New Short-Wavelength Laser Emissions From Optically Pumped $^{13}CD_3OD$

M. Jackson, H. Hockel, M. Lauters, E. C. C. Vasconcellos, M. D. Allen, and K. M. Evenson

***Abstract*—We report the discovery of 15 new laser emissions from $^{13}CD_3OD$ when optically pumped with a CW CO_2 laser. The wavelengths of these lines, ranging from 57.5 to 135.2 μm, are reported along with their polarization relative to the CO_2 pump laser, operating pressure and relative intensity. A three-laser heterodyne system was then used to measure the frequencies of 12 optically pumped laser emissions from this methanol isotope. These emissions range from 65.7 to 151.8 μm and are reported with fractional uncertainties up to $\pm 2 \cdot 10^{-7}$.**

***Index Terms*—$^{13}CD_3OD$, CO_2 laser, frequency measurements, optically pumped molecular laser (OPML).**

I. INTRODUCTION

THE first recognition of $^{13}CD_3OD$ as a source of far-infrared (FIR) laser emissions was by Vasconcellos and Evenson in 1985 [1]. Since then, over 100 laser lines from $^{13}CD_3OD$ in the range from 46.4 to 1194.0 μm have been discovered [2]–[7]. These lines provided the motivation for the theoretical treatment of this molecule, as well as the assignment of IR and FIR transitions [8]–[13]. This, combined with a newly designed short wavelength ($\lambda < 150$ μm) optically pumped molecular laser (OPML) system [14], has stimulated a reinvestigation of this methanol isotope as a source of optically pumped laser emissions.

II. EXPERIMENTAL DETAILS

The optically pumped molecular laser system consists of a carbon dioxide (CO_2) pump laser and a FIR laser cavity, as shown in Fig. 1. The CO_2 laser is 1.5-m long and includes a partially ribbed cavity surrounded by a water-cooled jacket. The Pyrex glass tube has an inner diameter of 18 mm and contains five equally spaced glass ribs whose inner diameters increase from 16.5 to 17.5 mm. The laser uses the zeroth-order output coupling from a 133-line/millimeter grating with 3% output coupling in zeroth order. Both the 9- and 10-μm branches exhibit lines out to $9R58$, $9P60$, $10R58$, and $10P60$, with powers up to 30 W [15]–[17].

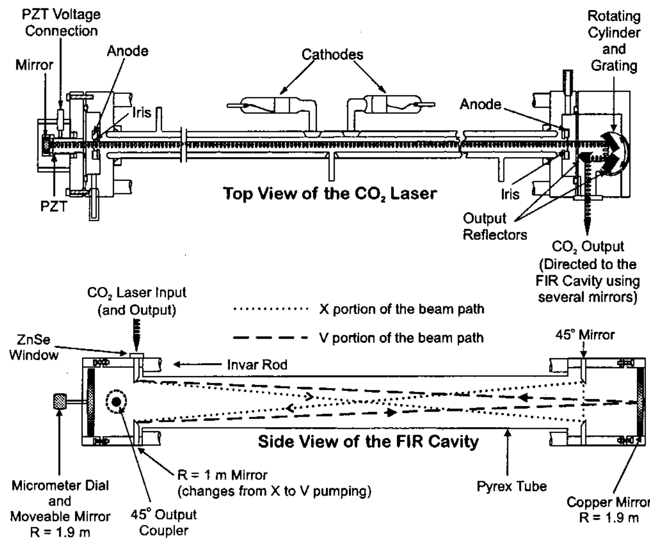

Fig. 1. Optically pumped molecular laser system.

The CO_2 laser radiation is focused into a 2-m long, nearly confocal FIR cavity having an X-V pumping geometry [14]. This geometry, illustrated in Fig. 1, uses three copper mirrors, 19 mm in diameter, a gold-coated copper mirror with a radius of curvature of 1 m, and one of the FIR cavity mirrors. Once entering the FIR cavity, the CO_2 radiation is first reflected across the vertical plane of the cavity by a 45° mirror. At the other end, two identical 45° mirrors redirect the CO_2 beam to the bottom of the input chamber. The gold-plated copper mirror then reflects the CO_2 beam to the main FIR cavity mirror. The CO_2 beam is reflected from the FIR mirror, to the input 45° mirror, and out of the FIR system. On the other hand, the FIR laser radiation is coupled horizontally out of the cavity, through a polypropylene window by means of a 45° copper mirror and focused by an off-axis parabolic mirror onto a metal–insulator–metal (MIM) point-contact diode.

