

# Methanol and the Optically Pumped Far-Infrared Laser

Li-Hong Xu, Ronald M. Lees, Elza C. C. Vasconcellos, Sandra C. Zerbetto, Lyndon R. Zink, and Kenneth M. Evenson

**Abstract**—New results on the generation and spectroscopic analysis of optically pumped far-infrared (FIR) laser emission from CH<sub>3</sub>OH have been obtained as part of a systematic study of methanol isotopomers as FIR laser sources utilizing the extended line coverage available from a recently developed high-resolution CO<sub>2</sub> laser of high efficiency. For normal CH<sub>3</sub>OH, six new short-wavelength lines have been found using a 2 m long Fabry–Perot FIR laser cavity. Accurate heterodyne frequency measurements are reported for 14 CH<sub>3</sub>OH FIR laser lines, nearly all above 100 cm<sup>-1</sup>, as well as accurate frequency offsets for most of the corresponding CO<sub>2</sub> pump lines. Spectroscopic assignments are presented for nine high-frequency FIR laser lines in four pump systems.

## I. INTRODUCTION

WE report new results on the generation and spectroscopic analysis of optically pumped far-infrared (FIR) laser emission from CH<sub>3</sub>OH. This paper is a major part of our systematic investigation of methanol isotopomers as FIR laser media utilizing a newly designed FIR laser system. The system combines several different FIR laser cavity designs with the extended line coverage available from a recently developed high-resolution CO<sub>2</sub> laser of high efficiency. With this system, new FIR laser lines pumped by CO<sub>2</sub> fundamental band lines of high *J*, CO<sub>2</sub> sequence band lines, and CO<sub>2</sub> hot-band transitions have been observed. The new FIR laser lines extend over a broad spectral region and contribute significantly to the frequency coverage of the optically pumped FIR laser. In the program so far, over 150 new lines have been observed for eight isotopic species of methanol (CH<sub>3</sub>OH, <sup>13</sup>CH<sub>3</sub>OH, CD<sub>3</sub>OH, <sup>13</sup>CD<sub>3</sub>OH, CD<sub>3</sub>OD, <sup>13</sup>CD<sub>3</sub>OD, CH<sub>3</sub>OD, and CH<sub>2</sub>DOH), and 76 of the new lines plus 23 previous lines with only wavelength observations have been measured in frequency by accurate heterodyne techniques.

Almost immediately after the first successful generation of FIR laser radiation by optical infrared (IR) pumping with a CO<sub>2</sub> laser 25 years ago, methanol and its isotopomers were

recognized as important sources because of their richness of IR pump absorptions, output power, and breadth of FIR spectral coverage. Up to now, more than 570 lines have been observed for the parent <sup>12</sup>CH<sub>3</sub><sup>16</sup>OH species alone and about 2000 lines in total for all of the isotopomers of methanol including <sup>13</sup>CH<sub>3</sub>OH, CH<sub>3</sub><sup>18</sup>OH, CD<sub>3</sub>OH, <sup>13</sup>CD<sub>3</sub>OH, CD<sub>3</sub>OD, <sup>13</sup>CD<sub>3</sub>OD, CH<sub>3</sub>OD, CH<sub>2</sub>DOH, CH<sub>2</sub>DOD, and CHD<sub>2</sub>OH [1]–[4]. The observed methanol FIR laser lines cover a wavelength range from 19–3030 μm, corresponding to 526–3.3 cm<sup>-1</sup> in wavenumber units or 16 THz to 99 GHz on the frequency scale. Therefore, methanol FIR lasers play an important role in bridging the full gap of radiation between the microwave and optical regions and have been widely used in a variety of research fields, such as laser magnetic resonance (LMR) spectroscopy, tunable FIR spectroscopy (TuFIR), and plasma diagnostics.

Several features contribute to the success of methanol isotopomers as excellent FIR laser media [5]. The large permanent dipole moments along both *a* and *b* axes lead to a strong FIR spectrum and liberal transition selection rules. The complexity of the energy level structure due to the large-amplitude torsional motion gives rich FIR and IR spectra, and the methanol IR absorption bands overlap well with the CO<sub>2</sub> laser bands. The favorable separation of the torsional energy states gives the possibility for high-frequency (short wavelength) torsional FIR lasing transitions; apart from the methanol isotopomers, only CH<sub>2</sub>F<sub>2</sub> and N<sub>2</sub>H<sub>4</sub> are presently known to be comparably prolific sources of laser lines above 2 THz. It is these characteristics of the methanol isotopomers that contribute greatly to the size of the FIR laser line catalog.

This paper deals with our new CH<sub>3</sub>OH FIR laser data and is organized as follows: Section II discusses the energy structure and the low resolution IR spectra of the methanol isotopomers; Section III presents the main features of the CO<sub>2</sub> pump laser and the characteristics of the two FIR laser cavities used in this paper; and Section IV describes and comments on the new results that we have obtained on FIR laser line observations and spectroscopic assignments for CH<sub>3</sub>OH.

## II. METHANOL ENERGY STRUCTURE AND IR SPECTRA

Methanol is a slightly asymmetric molecule possessing a large-amplitude internal rotation or torsional motion with a threefold torsional potential and a plane of symmetry. The tunneling motion of the OH framework with respect to the CH<sub>3</sub> top lifts the torsional degeneracy and splits the levels into *A* and *E* symmetry species. The torsional energy can be

Manuscript received August 21, 1995. This work was supported by the Natural Sciences and Engineering Research Council of Canada, NASA Grant W-18, 623, and the Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil.

L.-H. Xu is with the Department of Physical Sciences, University of New Brunswick, Saint John, NB E2L 4L5 Canada.

R. M. Lees is with the Department of Physics, University of New Brunswick, Fredericton, NB E3B 5A3 Canada.

E. C. C. Vasconcellos and S. C. Zerbetto are with the Instituto de Física "Gleb Wataghin," Departamento de Eletronica Quantica, UNICAMP, 13083-970 Campinas, S.P., Brazil.

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

Publisher Item Identifier S 0018-9197(96) 02037-4.

