Assignment of far-infrared laser lines of O-17 methanol by synchrotron FTIR spectroscopy and laser frequency measurements

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ABSTRACT

Analysis of synchrotron FTIR spectra has revealed new assignments for a number of optically pumped far-infrared laser lines from the $CH_3^{17}OH$ isotopologue of methanol, with definitive confirmation provided by recent accurate measurements of the laser frequencies. In this Note the lasing energy level systems are discussed, and the spectroscopic evidence for the assignments is presented.

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The isotopologues of methanol are among the most extensive sources of far-infrared laser (FIRL) lines optically pumped by CO_2 lasers [1–4]. In addition to their practical applications as sources of intense THz radiation, the FIRL lines have served as a valuable window into the spectroscopy of the excited vibrational states, giving direct information on transitions among the levels of the complicated excited energy manifolds. Thus, assignment of the energy level systems producing the FIRL lines has been a very profitable guide to the excited state energy structures and an interesting spectroscopic challenge. The first observation of FIR laser lines from the O-17 isotopologue of methanol was reported not long ago [5], and accurate frequencies for all observed laser lines have very recently been measured [6]. With the high-resolution infrared and FIR spectra recorded previously on the Far-infrared beamline at the Canadian Light Source synchrotron in Saskatoon [7,8], we have been able to deduce assignments for a number of the lasing systems from our experimental energy term values for levels of the excited CO-stretching vibrational state. The excellent agreement between the measured frequencies and our spectroscopic calculated wavenumbers definitively confirms the transition identifications.

As with other methanol isotopologues, the CO-stretching absorption band of $CH_3^{17}OH$ overlaps well with the CO_2 laser bands. A close coincidence between a CO_2 line and a methanol absorption then allows optical pumping up to a particular excited level in the CO-stretching state and subsequent far-infrared lasing on allowed transitions down to other lower levels. Thus, the FIRL observations serve as a "periscope" to look up into various locations within the CO-stretching manifold and give very specific information on its energy structure. For example, Fig. 1 shows the details of the energy level system pumped by the 9P14 CO_2 laser line at a frequency offset of 21 MHz, in which three FIRL lines were observed [5] with wavenumbers forming a triad pattern with $L_c \approx L_b - L_a$. In order to take advantage of the insights provided by these FIRL observations, careful spectroscopic analysis is then also needed to identify the transitions involved and attach the relevant quantum numbers to the levels as shown in Fig. 1.

Initial discovery and characterization of an FIRL line usually involve scanning of the moveable end mirror of a Fabry–Perot-type laser cavity over a number of resonances of the laser line and determination of the wavelength from the distance travelled by the mirror [5]. It is difficult in such measurements to get precision of better than about ±0.5 μm, which may be insufficient for unambiguous spectroscopic identification of the pump and lasing transitions in rich and complex spectra like those of methanol. In the present case, however, following the initial wavelength measurements [5] all of the laser frequencies have been directly measured by a three-laser heterodyne technique in which radiation from two frequency-stabilized CO_2 lasers is mixed with the unknown FIRL line on a Metal-insulator-metal (MIM) point-contact diode and the beat note detected on a spectrum analyzer [6]. The resulting
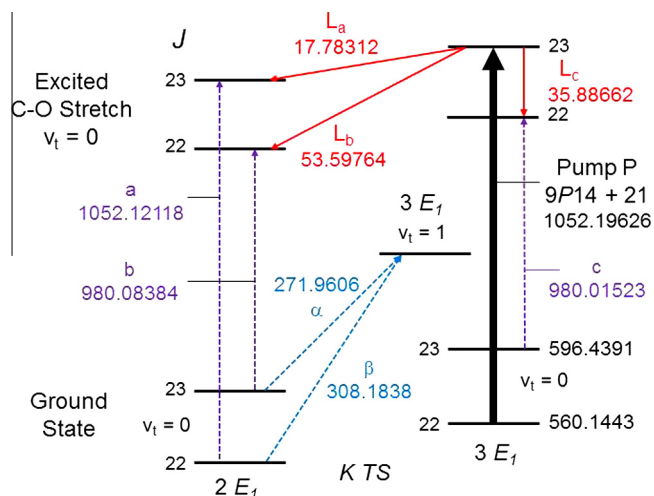
Fig. 1. Energy level and transition diagram for the FIRL system pumped by the 9P14 CO_2 line at +21 MHz offset, with the experimental wavenumbers for the three frequency-measured FIR laser lines. The observed spectroscopic wavenumbers are shown for the IR and FIR transitions, and term values from the Ritz analysis are given for the lower $v_t = 0$, $3E_1$ ground-state levels.

