Accurate Frequency of the 119 μm Methanol Laser from Tunable Far-Infrared Absorption Spectroscopy

M. INGUSCIO, L. R. ZINK, K. M. EVENSON, AND D. A. JENNINGS

Abstract—We report on high accuracy absorption spectroscopy of CH₃OH in the far infrared. In addition to 22 transitions in the ground state, we have measured the frequency of the (n, 7, /, K), (0, 1, 16, 8) → (0, 2, 15, 7) transition in the A₁ excited vibrational level, which is responsible for the laser emission at 119 μm. The measured frequency is 2 522 782.57(10) MHz at “zero pressure,” with a pressure shift of 6.1(32) kHz/Pa (0.805(420) MHz/torr). An accurate remeasurement of the laser emission frequency has also been performed, and the results are in good agreement.

INTRODUCTION

FOLLOWING the invention of the optically pumped far-infrared (FIR) laser in 1970 [1], over 1000 CW FIR laser lines have been discovered. These lasers have found wide applications in several fields of physics: atomic and molecular spectroscopy, astrophysics, and metrology. The most powerful line yet discovered is the 119 μm line of methanol, and it is also the most widely used in the many applications of far-infrared lasers. Many of these applications are possible because of the very good fractional frequency reproducibility (about ± 2 × 10⁻²) displayed by the optically pumped lasers. A survey of the measured frequencies and the techniques of frequency measurement was recently reported [2] together with a discussion of accuracies and limitations.

The uncertainty in the frequency reproducibility of the free running laser is mainly determined by the resettability of its frequency to the maximum (center) of the gain curve. For well-designed apparatus and careful measurements, the frequency reproducibility can be of the order of two parts in 10⁶. However, in a few cases, measurements of the frequency of the same laser line in different laboratories have differed by more than the stated uncertainties. Possible causes of these differences are shifts or asymmetries introduced in the gain curve by pump laser detunings or saturation effects in the pump transition, and mode or line competition affecting the shape of the gain curve, thus leading to erroneous determination of the line center. Pressure shifts have been demonstrated to be insignificant [3] in the range of operation of these lasers if careful measurement procedures are followed.

In most cases knowledge of the accurate molecular transition frequencies from independent spectroscopic data is not available because alternative sources for high resolution, high accuracy spectroscopy in the FIR were not available until recently. As a consequence, the molecular transition frequency had to be inferred from measurements of the laser output. An accurate value of the molecular transition frequency is also a valuable help in assigning the various lines.

Harmonic generation and mixing techniques are now used to generate tunable radiation in the FIR [4] and are employed in several spectrometers. In the experiments to be described, difference frequency generation in a metal-insulator-metal (MIM) diode irradiated by two CO₂ lasers [5] allows nearly complete coverage of the region from 50 μm to 1 mm with frequency accuracies of a few parts in 10⁶. The purpose of this paper is to report on the application of this spectroscopic technique to the measurement of methanol transitions, including a measurement of the rotational transition at 119 μm in the excited vibrational state. A deviation from the previously measured frequency of the laser was observed; as a consequence, a remeasurement of the frequency of the laser was performed in order to investigate causes of the difference and to improve the accuracy.

EXPERIMENTAL DETAILS

In the present paper two different experimental apparatus were used. The first was the tunable far-infrared (TuFIR) spectrometer [5] necessary for the measurement of absorption transitions in ground and excited vibrational states of CH₃OH. The second apparatus used a CH₃OH optically pumped laser with transverse pumping used for the remeasurement of the frequency of the 119 μm laser radiation.

In the TuFIR spectrometer, two drive lasers, CO₂ laser I and a CO₂ waveguide laser, are combined on a beam splitter and then focused onto a MIM diode, in which the FIR radiation is generated. Laser I is frequency modulated; thus, following lock-in detection the FIR radiation is also frequency modulated, and the derivative of the absorption signal is observed. A third CO₂ laser (laser II) is...
used to control the frequency of the waveguide laser by using a frequency offset lock. Both CO2 lasers I and II are frequency stabilized using the saturated fluorescence technique [6]. Optoacoustic modulators operating at 90 MHz are used to isolate the lasers from the MIM diode and to provide an additional 180 MHz of tunability. The accuracy of the FIR frequency generated is 35 kHz, with a frequency stability of 35 kHz.