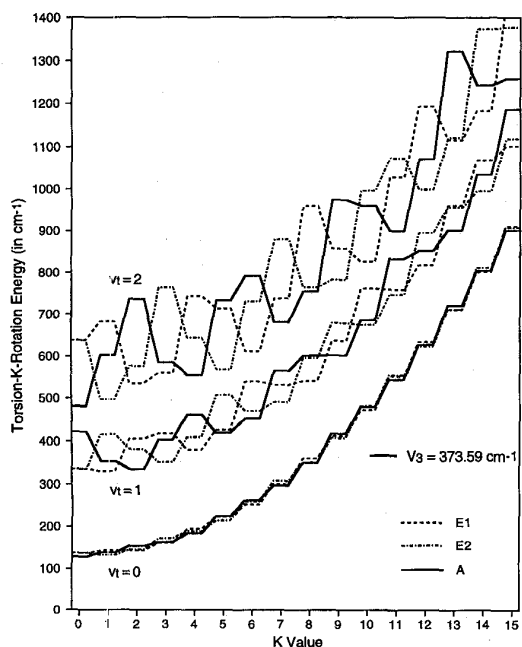


Fig. 1. Torsion- $K$ -rotation energy level structure for the lowest three torsional states of  $\text{CH}_3\text{OH}$ . The height  $V_3$  of the top of the barrier to internal rotation is also indicated.

approximately expressed as

$$E_{tor} = FP_\gamma^2 + \frac{1}{2}V_3(1 - \cos 3\gamma), \quad (1)$$

where  $F$  is the reduced rotational constant equal to the inverse of the reduced moment of inertia of the top ( $\text{CH}_3$ ) and framework ( $\text{OH}$ ),  $P_\gamma$  is the torsional angular momentum conjugate to the torsional angle  $\gamma$ , and  $V_3$  is the torsional potential barrier ( $\sim 373 \text{ cm}^{-1}$  for the normal species). The first excited torsional levels ( $v_t = 1$ ) straddle the top of the barrier. This torsional energy is superimposed on top of the zero-order rotational energy

$$E_{rot} = \frac{1}{2}(B + C)J(J + 1) + [A - \frac{1}{2}(B + C)]K^2, \quad (2)$$

where  $A$ ,  $B$ , and  $C$  are the rotational constants, and  $K$  is the projection of the overall angular momentum  $J$  along the  $a$ -axis parallel to the methyl top axis. The  $J$ -independent part of the torsion- $K$ -rotation energy for the  $v_t = 0-2$  levels is displayed in Fig. 1. The complex structure is very broadly spread in energy, explaining the success of methanol as a lasing medium in covering such a wide range of wavelengths through transitions both within and across the different torsional states.

Both IR and FIR spectra of methanol are very rich due to this torsional complexity and the liberality of the selection rules summarized in Table I. Transitions can occur within a  $K$  energy ladder with  $\Delta K = \Delta v_t = 0$  ( $a$ -type) or between different  $K$  stacks with  $\Delta K \geq 1$  and no restriction on the change  $\Delta v_t$  of torsional quantum number ( $b$ -type). The same selection rules apply to IR transitions between different vibrational states.

Low-resolution and normal mode studies [6]–[7] show that several vibrational bands are located in the region of the 9 and 10  $\mu\text{m}$   $\text{CO}_2$  laser bands. The overlap between the IR

TABLE I  
SUMMARY OF TRANSITION SELECTION RULES  
AND TRANSITION STRENGTHS FOR METHANOL

| Type                     | $\Delta K$ | $\Delta v_t$ | $\Delta J$ | Branch | Transition Strength $S^a$        |   |
|--------------------------|------------|--------------|------------|--------|----------------------------------|---|
| $a$ -type<br>( $\mu_a$ ) | 0          | 0            | +1         | Q      | $A^\pm \leftrightarrow A^{+\pm}$ | $(2J+1)K^2/J(J+1)$  |
|                          |            |              | -1         | R      | $A^\pm \leftrightarrow A^\pm$    | $[(J+1)^2 - K^2]/J(J+1)$  |
|                          |            |              |            | P      | $A^\pm \leftrightarrow A^\pm$    | $(J^2 - K^2)/J$   |
| $b$ -type<br>( $\mu_b$ ) | $\pm 1$    | even         | +1         | Q      | $A^\pm \leftrightarrow A^{+\pm}$ | $(1/4)\langle K \pm 1   K \rangle^2 (2J+1) [1 - K(K \pm 1)/J(J+1)]$ |
|                          |            |              | +1         | R      | $A^\pm \leftrightarrow A^\pm$    | $(1/4)\langle K \pm 1   K \rangle^2 (J+1 \pm K)(J+2 \pm K)/J(J+1)$  |
|                          |            |              | -1         | P      | $A^\pm \leftrightarrow A^\pm$    | $(1/4)\langle K \pm 1   K \rangle^2 (J - \pm K)(J - \pm K - 1)/J$   |
|                          |            |              | 0          | Q      | $A^\pm \leftrightarrow A^\pm$    | $(1/4)\langle K \pm 1   K \rangle^2 (2J+1) [1 - K(K \pm 1)/J(J+1)]$ |
|                          | $\pm 1$    | odd          | +1         | R      | $A^\pm \leftrightarrow A^{+\pm}$ | $(1/4)\langle K \pm 1   K \rangle^2 (J+1 \pm K)(J+2 \pm K)/J(J+1)$  |
|                          |            |              | -1         | P      | $A^\pm \leftrightarrow A^{+\pm}$ | $(1/4)\langle K \pm 1   K \rangle^2 (J - \pm K)(J - \pm K - 1)/J$   |

<sup>a</sup>  $\langle K' | K \rangle$  denotes a torsional overlap matrix element.

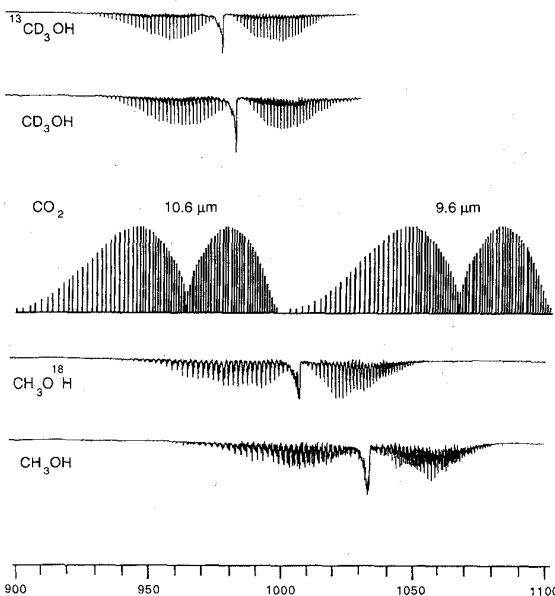


Fig. 2. Superimposed  $\text{CO}$ -stretching bands of several isotopomers of methanol and the  $\text{CO}_2$  laser spectrum.

absorption bands and the  $\text{CO}_2$  laser spectrum is excellent, and more than 100 pump coincidences between  $\text{CH}_3\text{OH}$  absorptions and  $\text{CO}_2$  laser lines have now been observed. Exchange of  $H$  by  $D$ , of an ordinary  $^{12}\text{C}$  carbon atom by the  $^{13}\text{C}$  isotope, or of  $^{16}\text{O}$  by  $^{18}\text{O}$  in  $\text{CH}_3\text{OH}$  shifts the vibrational bands somewhat, but the IR absorption still falls within the  $\text{CO}_2$  laser spectrum as shown in Fig. 2. However, the shifts in molecular rotational and vibrational levels with isotopic substitution are sufficient to generate entirely new sets of pump coincidences and FIR laser lines. Table II lists the vibrational assignments for the various isotopomers of methanol in the  $\text{CO}_2$  laser spectral region, collected from [6] and [7]. Note that combination and hot bands are not considered in this table.