laser frequency accuracies of order ±0.5 MHz then provide very stringent and definitive tests for proposed assignments of the lasing transition systems.

On the spectroscopic side, identification of the FIRL and pump transitions requires thorough analysis of both the IR and FIR spectral regions. The IR investigation identifies molecular absorptions lying close to CO_2 laser lines that could act as potential pumping transitions. The FIR studies serve to establish level energies for the ground vibrational state, which can then be combined with the IR results to determine term values for the excited vibrational states and permit prediction of possible FIRL wavenumbers. Here, our spectra were recorded with synchrotron source radiation at 0.00096 cm^{-1} resolution in the 65–1200 cm^{-1} region on the Bruker IFS125HR Fourier transform spectrometer on the Far-infrared beamline at the Canadian Light Source in Saskatoon. Simultaneous analysis of both the FIR and CO-stretching assigned transition wavenumbers utilizing the Ritz approach then generated an extensive database of ground-state and CO-stretching level energies with an estimated accuracy of better than ±0.0002 cm^{-1} [7,8].

So far, six FIRL systems have been discovered for $CH_3{}^{17}OH$ [5,6], and we have identified the pump and lasing transitions for four of them. The transition and energy level labeling in our notation

includes the vibrational state v (= co for the CO stretch and gd for the ground vibrational state), the torsional quantum number v_t, the torsional symmetry $TS = A$, E_1 or E_2, and the rotational quantum number J with its axial a-component K. Levels of A torsional symmetry with $K \neq 0$ are split into doublets by the molecular asymmetry, and the components are distinguished as A^+ or A^- when they are resolved.

Table 1 presents the information on the four assigned systems, including the CO_2 pumping line with offset, the observed FIRL line wavelengths and wavenumbers calculated from the measured frequencies, the IR transition wavenumber and its assignment as determined from our synchrotron FTIR spectroscopy, our assignments for the lasing transitions, and the wavenumbers calculated for those transitions from our spectroscopic CO-stretching term values. Fig. 1 illustrates two of the routes by which assignments can be reached. On the left of the diagram, we can construct a 6-sided closed loop of transitions, including the laser lines L_a and L_b. If all transitions in the loop are correctly assigned, the wavenumbers should sum to zero going around the loop, and from the data shown in Fig. 1 this is indeed the case to within the net measurement uncertainty:

$$\delta = a + L_a - L_b - b + \alpha - \beta = -0.00038 \text{ cm}^{-1}$$

On the right side of Fig. 1, we can employ the IR wavenumbers and the ground-state energies shown to obtain the wavenumber of laser line L_c via combination differences as:

$$L_c = P + 560.1443 - 596.4391 - c = 35.88623 \text{ cm}^{-1}$$

The close agreement here and in Table 1 between the experimentally measured and spectroscopic FIRL wavenumbers gives strong confirmation of the assignment schemes, and attests to the good accuracy of the Fourier transform data from the synchrotron Far-infrared beamline.

Traditionally there has been a very fruitful interplay between FIRL measurements and FTIR spectroscopy. The spectroscopic observations can locate molecular absorptions lying close to the CO_2 laser lines and, by combining the IR data with FIR results for the ground state, we can construct combination loops as in Fig. 1 to make accurate predictions of potential FIR laser lines. For their part, the FIR laser observations can give important clues as to possible assignments for the pump and lasing transitions and serve as a valuable guide to the spectroscopic analysis. This has certainly been the case here for the $CH_3{}^{17}OH$ results, in which the two techniques have come together to give the very satisfying agreement and mutual confirmation seen in Table 1.

