

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 CH_3OH in the far infrared. In addition to 22 transitions in the ground state, we have measured the frequency of the $(n, \tau, J, K), (0, 1, 16, 8) \rightarrow (0, 2, 15, 7)$ transition in the ν_5 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 $\pm 2 \times 10^{-7}$) 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 10^7 . 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 in-

significant [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 CO_2 lasers [5] allows nearly complete coverage of the region from 50 μm to 1 mm with frequency accuracies of a few parts in 10^8 . 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 CH_3OH . The second apparatus used a CH_3OH 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, CO_2 laser I and a CO_2 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 CO_2 laser (laser II) is

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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 spectral purity of about 10 kHz, making the source ideal for high resolution FIR spectroscopy. After a single pass through a Pyrex absorption cell (55 cm long and 19 cm in diameter), the radiation is detected with a liquid helium cooled germanium bolometer. CH₃OH gas pressure in the sealed absorption cell was measured by a calibrated capacitance manometer.

The optically pumped FIR laser is pumped nearly transversely and is similar to that used in the most recent laser magnetic resonance spectrometer [7]; however, it does not have a beam splitter. We mention here the main features. The resonator is an open structure with two spherical gold coated end mirrors. The gain cell is pumped transversely by a grating tuned CO₂ laser. A good overlap between pump and FIR is accomplished in a nearly confocal geometry with the use of a cylindrical copper tube as the CO₂ reflector. The CO₂ beam entering the tube at 75° with respect to the laser axis is cylindrically refocused with every reflection from the copper wall. Invar spacers are used in the resonator to provide good thermal stability. The output coupling is obtained from a 45°, 6 mm diameter, copper mirror which can be slid towards the center for increased coupling [7]. Single mode is obtained by means of an intracavity adjustable iris. The FIR laser frequency is measured by heterodyning the laser output with the radiation from the two CO₂ lasers used in the TuFIR spectrometer, in a point contact diode [8].

EXPERIMENTAL RESULTS

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 I. 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 *K* 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 I we explored a pressure region up to about 50 Pa, and the

TABLE I
LIST OF SOME OF THE CH₃OH GROUND STATE ABSORPTION LINES OBSERVED BY THE TUNABLE FAR-INFRARED SPECTROMETER. FOR REFERENCE, THE LESS ACCURATE DATA FROM FOURIER TRANSFORM SPECTRA ARE ALSO REPORTED

	TU-FIR MEASUREMENTS		FTS1	FIT	FTS2
	(MHz)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
1)	912 108.568(50)	30.4246669(16)	30.4244	30.4251	
2)	999 416.100(50)	33.3369624(17)	33.3371	33.3368	
3)	1 154 173.612(50)	38.4990877(17)			
4)	1 154 185.212(50)	38.4994746(17)	38.5002		38.4992
5)	1 154 198.677(50)	38.4999237(17)		38.4986	
6)	1 154 226.377(50)	38.5008477(17)		38.5007	
7)	1 156 219.245(150)	38.5673226(50)	38.5661	38.5661	38.56729
8)	1 156 225.006(150)	38.5675148(50)			
9)	1 191 948.650(50)	39.7591273(17)	39.7594	39.7593	39.75888
10)	1 193 712.271(100)	39.8179554(34)	39.8174		39.81775
11)	1 350 197.368(50)	45.0377363(17)			45.0386
12)	1 350 277.975(50)	45.0404251(17)	45.0401		45.04096
13)	1 350 315.008(50)	45.0416604(17)			
14)	2 444 957.467(50)	81.5550025(17)	81.5539	81.5548	81.55474
15)	2 445 388.911(50)	81.5693939(17)	81.5682	81.5691	81.56912
16)	2 447 941.161(50)	81.6545278(17)	81.6531		81.6542
17)	2 473 572.735(50)	82.5095051(17)			82.50942
18)	2 473 607.960(500)	82.510680(17)	82.5111		
19)	2 504 420.116(100)	83.5384630(34)	83.5362		83.5382
20)	2 504 428.416(100)	83.5387340(34)			
21)	2 551 161.010(50)	85.0975714(17)			85.0975
22)	2 551 173.316(50)	85.0979819(17)			

FTS 1 Fourier Transform, IR0E, Florence, 1984
 FTS 2 Fourier Transform, IR0E, Florence, 1986
 FIT Computed from the Fit of FTS 1

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 271 kHz/Pa, computed 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 $\nu_5 = 1$ 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 $\sim 1\%$, yielding a somewhat larger uncertainty in the center frequency

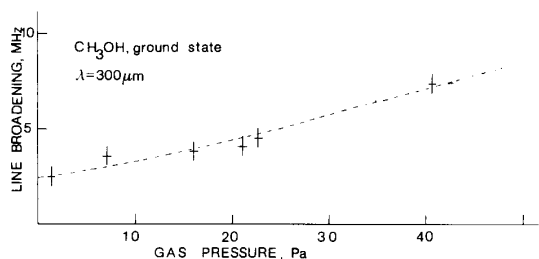


Fig. 1. Pressure broadening of CH₃OH ground state transition at 999 416.1 MHz (line 2 in Table I).