### III. OPTICALLY PUMPED FIR LASERS

In the general scheme of an optically pumped methanol FIR laser, molecules are pumped to a certain excited vibration-rotation-torsion level  $(v_t \tau K, J)^v$  by a selective  $\text{CO}_2$  pump laser line which is in coincidence with a molecular IR absorption line. (In our notation,  $v_t$  is the torsional quantum number,  $\tau$  labels the torsional symmetry,  $K$  is the projection of total angular momentum  $J$  along the  $a$ -axis, and  $v$  is the vibrational

TABLE II  
LOW-RESOLUTION VIBRATIONAL ASSIGNMENTS  
FOR METHANOL ISOTOPOMERS ([6] AND [7])

| Molecule                    | $A'$             |                     |                                |                                | $A''$               |                                |
|-----------------------------|------------------|---------------------|--------------------------------|--------------------------------|---------------------|--------------------------------|
|                             | $\nu(\text{CO})$ | $\rho(\text{CH}_3)$ | $\delta(\text{CH}_3)\text{-s}$ | $\delta(\text{CH}_3)\text{-a}$ | $\rho(\text{CH}_3)$ | $\delta(\text{CH}_3)\text{-a}$ |
| $\text{CH}_3\text{OH}$      | 1033.5           | 1074.5              |                                |                                | 1145.0              |                                |
| $^{13}\text{CH}_3\text{OH}$ | 1018.1           | 1068.1              |                                |                                | [1144.0]            |                                |
| $\text{CD}_3\text{OH}$      | 984.4            |                     | 1130.6                         | 1068.2                         | 897.5               | 1068.2                         |
| $^{13}\text{CD}_3\text{OH}$ | 980.2            |                     | 1111.5                         | [1059.0]                       | [878.2]             | [1060.3]                       |
| $\text{CH}_2\text{OD}$      | 1038.4           |                     |                                |                                | 1142.0              |                                |
| $\text{CD}_2\text{OD}$      | 981.8            | 1070.5              | 1134.3                         | 1027.9                         | 895.0               | 1070.5                         |
| $^{13}\text{CD}_2\text{OD}$ | 974.9            | 1064.5              | 1113.6                         | 1024.0                         | [878.2]             | [1060.3]                       |

(The methanol symmetry is  $C_s$ , hence the 12 normal vibrations are represented by  $T = 8A' + 4A''$ .

s - symmetric, a - antisymmetric. Wavenumbers in brackets are calculated from force constants.)

quantum number.) Population inversion is then achieved relative to lower rotational levels in the excited vibrational state, where the population is very small before the optical pumping, or sometimes in the ground vibrational state due to depletion of the lower level population by the optical pumping. Stimulated emission can thus occur between those levels with inverted populations. The FIR laser lines can be of either *a* or *b* type, as given by the selection and intensity rules in Table I, and a typical pumping scheme and the possible FIR emissions are shown in Fig. 3. The dashed arrows indicate allowed but weak FIR transitions that do not always lase. So far, most observed transitions belong to three-level systems, shown schematically in Fig. 4(a) and (b), where the lasing occurs directly from the upper level into which the pump energy is deposited. For the three-level system depicted in Fig. 4(a), the pumping is from the ground state to the excited state and the FIR lasing takes place within that same state or to a nearby vibrational state. More recently, a new scheme in which the pump coincides with a  $\nu = 2 \leftarrow 1$  hot band transition was proposed and is shown in Fig. 4(b) [8]. Many of the systems are associated with the important Fermi or Coriolis perturbation mechanisms [9] so provide spectroscopic information that is invaluable for understanding interactions among the excited vibrational states. Currently, however, over half of the FIR lasing transitions still remain unidentified in spite of much spectroscopic effort. We thus speculate that FIR laser action might occur by the four-level process shown in Fig. 4(c), where energy and population both flow out of the upper state prepared by the IR pumping and along an interaction channel over to another state from which the FIR lasing takes place at a later time. We are actively seeking spectroscopic confirmation of this type of process, which would represent a significant new technique for the study of intramolecular vibrational energy redistribution (IVR) mechanisms in methanol.

The FIR radiation is linearly polarized either parallel or orthogonal to the pump radiation depending on the sum of  $\Delta J_{\text{pump}}$  and  $\Delta J_{\text{FIR}}$ , the  $J$ -value changes in the pump and FIR laser transitions. The rule for the relative polarization of the pump and emission fields was stated by Henningsen [10] as

$$\Delta J_{\text{pump}} + \Delta J_{\text{FIR}} = \begin{cases} \text{even} & \Rightarrow \parallel \\ \text{odd} & \Rightarrow \perp \end{cases} \quad (3)$$

Polarization information from the observed FIR laser emissions often gives clues to their identification. As indicated in

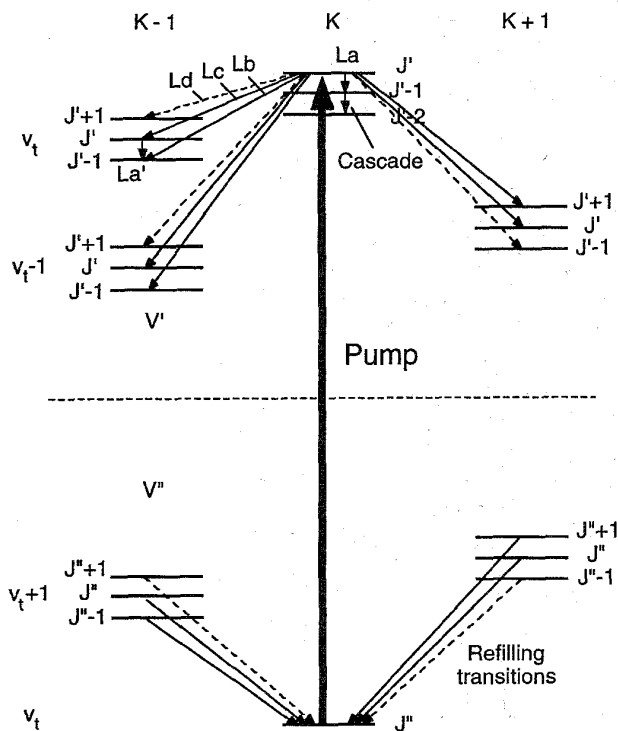


Fig. 3. Schematic diagram of IR-pump/FIR-laser energy level scheme with possible FIR laser transitions.