Preliminary wavelength measurements of the FIR radiation were made by tuning the Fabry–Perot cavity with the moveable end mirror and measuring the mirror displacement for ten wavelengths of that laser mode. The value obtained has an uncertainty of ±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 FIR emissions with respect to the CO_2 laser lines were measured with a multi-Brewster-angle polarization selector.

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M. Jackson, H. Hockel, and M. Lauters are with the Department of Physics, University of Wisconsin–La Crosse, La Crosse, WI 54601 USA.

E. C. C. Vasconcellos is with the Instituto de Física "Gleb Wataghin," Departamento de Eletrônica Quântica, Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas, São Paulo, Brazil.

M. D. Allen and K. M. Evenson are with the Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303 USA.

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The frequencies of optically pumped FIR laser lines were accurately measured using the three-laser heterodyne technique discussed in detail in [18] and [19]. Here, two CO_2 laser frequencies were combined to create a difference frequency in the FIR region. The particular lines chosen to generate the difference frequency were based on the wavelength measurement of the unknown FIR emission. These CO_2 frequencies were stabilized by locking each laser to a saturation dip in the 4.3-μm fluorescence signal from an external reference cell. The beat note, monitored by means of a spectrum analyzer, was used to determine the unknown frequency $\nu_{\rm FIR}$ through the relation

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

where

n_1, n_2, m integers that correspond to the respective harmonics (first-order, second-order, etc.) generated in the MIM diode;

$\nu_{\mu\rm wave}$ microwave frequency;

$\nu_{\rm beat}$ beat frequency.

A MIM point-contact diode was used as a harmonic mixer, combining the signals from the laser and microwave sources. The signal from the MIM diode was fed into a preamplifier connected to a spectrum analyzer to measure the intermediate-frequency beat note as compared with a synthesizer-generated marker. When necessary, a microwave source operating between 2 and 18 GHz was used. The values of $n_1, n_2, m,$ and the $\pm$ sign in (1) were determined experimentally by either tuning the FIR laser cavity or by increasing (or decreasing) the microwave frequency slightly in order to get a small shift in the beat note on the spectrum analyzer.

The uncertainty of a frequency measurement is at least $\Delta\nu/\nu = \pm 2 \cdot 10^{-7}$. It is due mainly to the uncertainty in the setting of the FIR laser cavity to the center of its gain curve. To minimize this uncertainty, we tuned the FIR laser across its gain curve and observed the change to the beat note on the spectrum analyzer. The value of this frequency was calculated from the average of ten measurements recorded with varying microwave frequencies. In addition, these measurements were made with at least two different sets of CO_2 laser lines.

The sample of $^{13}CD_3OD$, 99% ^{13}C, and 99% D enriched, was obtained from Cambridge Isotope Laboratories. Due to the fast exchange of deuterium and hydrogen in the hydroxyl group [2], contamination of the sample with $^{13}CD_3OH$ was possible. To limit this effect, the $^{13}CD_3OD$ sample was pumped through the FIR cavity for several minutes before the search for new OPML emissions began. In addition, several Strong (S) and Very Strong (VS) lines belonging to $^{13}CD_3OH$ were searched for as a check, but none were observed. Even so, some doubts may remain regarding the origin of these lines until they are spectroscopically assigned.

III. Results

Table I lists the wavelengths of the FIR laser emissions discovered in this investigation. The polarization relative to the pump laser, operating pressure and relative intensity are listed. The intensity of the FIR output is given as a listing ranging from Very Very Strong (VVS) to Very Weak (VW). In this work, a VVS line is expected to provide a power greater than 10 mW when all the parameters (pump laser, FIR resonator, coupling mirror, pressure, etc.) have been optimized. The FIR cavity was optimized to the best of our ability, but in no way should it be taken as an absolute measure since the relative intensities of FIR emissions are subject to the experimental apparatus used [20]. The lines labeled with VS, S, M, W, and VW range in power between 10–1 mW, 1–0.1 mW, 0.1–0.01 mW, 0.01–0.001 mW, and below 1 μW, respectively.

