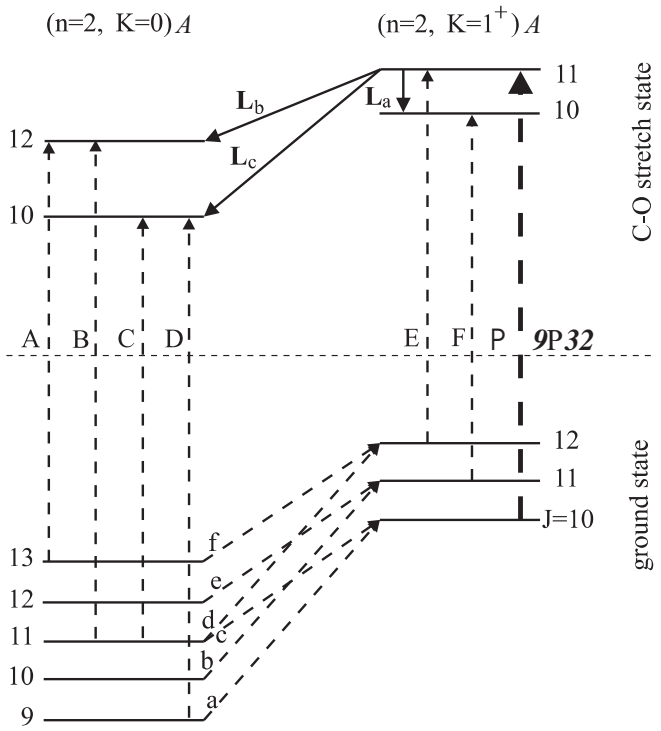

FIGURE 2 Laser system pumped by the CO_2 pump line $9P32$. The experimental FIR laser wavenumbers are $L_b = 104.7572\,cm^{-1}$ and $L_c = 140.3846\,cm^{-1}$. The IR (upper-case letter) and FIR (lower-case letter) FT absorption transition wavenumbers (in cm^{-1}) are: $A = 995.4067$,$B = 1034.6032$, $C = 998.9750$, $D = 1031.9054$, $E = 999.4779$, $F = 1001.2474$, $\mathbf{P} = 1035.4706$, $a = 136.8191$, $b = 138.3522$, $c = 103.8887$, $d = 139.8818$, $e = 102.2885$ and $f = 100.6860$

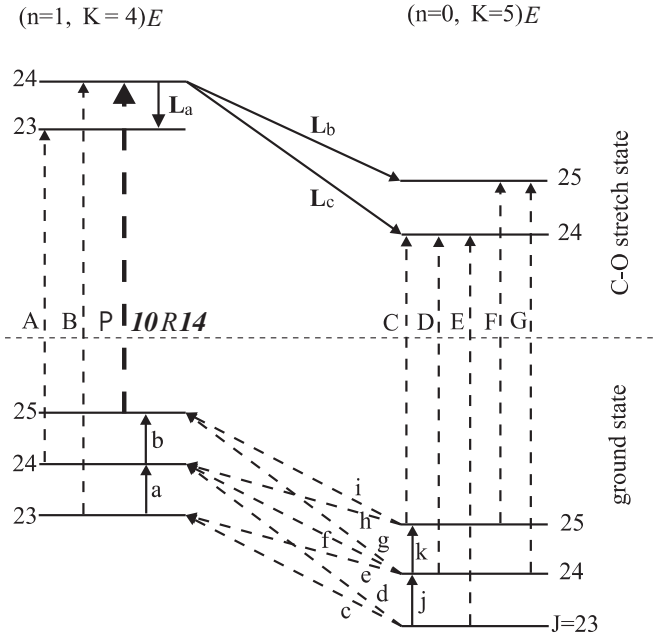

FIGURE 3 Laser system pumped by the CO_2 pump line $10R14$. The experimental FIR laser wavenumbers are $L_a = 37.05\,cm^{-1}$, $L_b = 116.0481\,cm^{-1}$ and $L_c = 154.8246\,cm^{-1}$. The IR (upper-case letter) and FIR (lower-case letter) FT absorption transition wavenumbers (in cm^{-1}) are: $A = 973.9444$, $B = 1048.6439$, $C = 973.5891$, $D = 1012.8362$, $E = 1050.5231$, $F = 1012.3657$, $G = 1051.6132$, $\mathbf{P} = 971.9312$, $a = 37.5780$, $b = 39.1350$, $c = 156.7040$, $d = 194.2821$, $e = 119.0176$, $f = 156.5958$, $g = 195.7302$, $h = 117.3480$, $i = 156.4825$, $j = 37.6860$ and $k = 39.2477$

for the $104.7572\,cm^{-1}$ emission confirms its initial observation [15], reinforcing the previously proposed assignment.

The second assigned system, proposed by Moraes and co-workers [15], involves the $10R14$ CO_2 line and is shown in Fig. 3. In this system, the pump transition is between the $(1, 4; 25)^0$ and $(1, 4; 24)^{co}$ energy levels, both belonging to E symmetry. The proposed assignment for the known $269.9\,\mu m$ ($37.05\,cm^{-1}$) FIR laser line led to the prediction of the $86.5\,\mu m$ ($115.87\,cm^{-1}$) line. The recent observation of this laser emission [10] has led to its frequency measurement. The wavenumbers calculated by the Ritz program for these three FIR lines pumped by $10R14$ CO_2 line were 37.1214 (L_a in Fig. 3), 116.0482 (L_b) and $154.8247\,cm^{-1}$ (L_c). The frequency measurements presented here for the L_b and L_c lines are in exact agreement with the values derived, confirming the assignment for this laser system.

4 Discussion and conclusions

We report twelve frequency measurements of optically pumped $^{13}CH_3OH$, eleven of which are new, with one belonging to a new short-wavelength emission. For each line, the wavelength, frequency, wavenumber and polarization relative to the pump laser are given. Since several of these lines have wavelengths below $100\,\mu m$, they will be useful for filling the gaps currently existing in this portion of the FIR region. The available data has been compared to a Ritz analysis of the high-resolution Fourier-transform absorption spectrum of $^{13}CH_3OH$, resulting in the confirmation of two previously reported laser systems. With at least one frequency-measured FIR laser line, the assignments of these laser systems are now considered to be definitive.

ACKNOWLEDGEMENTS The authors are pleased to acknowledge the following programs for financial support: the National Science Foundation (CRIF – #9982001 and RUI – #0078812), the Wisconsin Space Grant Consortium (Faculty Research Seed Grant and Undergraduate Research Award), Sigma Xi (Grants-in-Aid of Research), the College of Science and Allied Health (Faculty Research Grant and Undergraduate Research Grant), the University of Wisconsin–La Crosse (Undergraduate Research Grant), and CNPq, São Paulo, Brasil.

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