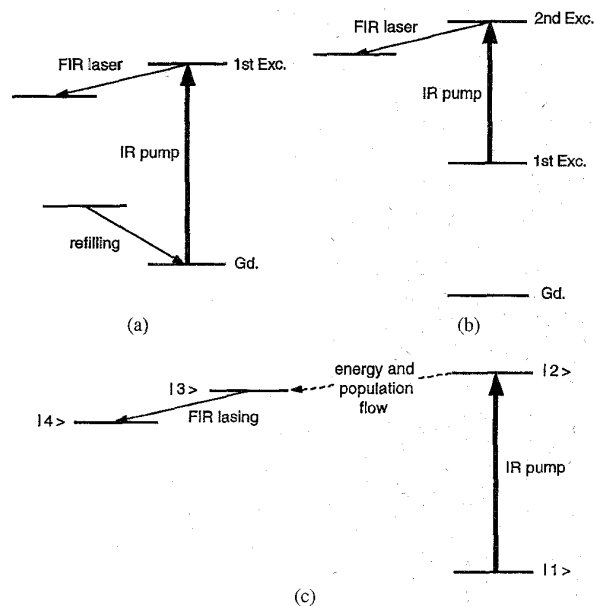


Fig. 4. Possible IR-pump/FIR-laser transition scheme with (a) Pumping in the vibrational fundamental band. (b) Pumping in the hot band. (c) Indirect pumping via a speculative four-level mechanism in which energy and population both flow from pumped level |2> to lasing level |3> along interaction channels coupling the levels.

Fig. 3, a triad of emission lines whose wavenumbers obey the approximate combination relation

$$L_a + L_c - L_b \approx 0 \quad (4)$$

may be observed. In the triad,  $L_a$  and  $L_b$  have the same

$\Delta J_{\text{FIR}}$  and therefore have the same polarization, while  $L_c$ , the  $Q$ -branch transition in the excited state, has the opposite polarization from  $L_a$  and  $L_b$ . Observation of a triad greatly aids the FIR laser assignment since the  $\alpha$ -type laser emission frequency gives  $J$  information for the upper pumped level from the approximate relation

$$J_{\text{upper}} \approx \frac{L_a}{2B'}, \quad (5)$$

where  $B'$  is the effective excited state rotational constant. The polarization of  $L_c$  then determines  $\Delta J_{\text{pump}}$ , and the  $L_c$  wavenumber can often give the other quantum numbers ( $v_i \tau K$ ) since the excited state energy structure is generally not too different from the known ground state levels in the absence of perturbations.

As seen in the literature, searches for FIR laser emission from various molecular gases are often aimed at uncovering the excited-state energy structure of the molecule in question. In our case, the observation and identification of FIR laser emissions have provided important confirmation of the IR assignments in a number of doubtful cases where line series were perturbed or strongly blended. The traditional IR assignment techniques often lose their power in the very condensed C–O stretch band, particularly for medium or high  $J$  where line overlap in the congested  $J$ -multiplets of the  $R$  and  $P$  subbranches can be very serious.

The experimental work was carried out at the Time and Frequency Division, National Institute of Standards and Technology, in Boulder. The optically pumped FIR laser system used in this work consisted of a CO<sub>2</sub> pump laser and two different FIR laser cavity designs that will be briefly discussed below. The CO<sub>2</sub> pump laser had a 1.5 m cavity and a ribbed discharge tube that increases the effective resolution of the grating in the cavity by preventing wall bounces and thereby eliminating waveguide modes [11]. Output coupling in the laser is derived in zero order from specially blazed gratings of 135, 150, 163, or 171 lines/mm. The zero-order output coupling from the 135 line/mm grating was measured to be approximately 5%, and the others behaved comparably. Altogether, this CO<sub>2</sub> system lases on more than 250 lines including the regular 9.4 and 10.4  $\mu\text{m}$  bands from  $J = 0$  to  $J = 62$ , many of the 10.8  $\mu\text{m}$  hot-band lines, many of the 10  $\mu\text{m}$  sequence-band lines, some of the 9  $\mu\text{m}$  sequence lines, and a substantial number of the new 9  $\mu\text{m}$  hot-band lines, with typical powers of order 25 W for the regular lines, 11 W for the hot-band lines, and 6 W for the sequence band lines [12].

Two FIR laser cavities were used in this paper. One was a 2 m long metal-dielectric rectangular waveguide cavity pumped longitudinally through a 1 mm hole in a flat copper end mirror and is described in detail in [13]. The other was a low-loss (<0.5% diffraction loss for wavelengths below 150  $\mu\text{m}$ ) FIR Fabry–Perot cavity consisting of a 2 m long Pyrex tube of 36 mm diameter closed by a fixed copper flat mirror and a gold-coated concave mirror with 4 m radius-of-curvature and operated in a folded confocal geometry [14]. In both cavities, the end mirror was attached to a precision micrometer in order to tune the cavity into resonance with the FIR laser modes. The FIR laser radiation

was coupled out of the cavity by a 45° copper mirror and detected by a metal-insulator-metal (MIM) diode or a pyroelectric detector. The amplitude of the detector signal was recorded as an estimate of the relative intensity of each FIR laser line. A quartz disc was frequently placed in front of the MIM diode in order to block unwanted CO<sub>2</sub> laser carrier.

In searching for new FIR laser lines, the first step was to monitor the optoacoustic response of the laser gas to the chopped CO<sub>2</sub> pumping radiation by means of a microphone placed inside the FIR laser cavity, in order to find CO<sub>2</sub> lines having good coincidences with molecular absorptions. The FIR laser cavity length was then tuned into resonance with the laser modes. The FIR laser wavelength was determined to within an uncertainty of approximately  $\pm 0.5 \mu\text{m}$  by measuring the distance travelled by the micrometer for 10 or more wavelengths. For most of the new FIR laser lines, the frequencies were measured to higher precision by using the heterodyne technique described in [15]. In this technique, two frequency-stabilized CO<sub>2</sub> lasers are locked to the Lamb-dips at their respective line centers. The beams from these lasers, which have frequencies  $\nu_{\text{CO}_2(\text{I})}$  and  $\nu_{\text{CO}_2(\text{II})}$  and moderate power, are mixed on a MIM diode with the unknown FIR laser radiation  $\nu_{\text{FIR}}$  plus a microwave signal  $\nu_{\mu\text{wave}}$  supplied in the 2–18 GHz range from a synthesized signal generator. A spectrum analyzer is then employed to search for a resulting beat note at the frequency given by the equation:

$$\nu_{\text{FIR}} = |n_1\nu_{\text{CO}_2(\text{I})} - n_2\nu_{\text{CO}_2(\text{II})} \pm m\nu_{\mu\text{wave}} \pm \nu_{\text{beat}}, \quad (6)$$

where  $n_1$ ,  $n_2$ , and  $m$  are integers corresponding to the respective harmonics generated in the MIM diode, and  $\nu_{\text{beat}}$  is the beat frequency. The CO<sub>2</sub> frequencies and harmonic orders are chosen to give a beat note below 1.5 GHz. The intensity of the beat signal decreases as the harmonic orders increase; hence, we generally aim to satisfy the optimum condition  $n_1 = n_2 = m = 1$ . However, when measuring the higher frequency ( $\lambda < 50 \mu\text{m}$ ) methanol lines, this was not possible. For the 26.2  $\mu\text{m}$  line at 11.4 THz [16], for example, we obtained the beat note with  $n_1 = n_2 = 3$  and  $m = 1$ . The beat note is amplified and displayed on a spectrum analyzer, using a peak-hold feature that records the peak signal as the FIR laser is tuned over its gain curve. The center frequency of the gain curve is then measured with a marker derived from an accurate oscillator. The estimated  $1\sigma$  accuracy of the FIR laser frequency measurements is  $\Delta\nu/\nu = 2 \times 10^{-7}$ , due mainly to the precision of the resettability of the FIR laser.

With the rich spectral output available from the efficient, high-resolution CO<sub>2</sub> laser [11], [17] we found it important to measure the precise IR pump offset for each FIR laser line in order to be absolutely sure of the identity of the CO<sub>2</sub> pump transition. When the latter was located in a dense region of the CO<sub>2</sub> laser spectrum, one could have regular, hot-band and sequence-band laser lines all crowded closely together with significant output powers and not readily distinguishable simply from the setting of the CO<sub>2</sub> laser tuning micrometer. The offset measurements were performed by adjusting the system to the peak of the FIR emission and then beating the CO<sub>2</sub> pump laser frequency  $\nu_{\text{pump}}$  against a second Lamb-dip-stabilized CO<sub>2</sub> reference laser frequency  $\nu_{\text{ref}}$  in a MIM diode.

TABLE III  
NEW OPTICALLY PUMPED FIR LASER LINES OF CH<sub>3</sub>OH WITH FREQUENCY AND OFFSET MEASUREMENTS

| CO <sub>2</sub> Pump | ν <sub>CO2</sub><br>[cm <sup>-1</sup> ] | Offset <sup>a</sup><br>[MHz] | FIR Laser Line      |                                    |                                     | Rel. Pressure<br>[Pa] | Rel Int<br>[mV] | Ref. |      |      |
|----------------------|---|------------------------------|---------------------|------------------------------------|-------------------------------------|-----------------------|-----------------|------|------|------|
|                      |   |                              | λ [μm] <sup>b</sup> | ν [cm <sup>-1</sup> ] <sup>c</sup> | ν <sub>FIR</sub> [MHz] <sup>d</sup> |                       |                 |      | Pol. |      |
| 10R (04)             | 964.76898                               |                              | 57.4                |                                    |                                     | 16.5                  |                 | new  |      |      |
| 10R (32)             | 983.25225                               | -48                          | 48.283              | 207.11286                          | 6 209 087.2                         | ⊥                     | 32.0            | 0.5  | new  |      |
| 10R (46)             | 990.61963                               | +48                          | 41.630              | 240.21218                          | 7 201 380.0                         | ∥                     | 40.0            | 0.1  | 14   |      |
|                      |   |                              | +48                 | 50.389                             | 198.45711                           | 5 949 594.6           | ⊥               | 32.0 | 0.3  | 14   |
|                      |   |                              | (+15)               | 52.004                             | 192.29392                           | 5 764 826.7           | ⊥               | 32.0 | 0.1  | 2, 4 |
|                      |   |                              | +45                 | 61.819                             | 161.76189                           | 4 849 499.5           | ⊥               | 22.7 | 0.2  | 14   |
|                      |   |                              | (+15)               | 64.156                             | 155.87022                           | 4 672 871.5           |                 | 53.3 | 0.1  | 2, 4 |
| 10R (48)             | 991.56580                               | -16                          | 69.188              | 144.53396                          | 4 333 019.1                         | ∥                     | 21.3            | 0.2  | 14   |      |
|                      |   | -18                          | 97.981              | 102.06043                          | 3 059 694.8                         | ∥                     | 32.0            | 0.5  | 2, 4 |      |
| 10R (50)             | 992.48480                               |                              | 102.061             | 97.98084                           | 2 937 391.8                         | ∥                     | 16.0            | 0.1  | new  |      |
|                      |   |                              | 130.6               |                                    |                                     |                       |                 | 17.3 |      | new  |
| 10R (52)             | 993.37643                               | +40                          | 49.694              | 201.23294                          | 6 032 811.7                         | ∥                     | 20.0            | 0.2  | 14   |      |
|                      |   | +34                          | 60.676              | 164.81093                          | 4 940 907.5                         | ⊥                     | 45.3            | 0.1  | 14   |      |
|                      |   |                              | 104.3               |                                    |                                     |                       |                 |      | new  |      |
| 9P (56)              | 1010.04283                              | -25                          | 59.492              | 168.08929                          | 5 039 190.0                         | ⊥                     | 49.3            | 0.5  | 14   |      |
| 9P (34)              | 1033.48800                              | +35                          | 111.704             | 89.52265                           | 2 683 821.6                         | ∥                     | 22.7            | 1.2  | new  |      |

<sup>a</sup> Offsets in parentheses have not been measured but are literature values.

<sup>b</sup> Lines with wavelengths reported to one decimal place only have not been measured in frequency.

<sup>c</sup> Calculated from frequency measurement with  $1 \text{ cm}^{-1} = 29\,979.2458 \text{ MHz}$ .

<sup>d</sup>  $1\sigma$  relative uncertainty is  $\Delta\nu/\nu = 2 \times 10^{-7}$ .

For pumping with the regular CO<sub>2</sub> bands, the reference laser was locked to the same line as the main pump laser, and the beat frequency observed on the spectrum analyzer then gave the pump offset  $|\nu_{\text{pump}} - \nu_{\text{ref}}|$ . For sequence or hot-band pumping, the reference laser was locked to the closest regular-band CO<sub>2</sub> line and an additional microwave frequency  $\nu_{\mu\text{wave}}$  was mixed in to bring the beat note into the range of the spectrum analyzer. The offset was then obtained to an estimated experimental uncertainty of  $\pm 2 \text{ MHz}$  from the relation

$$\nu_{\text{pump}} = (\nu_{\text{ref}} \pm \nu_{\mu\text{wave}}) \pm \nu_{\text{beat}}. \quad (7)$$

#### IV. RESULTS AND DISCUSSION

Table III reports observations of six new FIR laser lines for CH<sub>3</sub>OH along with 14 new frequency measurements of lines previously reported in the literature. The newly measured lines cover the frequency range from 2.6–7.2 THz.