TABLE I
New Laser Emissions From Optically Pumped $^{13}CD_3OD$

Pump	Wavelength (μm)	Rel. Pol.	Pressure (mTorr)	Rel. Int.
9R30	68.837[a]	$\parallel$	170	M
	103.050[a]	$\perp$	130	M
9R20	111.653[a]	$\perp$	160	M
	135.243[a]	$\parallel$	160	M
9R8	122.233[a]	$\parallel$	115	M
9P32	100.430[a]	$\parallel$	140	M
9P44	114.6[b]	$\perp$	90	W
10R40	91.3[b]	$\perp$	140	M
	103.0[b]	$\parallel$	170	M
10R30	76.4[b]	$\perp$	250	M
10R24	81.8[b]	$\parallel$	250	M
10R20	65.716[a]	$\perp$	150	M
10R18	109.0[b]	$\perp$	160	W
10R16	57.5[b]	$\parallel$	160	M
	105.492[a]	$\perp$	165	M

[a] Wavelength derived from Table II.
[b] Wavelength uncertainty is $\pm$ 0.5 μm.

TABLE II
New Frequency Measured Laser Emissions From Optically Pumped $^{13}CD_3OD$

Pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Ref.
9R30	68.837	4 355 080.6[(a)]	145.2699	new
	103.050	2 909 204.6[(a)]	97.0406	new
9R20	111.653	2 685 044.8[(a)]	89.5635	new
	135.243	2 216 701.0[(a)]	73.9412	new
9R8	122.233	2 452 635.3[(b)]	81.8111	new
9P14	109.996	2 725 481.6[(c)]	90.9123	[7]
9P24	150.896	1 986 747.5[(a)]	66.2708	[1]
9P28	151.832	1 974 500.7[(a)]	65.8623	[1]
9P32	100.430	2 985 091.5[(a)]	99.5719	new
10R20	65.716	4 561 935.4[(a)]	152.1698	new
	70.467	4 254 362.4[(b)]	141.9103	[23]
10R16	105.492	2 841 850.2[(a)]	94.7939	new

[(a)] $\Delta\nu/\nu = \pm\, 2 \cdot 10^{-7}$.
[(b)] $\Delta\nu/\nu = \pm\, 4 \cdot 10^{-7}$.
[(c)] $\Delta\nu/\nu = \pm\, 6 \cdot 10^{-7}$.

Table II gives the frequency measurements of the OPML emissions. All frequency measurements are new and are arranged in order by their CO_2 pump lines. The wavelengths and wavenumbers were calculated from the average frequency using 1 cm^{-1} = 29 979.2458 MHz. The FIR frequencies were measured for the first time in this work under optimal operating conditions. A slight shift in frequency (possibly a few megahertz) may still occur due to the type of FIR cavity and pumping geometry used [20]–[22].

IV. Conclusion

We report the discovery of 15 new laser emissions from optically pumped $^{13}CD_3OD$. In addition, the frequencies of 12 OPML emissions have been measured for the first time. The new

OPML emissions will be useful for filling the gaps currently existing in the short-wavelength portion of the FIR region. Due to the accuracy with which the laser frequencies were measured, this work will be useful for future assignments of FIR laser emissions by calculation of combination loops from high-resolution Fourier transform data [24]–[26]. Finally, the information gained from these frequencies will help provide a more complete picture of this particular methanol isotope in the FIR region.

REFERENCES

[1] E. C. C. Vasconcellos and K. M. Evenson, "New far-infrared lines obtained by optically pumping $^{13}CD_3OD$," *Int. J. Infrared and Millimeter Waves*, vol. 6, pp. 1157–1167, 1985.

[2] E. M. Telles, J. C. S. Moraes, A. Scalabrin, D. Pereira, G. Carelli, N. Ioli, A. Moretti, and F. Strumia, "Optically pumped $^{13}CD_3OH$: Far infrared laser lines and assignment," *IEEE J. Quantum Electron.*, vol. 30, pp. 2946–2949, 1994.

[3] E. M. Telles, A. Scalabrin, and D. Pereira, "Frequency measurements of optically pumped far-infrared laser lines," *IEEE J. Quantum Electron.*, vol. 31, pp. 754–757, 1995.

[4] R. C. Viscovini, E. M. Telles, A. Scalabrin, and D. Pereira, "Large offset far-infrared laser lines generation from the C-O stretching Q-branch of $^{13}CD_3OD$," *Appl. Phys. B*, vol. 65, pp. 33–35, 1997.