The resonator is an open structure with two spherical gold coated end mirrors. The gain cell is pumped transversely with respect to the laser axis is cylindrically refocused by means of an intracavity adjustable iris. The FIR laser spectrum is measured by heterodyning the laser output with the radiation from the two CO2 lasers used in the FIR laser. The signal-to-noise ratio is over 10:1.

The results are shown in Fig. 1. Since the Doppler broadening of the transition is about 2.5 MHz, collisional broadening can be considered to be predominant only for pressure values of a few tens of pascals. As a consequence, we have fit the experimental data using the expression given in [12, case b], and obtained for the broadening parameter a value of 268[25] kHz/Pa (FWHM), in good agreement with the value 721 kHz/Pa, obtained using Anderson's model [13].

The precision of the center frequency measurements (±50 kHz uncertainty) makes possible an investigation of the pressure shift even though it is rather small, about 2% of the linewidth. By fitting the data of Fig. 2 we obtain a positive frequency shift of 4.1(4) kHz/Pa (0.540 MHz/torr). To our knowledge this is the first measurement of a pressure shift on a CH3OH transition.

Encouraged by the optimum signal-to-noise ratio in the absorption measurements in the ground state, we decided to perform measurements in the vibrational excited state. A typical experimental recording is shown in Fig. 3 for the ν2 = 1 transition at 118.8 μm (84.15 cm−1). This transition, measured here in absorption, is particularly important because it is responsible for one of the most important FIR laser lines. The signal-to-noise ratio is worse than that of the measurements in the ground state, because of the reduction of the population to ~1%, yielding a somewhat larger uncertainty in the center frequency.

### Table 1

<table>
<thead>
<tr>
<th>Transition</th>
<th>Amplitude</th>
<th>Value (kHz)</th>
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<tr>
<td>TUFIR Measurements</td>
<td>FTSl</td>
<td>FIT</td>
</tr>
<tr>
<td>1</td>
<td>912 106.568 (50)</td>
<td>30.4269691 (16)</td>
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<tr>
<td>2</td>
<td>999 116.100 (50)</td>
<td>33.3965621 (17)</td>
</tr>
<tr>
<td>3</td>
<td>1 154 173.612 (50)</td>
<td>36.490877 (17)</td>
</tr>
<tr>
<td>4</td>
<td>1 154 185.212 (50)</td>
<td>38.699146 (17)</td>
</tr>
<tr>
<td>5</td>
<td>1 154 196.677 (50)</td>
<td>38.699327 (17)</td>
</tr>
<tr>
<td>6</td>
<td>1 154 226.377 (50)</td>
<td>38.500847 (17)</td>
</tr>
<tr>
<td>7</td>
<td>1 156 219.245 (50)</td>
<td>38.577326 (50)</td>
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<td>8</td>
<td>1 156 225.064 (50)</td>
<td>38.575146 (50)</td>
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<tr>
<td>9</td>
<td>1 154 226.377 (50)</td>
<td>38.699327 (17)</td>
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<td>1 192 712.721 (100)</td>
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<td>2 501 161.010 (50)</td>
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<tr>
<td>22</td>
<td>2 301 173.364 (50)</td>
<td>65.057014 (17)</td>
</tr>
</tbody>
</table>

### A. Absorption Spectroscopy

The transition frequencies in the ground state of CH3OH were measured first. Generally, the gas pressure was chosen in order to optimize the signal-to-noise ratio (that is, at a value in which the collisional broadening is nearly equal to the Doppler broadening). The results are summarized in Table 1. The assignment of the observed transitions can be deduced from the analysis of the Fourier transform spectra [9], [10]. The present frequency values can be used for the calibration of Fourier transform spectroscopy (FTS) recordings. FTS1 data are from [9], while FTS2 are from a more recent and more accurate recording [10]. The accuracy of FTS2 values is demonstrated to be a few times 10−4 cm−1. Some of the observed transitions show asymmetry type transitions. The TuFIR recording allows the resolution of the Δ splitting, unresolved in the FTS measurements, and makes possible a careful reinvestigation of the asymmetry splitting in methanol [11].