With the IR and FIR data sets available for CH<sub>3</sub>OH [18], [19], we have been able to assign the quantum numbers for the transitions associated with two of the new FIR laser pump systems and find new assignments for two additional previous systems. Nine of the FIR laser transitions have been identified, all high-frequency lines involving torsionally excited states. The results are given in Table IV and show excellent agreement between the accurate heterodyne FIR laser wavenumbers and those derived from combination difference relations based on our high-resolution spectroscopic data.

This type of result [20] has served as an extremely valuable check on the spectroscopic assignments, particularly for the weaker IR transitions in the torsionally excited subbands of the CO-stretching spectrum whose positions are significantly downshifted relative to the  $\nu_t = 0$  subbands by up to several units in  $J$ .

In the present paper, for example, we correct the assignment of the 9R(2) system pump transition reported in the earlier reviews as the  $A^+$  component of the  $R(113, 24)^{co}$  IR  $K$ -doublet [1], [20]. In actuality, the pump absorption is the  $A^-$  component, which fact emerges clearly from our combination loops when we account for the substantial  $K$ -doubling contribution to the energy of the lower  $(022^+, 24)^{co}$  level of the  $285.24496 \text{ cm}^{-1}$  FIR laser line. We have also confirmed the reported P(123, 24)<sup>co</sup> pump for the 10R(46) + 48 MHz system [21] for which a misassignment existed in earlier literature [20], [22]. In the previous spectroscopic work leading to the correct identification, several high-frequency FIR laser lines were predicted from combination loop relations [21], and we have now observed and measured three of these, thus confirming the assignment. This confirmation is important because the single  $a$ -type FIR laser line observed earlier is not very sensitive to the  $(\nu_t \tau K)$  quantum numbers so could not be identified unambiguously. Now, however, the observation and assignment of four high-frequency  $b$ -type laser lines leave absolutely no doubt about the identity of the P(123, 24)<sup>co</sup>

TABLE IV  
ASSIGNMENTS OF NEW CH<sub>3</sub>OH FIR LASER LINES OPTICALLY PUMPED BY A CO<sub>2</sub> LASER

| CO <sub>2</sub> Pump +<br>Offset [MHz] | $\nu_{\text{pump}}$<br>[cm <sup>-1</sup> ] | IR Absorption <sup>a</sup><br>P/Q/R | FIR Laser Transition <sup>b</sup><br>( $\nu_t \tau' K', J'$ ) $\nu'$ → ( $\nu_t \tau'' K'', J''$ ) $\nu''$ | $\nu_{\text{obs}}$<br>[cm <sup>-1</sup> ] | Rel<br>Pol <sup>b</sup> | $\nu_{\text{calc}}$ <sup>b</sup><br>[cm <sup>-1</sup> ] |
|--|--|-------------------------------------|--|---|-------------------------|---|
| 9R(02) + 25                            | 1066.03820                                 | R(114,23) <sup>co</sup>             | (114,24) <sup>co</sup> → (023,24) <sup>co</sup>  | 236.59015                                 | ⊥                       | 236.5901  |
|  |  |                                     | → (023,23) <sup>co</sup>   | 274.78829                                 | ∥                       | 274.7879  |
| 9R(02) - 13                            | 1066.03693                                 | R(113',24) <sup>co</sup>            | (113',25) <sup>co</sup> → [(113',24) <sup>co</sup> ]   |   | [∥]                     | [39.7691]   |
|  |  |                                     | → (122',24) <sup>co</sup>  | 105.40181                                 | ∥                       | 105.4020  |
|  |  |                                     | → (022',24) <sup>co</sup>  | 285.24496                                 | ∥                       | 285.2447  |
| 10R(32) - 48                           | 983.25065                                  | P(132,27) <sup>co</sup>             | (132,26) <sup>co</sup> → [(023,27) <sup>co</sup> ]   |   | [∥]                     | [164.1724]  |
|  |  |                                     | → (023,26) <sup>co</sup>   | 207.11286                                 | ⊥                       | 207.1128  |
| 10R(46) + 48                           | 990.62123                                  | P(123,24) <sup>co</sup>             | (123,23) <sup>co</sup> → [(032,23) <sup>co</sup> ]   |   | [⊥]                     | [203.3523]  |
|  |  |                                     | → (032,22) <sup>co</sup>   | 240.21218                                 | ∥                       | 240.2123  |
|  |  |                                     | → (014,24) <sup>co</sup>   | 123.84435                                 | ∥                       | 123.8450  |
|  |  |                                     | → (014,23) <sup>co</sup>   | 161.76189                                 | ⊥                       | 161.7618  |
|  |  |                                     | → (014,22) <sup>co</sup>   | 198.45711                                 | [∥] <sup>c</sup>        | 198.4575  |

<sup>a</sup> Pump assignments reported in Ref. [2]; the A<sup>±</sup> component was incorrectly identified for 9R(02) - 13 MHz.

<sup>b</sup> Values in brackets are predicted.

<sup>c</sup> The observed ⊥ polarization given in Table III is inconsistent with the present assignment.

IR pump, although one point needing to be rechecked is that our assignment for the 198.457 11 cm<sup>-1</sup> laser line requires ∥ polarization rather than the observed ⊥ polarization given in Table III.

The most important of the new FIR laser lines, spectroscopically speaking, may turn out to be those pumped by the 10R(46) + 15 MHz and the 10R(52) CO<sub>2</sub> lines. Although they are not yet assigned, we can make some pertinent comments about their origins and significance. The two FIR laser lines observed for each system must be *b*-type members of the triads of Fig. 3; hence, their difference represents the *a*-type line  $L'_a$  in the excited state according to Fig. 3 and (4). The experimental differences of 36.423 70 and 36.422 01 cm<sup>-1</sup> obtained from Table III for the 10R(46) and 10R(52) pumps are very similar, implying that the *J* values in the two systems must be identical despite the significant difference in pump wavenumber. The upper-level *J* value and effective *B*-value for the  $L'_a$  transitions are calculated from (5) to be  $J_{\text{upper}} = 23$  and  $B = 0.7918$  cm<sup>-1</sup>, assuming the FIR laser lines correspond to the  $L_c$  and  $L_b$  transitions of Fig. 3 for each system. This *B*-value would be expected for the  $\nu_t = 3$  torsional state of the excited CO-stretching mode. Effective *B*-values decrease with  $\nu_t$  and are equal to 0.7935 cm<sup>-1</sup> for the  $\nu_t = 2$  CO-stretch levels [23]. The further reduction of 0.0017 cm<sup>-1</sup> observed here is consistent with the calculated decrease from about 0.804 to 0.802 cm<sup>-1</sup> in the ground state *B*-values in going from  $\nu_t = 2$  to  $\nu_t = 3$ ; hence, it is likely that the lower levels of the FIR laser transitions for the two systems are  $\nu_t = 3$  CO-stretching levels. The identity of the upper level of the lasing and IR pump transition is not clear, and there is a strong possibility of interaction and perturbation given the greater density of states at this level