[5] R. C. Viscovini, A. Scalabrin, and D. Pereira, "$^{13}CD_3OD$ optically pumped by a waveguide CO_2 laser: New FIR laser lines," *IEEE J. Quantum Electron.*, vol. 33, pp. 916–918, 1997.

[6] E. C. C. Vasconcellos, S. C. Zerbetto, L. R. Zink, and K. M. Evenson, "Laser lines and frequency measurements of fully deuterated isotopomers of methanol," *Int. J. Infrared and Millimeter Waves*, vol. 19, pp. 465–473, 1998.

[7] R. C. Viscovini, E. M. Telles, A. Scalabrin, and D. Pereira, "Characterization of new FIR laser lines from CD_3-rocking and asymmetric CD_3 deformation modes of $^{13}CD_3OD$," *IEEE J. Quantum Electron.*, vol. 35, pp. 1613–1615, 1999.

[8] F. C. Cruz, A. Scalabrin, D. Pereira, P. A. M. Vazquez, Y. Hase, and F. Strumia, "The infrared absorption spectra and normal coordinate analysis of $^{13}CH_3OH$, $^{13}CD_3OH$, and $^{13}CD_3OD$," *J. Mol. Spectrosc.*, vol. 156, pp. 22–38, 1992.

[9] M. Jackson, G. R. Sudhakaran, and E. Gansen, "Far-infrared laser stark spectroscopy of $^{13}CD_3OD$," *J. Mol. Spectrosc.*, vol. 176, pp. 439–441, 1996.

[10] R. C. Viscovini, A. Scalabrin, and D. Pereira, "Infrared optoacoustic spectroscopy of $^{13}CD_3OD$ around the $10R$ and $10P$ CO_2 laser lines," *Int. J. Infrared and Millimeter Waves*, vol. 17, pp. 1821–1838, 1996.

[11] I. Mukhopadhyay, "Molecular parameters of $^{13}CD_3OD$," *Spectroc. Acta A*, vol. 53, pp. 979–980, 1997.

[12] R. C. Viscovini, F. C. Cruz, J. C. S. Moraes, A. Scalabrin, and D. Pereira, "Vibrational and rotational spectroscopy of $^{13}CD_3OD$," *Int. J. Infrared and Millimeter Waves*, vol. 20, pp. 193–201, 1999.

[13] R. C. Viscovini, A. Scalabrin, and D. Pereira, "Infrared optoacoustic spectroscopy of $^{13}CD_3OD$ around $9P$ laser lines," *Int. J. Infrared and Millimeter Waves*, vol. 21, pp. 621–632, 2000.

[14] M. Jackson, E. M. Telles, M. D. Allen, and K. M. Evenson, "Short-wavelength far-infrared laser cavity yielding new laser emissions in CD_3OH," *Appl. Phys. B*, vol. 72, pp. 815–819, 2001.

[15] K. M. Evenson, C.-C. Chou, B. W. Bach, and K. G. Bach, "New CW CO_2 laser lines: The 9-μm hot band," *IEEE J. Quantum Electron.*, vol. 30, pp. 1187–1188, 1994.

[16] C.-C. Chou, K. M. Evenson, L. R. Zink, A. G. Maki, and J.-T. Shy, "New CO_2 laser lines in the 11-μm wavelength region: New hot bands," *IEEE J. Quantum Electron.*, vol. 31, pp. 343–345, 1995.

[17] E. M. Telles, H. Odashima, L. R. Zink, and K. M. Evenson, "Optically pumped FIR laser lines from CH_3OH: New laser lines, frequency measurements, and assignments," *J. Mol. Spectrosc.*, vol. 195, pp. 360–366, 1999.

[18] F. R. Petersen, K. M. Evenson, D. A. Jennings, J. S. Wells, K. Goto, and J. J. Jiminez, "Far infrared frequency synthesis with stabilized CO_2 lasers: Accurate measurements of the water vapor and methyl alcohol laser frequencies," *IEEE J. Quantum Electron.*, vol. 11, pp. 838–843, 1975.

[19] L.-H. Xu, R. M. Lees, E. C. C. Vasconcellos, S. C. Zerbetto, L. R. Zink, and K. M. Evenson, "Methanol and the optically pumped far-infrared laser," *IEEE J. Quantum Electron.*, vol. 32, pp. 392–399, 1996.

[20] D. T. Hodges, "A review of advances in optically pumped far-infrared lasers," *Infrared Phys.*, vol. 18, pp. 375–384, 1978.