For some of the transitions we have performed the measurements at different pressures to investigate pressure broadening and shifts. For instance, for line 2 in Table 1 we explored a pressure region up to about 50 Pa, and the
Fig. 1. Pressure broadening of \( \text{CH}_3\text{OH} \) ground state transition at 999.416 MHz (line 2 in Table I).

Fig. 2. Pressure shift of the same transition of Fig. 1.

Fig. 3. Experimental recording of the absorption at 118.8 \( \mu \)m in the \( \text{CH}_3\text{OH} \) \( v=1 \) excited vibrational state. The gas pressure was 10 Pa.

determination (\( \pm 100 \) kHz). The Doppler effect at this frequency is the predominant cause of broadening, nevertheless, we could investigate the effect of collisions both on the width and on the center frequency. We performed measurements from 4 to 60 Pa and the results are shown in Fig. 4. The experimental data were analyzed again using [12, case b)]. The measured pressure broadening parameter (FWHM) is 226(22) kHz/Pa (30 MHz/torr). This is in good agreement with the computed value of 221 kHz/Pa from [13].

In almost the same range of pressure we carefully measured the center frequency, and the results are plotted in Fig. 5. Here the spread in the measurements is somewhat larger than for measurements in the ground state (Fig.2). Nevertheless it has been possible to extract a pressure shift value, of +6.1(32) kHz/Pa (0.80(40) MHz/torr). Also, in this case, the theoretical prediction of +4.5 kHz/Pa (13) is in good agreement. To the best of our knowledge, this is the first extension of Anderson’s model to such a high frequency, and the pressure broadening and shift measurements indicate the applicability of this model in the FIR. With limitation to the pressure broadening, the model has also recently been successfully applied to FIR transitions of atmospheric interest in the OH radical [14].

The correctness of the model is important in evaluating shifts of transitions for which direct measurements are not available. For instance, the pressure shift of the \( \text{CH}_3\text{OH} \) lasing transition at 170.6 \( \mu \)m has been the subject of some controversy, with one group claiming a 112 kHz/Pa (15 MHz/torr) shift [15] and another observing a negligible shift [3]. In the present paper we have attempted to make the same direct measurements on the 170 \( \mu \)m line as the 119 \( \mu \)m line; however, accurate measurements were prevented by the occurrence of a nearby strong absorption originating from a ground state transition (about 10 MHz higher in frequency). On the other hand, since the 170.6 \( \mu \)m transition has the same upper level as the 119 \( \mu \)m transition, shifts similar to those of the 119 \( \mu \)m line are expected. Anderson’s model in fact predicts [13] a small shift of 4.5 kHz/Pa (600 KHz/torr) for the 170.6 \( \mu \)m line, in support of measurements in [3].

The frequency of the 119 \( \mu \)m transition extrapolated to “zero pressure” is 2 522 782.567 (65) MHz and is con-
consistent with the value 2 522 781.6 (12) MHz reported in the original measurement [8] of the longitudinally pumped laser output. The uncertainty interval of that laser measurement is 5 × 10⁻⁸. In comparison, we have found the reproducibility of transversely pumped FIR lasers to be about 2 × 10⁻⁸. This is confirmed in the measurement by Blaney et al. [16], who obtained a value of 2 522 782.0 (7) MHz using a transversely pumped FIR laser. A comparison of that laser frequency with the present TuFIR measured frequency is illustrated in Fig. 6.

The frequencies of methanol of the 119 μm line cannot be computed a priori to an accuracy better than the laser frequency measurement. However, recent measurements were reported in the excited ν₂ state of CH₃F [17], but in that case the frequency was lower than 1 THz and the molecular constants [18] are very precise for that molecule and the transition frequency can be computed with much better accuracy than the laser output measurement.