of excitation. However, the tiny absorption peak observed in our IR spectrum at the position of the 10R(52) CO<sub>2</sub> transition suggests pumping from a high torsional level of the ground state with a small Boltzmann factor. It would be rewarding and of great spectroscopic interest to identify such highly excited levels from the FIR laser emission because direct detection and analysis of such weak pump absorptions in our spectrum will certainly be extremely difficult.

The spectroscopic challenge is even greater for the 10R(46) + 15 MHz pump identification because it is not clear which transitions the FIR laser lines correspond to in Fig. 3. The IR pump wavenumber suggests that the pump absorption must be a P-branch transition, in which case the polarization rules of (3) would require ∥ polarization for lines  $L_b$  and  $L_d$  and ⊥ polarization for line  $L_c$ . The ⊥ polarization reported for the 192.293 92 cm<sup>-1</sup> line in Table III would then make it the Q-branch transition  $L_c$  so that the 155.870 22 cm<sup>-1</sup> line would be  $L_d$  and  $J_{\text{upper}}$  would equal 22 instead of 23. However, the polarization measurements are incomplete for the 10R(46) + 15 MHz system, so the possibility that the FIR laser lines are the  $L_b$  and  $L_c$  pair cannot be ruled out, and further complication is added to the search for the assignments. It would thus be useful to return to the 10R(46) system in the future to resolve this uncertainty and to reinvestigate the inconsistency between the observed ⊥ polarization and the ∥ polarization required by the assignment for the 198.457 11 cm<sup>-1</sup> line pumped by 10R(46) at + 48 MHz offset.

## V. CONCLUSION

The present paper, in conjunction with other complementary results in three recent reports [14], [16], [17], serves to

summarize the new FIR laser line observations for CH<sub>3</sub>OH and thus to update the previous reviews of FIR laser emission for methanol isotopomers [1]–[4]. In this paper, we have reported six new FIR lines for CH<sub>3</sub>OH, and accurate heterodyne frequency measurements for 14 lines, nearly all of high frequency above 100 cm<sup>-1</sup>. Transition assignments are also presented for nine high-frequency lines in four systems and a partial analysis presented for pairs of lines in two other systems suggesting that the FIR laser emission may be associated with highly excited  $v_t = 3$  levels in the CO-stretching state.

With the results of the new study, 662 FIR laser lines have now been observed for the parent <sup>12</sup>CH<sub>3</sub><sup>16</sup>OH species so far. To date, we have met the spectroscopic challenge of identifying this extensive emission approximately halfway, with roughly 50% of the known lines having been assigned. In this regard, the new frequency and offset measurements are extremely important in supplying precise benchmark information about transitions in excited vibrational states against which proposed spectroscopic assignments can be rigorously tested and a full and accurate map of the torsion-rotation energy level manifold built up for the excited states.