[21] M. Inguscio, L. R. Zink, K. M. Evenson, and D. A. Jennings, "Accurate frequency of the 119 μm methanol laser from tunable far-infrared absorption spectroscopy," *IEEE J. Quantum Electron.*, vol. 26, pp. 575–579, 1990.

[22] E. M. Telles, L. R. Zink, and K. M. Evenson, "Frequencies of optically pumped sub-doppler far-infrared laser lines of methanol," *J. Mol. Spectrosc.*, vol. 191, pp. 206–208, 1998.

[23] K. M. Evenson, private communication.

[24] J. O. Henningsen, "Assignment of laser lines in optically pumped CH_3OH," *IEEE J. Quantum Electron.*, vol. QE-13, pp. 435–441, 1977.

[25] J. O. Henningsen, "Molecular spectroscopy by far-infrared laser emission," in *Infrared and Millimeter Waves—Coherent Sources and Applications, Part I*, K. J. Button, Ed., 1982, vol. 5, ch. 2, pp. 29–128.

[26] R. M. Lees, "Far-infrared laser spectroscopy of methanol: A probe for vibrational mode coupling," in *Proc. SPIE, Millimeter and Submillimeter Waves II*, vol. 2558, M. N. Afsar, Ed., 1995, pp. 262–284.

M. Jackson received the B.S. degree in physics from the State University of New York (SUNY) at Oswego in 1992 and the Ph.D. degree in physics from New Mexico State University at Las Cruces in 1998.

Since 1999, he has been an Assistant Professor in the Department of Physics, University of Wisconsin at La Crosse. His research interests include infrared and far-infrared lasers and their application to molecular spectroscopy.

H. Hockel received the B.S. degree in physics from the University of Wisconsin–La Crosse in 2001. She is currently working toward the Ph.D. degree at the School of Optics/CREOL, University of Central Florida at Orlando.

M. Lauters received the B.S. degree in physics from the University of Wisconsin–La Crosse in 2001. He is currently working toward the Ph.D. degree at the Optical Sciences Center, University of Arizona at Tucson.

E. C. C. Vasconcellos received the B.S. degree from the University of São Paulo, São Paulo, Brazil, in 1965, the M.S. degree from and the University of Brasília in 1969, and the Ph.D. degree from the Universidade Estadual de Campinas (UNICAMP), São Paulo, Brazil, in 1978, all in physics.

She joined the Universidade Estadual de Campinas (UNICAMP), São Paulo, Brazil, in 1974, where she currently works in the Institute of Physics. She was Head of the Quantum Electronics Department of the "Gleb Wataghin" Institute of Physics during 1991 and 1992. She spent her sabbatical leaves in 1993 and 1997 with the Laser Spectroscopy Group in the Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO. Her research interests include lasers in the infrared and far-infrared regions, with application to molecular and solid-state spectroscopy.

M. D. Allen received the B.S. degree in chemistry from Fort Lewis College, Durango, CO, in 1991 and the Ph.D. degree in chemistry from Arizona State University at Tempe in 1997.

He was a National Research Council Postdoctoral Fellow from 1997 to 1999 and then a Professional Research Experience Plan (PREP) post-doctorate with the Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO during 1999–2000. He is currently a Software Engineer at Xilinx Corporation, Longmont, CO.

K. M. Evenson received the B.S. degree in physics from Montana State University at Bozeman in 1955. He was a Fulbright Scholar at Tübingen University, Germany, in 1955–1956. He received the M.S. and Ph.D. degrees from Oregon State University at Corvallis in 1960 and 1963, respectively.

Since 1963, he has been with the National Institute of Standards and Technology (NIST), Boulder, CO. His research has included the definitive laser measurement of the speed of light, direct (heterodyne) laser frequency measurements, including the first measurement of the frequency of visible light leading to the redefinition of the meter, and the invention of laser magnetic resonance and its application to the spectroscopy of unstable molecules and free radicals.

Dr. Evenson is a NIST Fellow in the Time and Frequency Division and has received the Department of Commerce Silver and Gold Medals, the National Bureau of Standards Stratton and E. U. Condon Awards. He delivered the Spiers Memorial Lecture in 1983 to the Royal Society of London and won the Humboldt Prize in 1986. He is a Fellow of the American Physical Society and was the 1991 winner of the APS Earle K. Plyler Prize for Molecular Spectroscopy.