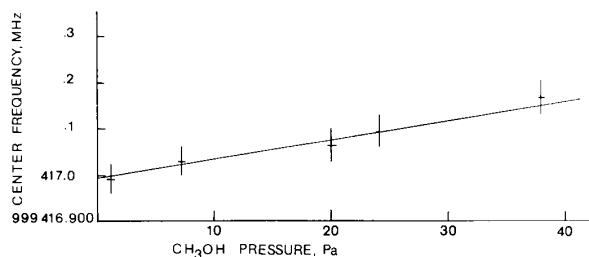


Fig. 2. Pressure shift of the same transition of Fig. 1.

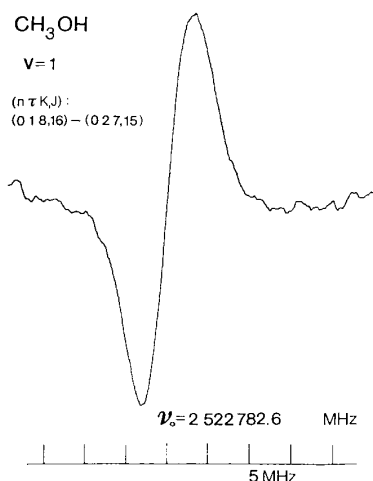


Fig. 3. Experimental recording of the absorption at 118.8 μm in the CH₃OH $\nu_s = 1$ excited vibrational state. The gas pressure was 10 Pa.

determination (± 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

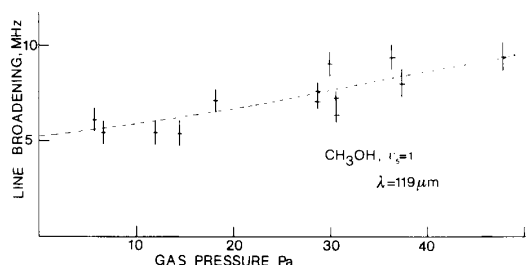


Fig. 4. Pressure broadening of the transition at 118.8 μm .

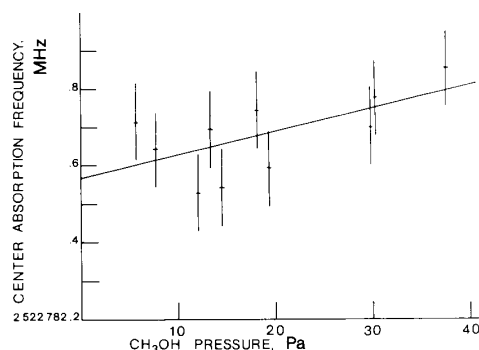


Fig. 5. Pressure shift of the 118.8 μm transition as directly measured in absorption.

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 CH₃OH lasing transition at 170.6 μm 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 μm line as the 119 μm 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 μm transition has the same upper level as the 119 μm transition, shifts similar to those of the 119 μm 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 μm line, in support of measurements in [3].

The frequency of the 119 μm transition extrapolated to "zero pressure" is 2 522 782.567 (65) MHz and is con-

sistent 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^{-7} . In comparison, we have found the reproducibility of transversely pumped FIR lasers to be about 2×10^{-7} . 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 ν_3 state of CH_3F [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 TEM_{00} 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 CO_2 laser emissions used to synthesize the FIR radiation in the TuFIR apparatus ($^{13}\text{CO}_2$, 9R22 and CO_2 , 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 metric 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

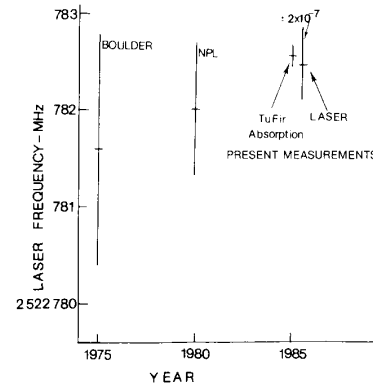


Fig. 6. Comparison of the frequency measurements reported for the CH_3OH transition at 118.8 μm . The higher accuracy of the present measurement from the laser output mainly originates from the use of a transverse optical pumping scheme. The direct absorption measurement yields a value accurate to better than one part in 10^7 .

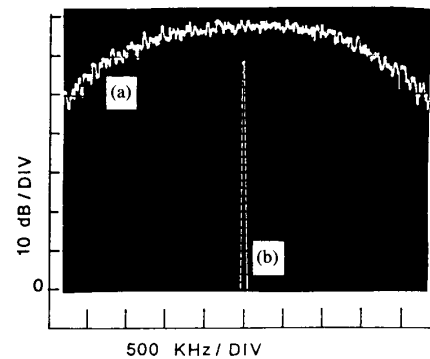


Fig. 7. New measurement of the CH_3OH 118.8 μm frequency using the laser. In (a) the symmetric tuning curve chosen for the measurement is shown. In (b), the beat note from mixing the laser output with two CO_2 lasers is shown. The recording in (a) is obtained by scanning the FIR cavity and storing the maximum heterodyne signal.

measurement under optimized conditions and at a pressure of 30 Pa, obtaining a frequency value of 2 522 782.464(220) 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.

The frequency of the laser output now determined under controlled and optimized conditions of operations is accurate to $\pm 2 \times 10^{-7}$ and is in agreement with the precise value obtained from TuFIR absorption spectroscopy. The spread of the frequency values at different pressures of operation is constrained within a few hundred kHz and the reproducibility of the measurements is well within two parts in 10^7 . 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, $\pm 5 \times 10^{-7}$.

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_3OH 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} .

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