#### REFERENCES

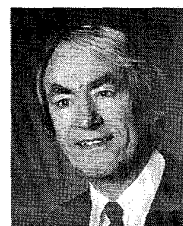
- [1] N. G. Douglas, *Millimeter and Submillimeter Wavelength Lasers*. Heidelberg: Springer-Verlag, 1989.
- [2] G. Moruzzi, J. C. S. Moraes, and F. Strumia, "Far infrared laser lines and assignments of CH<sub>3</sub>OH: A review," *Int. J. Infrared Millimeter Waves*, vol. 13, pp. 1269–1312, 1992.
- [3] D. Pereira, J. C. S. Moraes, E. M. Telles, A. Scalabrin, F. Strumia, A. Moretti, G. Carelli, and C. A. Massa, "A review of optically pumped far-infrared laser lines from methanol isotopes," *Int. J. Infrared Millimeter Waves*, vol. 15, pp. 1–44, 1994.
- [4] S. C. Zerbetto and E. C. C. Vasconcellos, "Far infrared laser lines produced by methanol and its isotopic species: A review," *Int. J. Infrared Millimeter Waves*, vol. 15, pp. 889–933, 1994.
- [5] M. Inguscio, G. Moruzzi, K. M. Evenson, and D. A. Jennings, "A review of frequency measurements of optically pumped lasers from 0.1 to 8 THz," *J. Appl. Phys.*, vol. 60, pp. R161–R192, 1986.
- [6] A. Serrallach, R. Meyer, and H. H. Günthard, "Methanol and deuterated species: Infrared data, valence force field, rotamers, and conformation," *J. Mol. Spectrosc.*, vol. 52, pp. 94–129, 1974.
- [7] F. C. Cruz, A. Scalabrin, D. Pereira, P. A. M. Velazquez, Y. Hase, and F. Strumia, "The infrared absorption spectra and normal coordinate analysis of <sup>13</sup>CH<sub>3</sub>OH, <sup>13</sup>CD<sub>3</sub>OH, and <sup>13</sup>CD<sub>3</sub>OD," *J. Mol. Spectrosc.*, vol. 156, pp. 22–38, 1992.
- [8] I. Mukhopadhyay, I. Ozier, and R. M. Lees, "High resolution spectrum of the C–O stretch overtone band in methyl alcohol," *J. Chem. Phys.*, vol. 93, pp. 7049–7053, 1990.
- [9] R. M. Lees, "FIR laser spectroscopy of methanol—A probe for vibrational mode coupling," in *Millimeter and Submillimeter Waves and Applications II, Proc. Soc. Photo-Optical Instrumentation Engineers*, vol. SPIE-2558, pp. 262–284, 1995.
- [10] J. O. Henningsen, "Assignment of laser lines in optically pumped CH<sub>3</sub>OH," *IEEE J. Quantum Electron.*, vol. QE-13, pp. 435–441, 1977.
- [11] K. M. Evenson, C.-C. Chou, B. W. Bach, and K. G. Bach, "New CW CO<sub>2</sub> laser lines: The 9- $\mu$ m hot band," *IEEE J. Quantum Electron.*, vol. QE-30, pp. 1187–1188, 1994.
- [12] A. G. Maki, C.-C. Chou, K. M. Evenson, L. R. Zink, and J.-T. Shy, "Improved molecular constants and frequencies for the CO<sub>2</sub> laser from new high- $J$  and hot-band frequency measurements," *J. Mol. Spectrosc.*, vol. 167, pp. 221–224, 1994.
- [13] M. Inguscio, F. Strumia, K. M. Evenson, D. A. Jennings, A. Scalabrin, and S. R. Stein, "Far-infrared CH<sub>3</sub>F Stark laser," *Opt. Lett.*, vol. 4, pp. 9–11, 1979.
- [14] E. C. C. Vasconcellos, S. C. Zerbetto, J. C. Holecck, and K. M. Evenson, "Short wavelength far-infrared laser cavity yielding new lines in methanol," *Opt. Lett.*, vol. 20, pp. 1392–1393, 1995.
- [15] F. R. Petersen, K. M. Evenson, D. A. Jennings, J. S. Wells, K. Goto, and J. J. Jimenez, "Far infrared frequency synthesis with stabilized CO<sub>2</sub> lasers: Accurate measurements of the water vapor and methyl alcohol laser frequencies," *IEEE J. Quantum Electron.*, vol. QE-11, pp. 838–843, 1975.
- [16] S. C. Zerbetto, L. R. Zink, K. M. Evenson, and E. C. C. Vasconcellos, "High-frequency far-infrared laser lines in optically pumped CH<sub>3</sub>OH," *Int. J. Infrared and Millimeter Waves*, vol. 16, 1995, to be published.
- [17] L.-H. Xu, R. M. Lees, K. M. Evenson, C.-C. Chou, J.-T. Shy, and E. C. C. Vasconcellos, "Spectroscopy of new CH<sub>3</sub>OH far-infrared laser lines pumped by new CO<sub>2</sub> laser lines," *Canad. J. Phys.*, vol. 72, pp. 1155–1164, 1994.
- [18] G. Moruzzi, F. Strumia, P. Carneseccchi, R. M. Lees, I. Mukhopadhyay, and J. W. C. Johns, "Fourier spectrum of CH<sub>3</sub>OH between 950 and 1100 cm<sup>-1</sup>," *Infrared Phys.*, vol. 29, pp. 583–606, 1989.
- [19] G. Moruzzi, F. Strumia, J. C. S. Moraes, R. M. Lees, I. Mukhopadhyay, J. W. C. Johns, B. P. Winnewisser, and M. Winnewisser, "The Fourier spectrum of CH<sub>3</sub>OH between 200 and 350 cm<sup>-1</sup>: Torsional transitions and evidence for state mixings," *J. Mol. Spectrosc.*, vol. 153, pp. 511–577, 1992.
- [20] G. Moruzzi, F. Strumia, R. M. Lees, and I. Mukhopadhyay, "CH<sub>3</sub>OH laser line assignments and frequency predictions," *Infrared Phys.*, vol. 32, pp. 333–347, 1991.
- [21] R. M. Lees, "Spectroscopic assignments of far infrared laser transitions in methanol," in *Proc. Nat. Conf. Lasers and Their Applicat.*, A. Hariri, Ed., Tehran, Iran, 1987, pp. 76–82.
- [22] J. O. Henningsen, *Molecular Spectroscopy by Far Infrared Laser Emission*. Copenhagen: JJ Tryktechnik A-S, 1984.
- [23] R. M. Lees, "Far-infrared and infrared spectroscopy of methanol applied to FIR laser assignments," in *Far-Infrared Science and Technology*, J. R. Izatt, Ed., Proc. Soc. Photo-Optical Instrumentation Engineers, vol. SPIE-666, pp. 158–170, 1986.



**Li-Hong Xu** received the B.Sc. honors degree in physics with a minor in modern optics in 1982 from Suzhou University, China, and the Diploma of the Information Processing Centre Program in Contemporary Experimental Optics from a consortium of seven Beijing universities in 1983. She received the Ph.D. degree in physics in 1992.

She joined the University of New Brunswick, Canada, in 1988 as a Visiting Scholar. From 1992 to 1994, she was a CEMAID postdoctoral fellow at U.N.B. in the Network of Centres of Excellence in

Molecular and Interfacial Dynamics and from 1994 to 1995 was a Visiting Scientist in the Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD. She is now on the faculty of the Department of Physical Sciences at U.N.B. Saint John. Her research interests include high-resolution infrared and far-infrared spectroscopy, notably of molecules with large amplitude internal motions, jet-cooled molecular beam studies, and far-infrared laser analysis.



**Ronald M. Lees** was born in Sutton, England, in 1939. He received the B.Sc. degree in honors mathematics and physics and the M.Sc. degree in physics from the University of British Columbia, Canada, in 1961 and 1965, respectively. He was a Commonwealth Scholar at the University of Bristol, England and received the Ph.D. degree in physics in 1967.

From 1966 to 1968, he was a Postdoctoral Fellow in the Spectroscopy Section at the National Research Council of Canada, after which he joined the University of New Brunswick, Fredericton. He has worked on microwave spectra of astrophysical molecules, collisional energy transfer in gases, and on high-resolution infrared and far-infrared spectra of methanol with recent emphasis on vibrational mode coupling and FIR laser assignment.

Dr. Lees is a member of the Canadian Association of Physicists, of which he was President in 1991–1992, the American Physical Society, the American Association of Physics Teachers, the Optical Society of America, and SPIE.



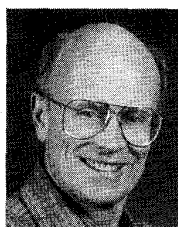
**Elza C. C. Vasconcellos** was born in Presidente Venceslau, SP, Brazil, on November 2, 1942. She received the B.S. and M.S. degrees in physics from the University of S ao Paulo and University of Brasilia in 1965 and 1969, respectively.

After completing her graduate courses and Ph.D. thesis in physics at the University of Southern California, Los Angeles, she returned to Brazil in 1974 to the Universidade Estadual de Campinas (UNICAMP) where she has a permanent position. She was the head of the Quantum Electronics Department during 1991–1992 and has spent her sabbatical leave in 1993 and 1994 at NIST in Boulder, CO. Her research interests include lasers in the infrared and far-infrared regions, with application to molecular and solid-state spectroscopy.



**Sandra C. Zerbetto** was born in Americana, SP, Brazil, on November 28, 1963. She received the B.S. and M.S. degrees in physics from the University of Campinas (UNICAMP) in 1988 and 1989, respectively. She is currently finishing her Ph.D. degree at UNICAMP.

**Lyndon R. Zink**, photograph and biography not available at the time of publication.



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

Since 1963, he has been with the National Institute of Standards and Technology, 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 Medal, the Gold Medal, and 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.