Table 1
Assignments for FIR laser lines of the $CH_3{}^{17}OH$ isotopologue of methanol optically pumped in the CO-stretching band by CO_2 laser lines.

CO_2 line ± offset (MHz)[a]	λ_{laser} (μm)	ν_{laser}[b] (cm^{-1})	IR pump[c] (v_t, K, J)^v TS	FIRL assignment		ν_{calc}[d] (cm^{-1})	Refs.
				$(v_t', K', J')^{v'}$	$\to (v_t'', K'', J'')^{v''}$		
9P14 + 21	278.655	35.88662	$R(0,3,22)^{co} E_1$	$(0,3,23)^{co}$	$\to (0,2,23)^{co}$	35.8864	[5,6]
[1052.19625]	562.331	17.78312	[1052.19626]		$\to (0,2,22)^{co}$	17.7828	[5,6]
	186.575	53.59764			$\to (0,2,22)^{co}$	53.5976	[5,6]
9P18 + 25	319.343	31.31428	$R(0,2,19)^{co} E_2$	$(0,2,20)^{co}$	$\to (0,2,19)^{co}$	31.3143	[5,6]
[1048.66164]	642.707	15.55920	[1048.66166]		$\to (0,1,20)^{co}$	15.5592	[5,6]
	214.664	46.58445			$\to (0,1,19)^{co}$	46.5847	[6]
9P32 + 17	227.945	43.87016	$R(0,5,9)^{co} E_1$	$(0,5,10)^{co}$	$\to (0,4,9)^{co}$	43.8703	[5,6]
[1035.47418]	353.739	28.26940	[1035.47417]		$\to (0,4,10)^{co}$	28.2697	[5,6]
10R40 − 10	357.319	27.98620	$P(0,0,19)^{co} A$	$(0,0,18)^{co}$	$\to (0,0,17)^{co}$	27.9863	[5,6]
[987.61985]	506.915	19.72718	[987.61984]		$\to (0,1^+,17)^{co}$	19.7272	[5,6]

[a] The wavenumber of the CO_2 pump line plus the reported offset is shown underneath in brackets, using the conversion factor 29979.2458 MHz/cm^{-1}.

[b] Wavenumber of the FIR laser line calculated from the reported FIR laser frequency.

[c] The experimental wavenumber for the IR pump transition as measured in the FTIR synchrotron spectrum is shown underneath in brackets.

[d] FIR laser wavenumber predicted from IR/FIR transition combination loops or from ground and excited state term values determined from the spectroscopic FIR and IR transition wavenumbers.

Acknowledgments

References

[1] S.C. Zerbetto, E.C.C. Vasconcellos, Int. J. Infrared Millim. W. 15 (1994) 889–933.

[2] G. Moruzzi, J.C.S. Moraes, F. Strumia, Int. J. Infrared Millim. W. 13 (1992) 1269–1312.

[3] D. Pereira, J.C.S. Moraes, E.M. Telles, A. Scalabrin, F. Strumia, A. Moretti, G. Carelli, C.A. Massa, Int. J. Infrared Millim. W. 15 (1994) 1–44.

[4] G. Moruzzi, B. Winnewisser, M. Winnewisser, I. Mukhopadhyay, F. Strumia, Microwave, Infrared, and Laser Transition of Methanol: Atlas of Assigned Lines from 0 to 1258 cm^{-1}, CRC Press, Boca Raton, FL, 1995.

[5] M. Jackson, A.J. Nichols, D.R. Womack, L.R. Zink, IEEE J. Quant. Electron. 48 (2012) 303–306.

[6] M. Jackson, M. Smith, C. Gerke, J. Barajas, IEEE J. Quant. Electron. 51 (2015) 1500105-1–1500105-5.

[7] G. Moruzzi, R.J. Murphy, R.M. Lees, A. Predoi-Cross, B.E. Billinghurst, Mol. Phys. 108 (2010) 2343–2353.

[8] G. Moruzzi, R.J. Murphy, J. Vos, R.M. Lees, A. Predoi-Cross, B.E. Billinghurst, J. Mol. Spectrosc. 268 (2011) 211–220.