The high frequency (2.5 THz) implies large Doppler shifts, which easily can cause misleading asymmetries in the laser gain curve. In addition this laser line is one of the strongest, and shifts from the molecular center frequency could also be caused by Raman effects or multimode operation of the laser. As a consequence of these considerations, we decided to repeat the laser frequency measurement.

B. Laser Output Frequency Measurements

As we have discussed in the experimental apparatus section, the FIR laser consisted of an open, nearly confocal resonator which easily allows single TEM₀₀ mode operation with the aid of the intracavity iris. Furthermore, the transverse, multireflection optical pumping scheme avoids Doppler tuning or splitting effects, even in this short wavelength region. To measure the frequency, the FIR laser output was mixed in the MIM diode with the same pair of CO₂ laser emissions used to synthesize the FIR radiation in the TuFIR apparatus (¹³ CO₂, 9R22 and CO₂, 10P14). The synthesized frequency is 2 522 798.258 (30) MHz and a heterodyne signal with the FIR laser was observed on the spectrum analyzer at a frequency of about 16 MHz. The beat note was recorded with more than 60 dB signal-to-noise ratio, with a diode impedance of about 350 Ω, typical for this diode [19]. The entire tuning curve could be recorded by means of micrometric scanning one of the end mirrors. The tuning range depended on the pressure of operation of the FIR laser and varied from about 1 to 10 MHz. A portion of the tuning curve recorded in these conditions is shown in Fig. 7 (a). As widely discussed in [3], for each of the several measurements that we have performed only the centers of symmetric curves were used. The center frequency was then determined with the aid of a synthesizer generated frequency marker, as shown in Fig. 7 (b). When the intracavity iris was not reduced in order to avoid multimode operation, the center of the curve could be shifted more than 1 MHz. This is consistent with similar results reported in [20]. We have repeated the center frequency measurement under optimized conditions and at a pressure of 30 Pa, obtaining a frequency value of 2 522 782.464 (22) MHz (two standard deviations). Repeating the same procedure for different pressures in the range 11–40 Pa, we observed maximum frequency differences of about 300 kHz which is consistent with the TuFIR absorption spectroscopy measurements of the frequency shifts shown in Fig. 5.

Fig. 6. Comparison of the frequency measurements reported for the CH₃OH transition at 118.8 μm. The higher accuracy of the present measurement from the laser output mainly originates from the use of a transverse optical pumping scheme. The direct absorption measurement yields a value accurate to better than one part in 10⁷.

Fig. 7. New measurement of the CH₃OH 118.8 μm frequency using the laser. In (a) the symmetric tuning curve chosen for the measurement is shown. In (b), the beat note from mixing the laser output with two CO₂ lasers is shown. The recording in (a) is obtained by scanning the FIR cavity and storing the maximum heterodyne signal.

The frequency of the laser output now determined under controlled and optimized conditions of operations is accurate to ±2 × 10⁻⁸ and is in agreement with the precise value obtained from TuFIR absorption spectroscopy. The spread of the frequency values at different pressures is constrained within a few hundred kHz and the reproducibility of the measurements is well within two parts in 10⁷. Improper operation of the laser can increase the uncertainty. We think that the previous frequency measurement [8] was affected by the longitudinal pumping scheme used in that apparatus; however, it was in agreement within the reported uncertainty, ±5 × 10⁻⁸.
CONCLUSION

In conclusion, we have demonstrated that tunable far-infrared spectroscopy (TuFIRS) is a powerful technique for precise measurements of transitions of polyatomic molecules, including excited levels. We obtained pressure broadening and pressure shift coefficients of methanol at FIR frequencies.

The direct absorption frequency measurement of the CH$_3$OH lasing transition at 118.8 μm has demonstrated a new measurement technique: the frequency of an optically pumped lasing transition in the THz region can be precisely measured from absorption spectroscopy. The direct absorption and laser output frequency measurements for such lasing lines yield an insignificant pressure shift and indicate a reproducibility (one sigma) of these laser frequencies of about 2 × 10$^{-7}$.

REFERENCES


M. Inguscio, photograph and biography not available at the time of publication.

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

K. M. Evenson, photograph and biography not available at the time of publication.

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