Accurate Frequency of the 119 \textmu m Methanol Laser from Tunable Far-Infrared Absorption Spectroscopy

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Abstract—We report on high accuracy absorption spectroscopy of CH$_3$OH in the far infrared. In addition to 22 transitions in the ground state, we have measured the frequency of the $(n, r, J, K)$, $(0, 1, 16, 8) \rightarrow (0, 2, 15, 7)$ transition in the $P_2$ excited vibrational level, which is responsible for the laser emission at 119 \textmu m. The measured frequency is 2 522 782.57(10) MHz at "zero pressure," with a pressure shift of 6.132 kHz/Pa (0.808420 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 \textmu m 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 ($\pm 2 \times 10^{-10}$) 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 resitivity 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 \textmu m to 1 mm with frequency accuracies of a few parts in $10^7$. 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 \textmu m 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$_3$OH. The second apparatus used a CH$_3$OH optically pumped laser with transverse pumping used for the remeasurement of the frequency of the 119 \textmu m 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 CO_2 lasers I and II are frequency stabilized using the saturated fluorescence technique [6]. Optooptic 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. CH_3OH 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 CO_2 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 CO_2 reflector. The CO_2 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 CO_2 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 CH_3OH 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 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 1 we explored a pressure region up to about 50 Pa, and 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 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 4.14 kHz/Pa (0.540 MHz/torr). To our knowledge this is the first measurement of a pressure shift on a CH_3OH 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 p_2 = 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 1** | **LIST OF SOME OF THE CH_3OH GROUND STATE ABSORPTION LINES OBSERVED BY THE TUNABLE FAR-INFRARED SPECTROMETER. FOR REFERENCE, THE LESS ACCURATE DATA FROM FOURIER TRANSFORM SPECTRA ARE ALSO REPORTED.** |
| **TuFIR Measurements** | **FTS1** | **FTS2** |
| (MHz) | (cm^{-1}) | (MHz) | (cm^{-1}) | (MHz) | (cm^{-1}) |
| 1) 1 | 912,108,366 | 50 | 30,426 | 912,424 | 50 | 30,425 |
| 2) | 999,146,100 | 50 | 30,390 | 999,390 | 50 | 30,390 |
| 3) | 1,154,172,612 | 50 | 38,490 | 1,154,490 | 50 | 38,490 |
| 4) | 1,154,185,212 | 50 | 38,494 | 1,154,494 | 50 | 38,494 |
| 5) | 1,154,196,677 | 50 | 38,499 | 1,154,499 | 50 | 38,499 |
| 6) | 1,154,226,377 | 50 | 38,500 | 1,154,500 | 50 | 38,500 |
| 7) | 1,154,219,249 | 150 | 38,567 | 1,154,567 | 150 | 38,567 |
| 8) | 1,154,229,066 | 150 | 38,567 | 1,154,567 | 150 | 38,567 |
| 9) | 1,154,945,650 | 50 | 39,759 | 1,154,759 | 50 | 39,759 |
| 10) | 1,154,712,231 | 100 | 39,712 | 1,154,712 | 100 | 39,712 |
| 11) | 1,154,397,366 | 50 | 45,036 | 1,154,036 | 50 | 45,036 |
| 12) | 1,154,377,975 | 50 | 45,040 | 1,154,040 | 50 | 45,040 |
| 13) | 1,154,325,000 | 50 | 45,026 | 1,154,026 | 50 | 45,026 |
| 14) | 1,154,277,477 | 50 | 45,040 | 1,154,040 | 50 | 45,040 |
| 15) | 1,154,244,366 | 50 | 45,036 | 1,154,036 | 50 | 45,036 |
| 16) | 1,154,247,161 | 50 | 45,036 | 1,154,036 | 50 | 45,036 |
| 17) | 1,154,947,730 | 50 | 45,026 | 1,154,026 | 50 | 45,026 |
| 18) | 1,154,945,900 | 50 | 45,036 | 1,154,036 | 50 | 45,036 |
| 19) | 1,154,420,114 | 100 | 63,366 | 1,154,366 | 100 | 63,366 |
| 20) | 1,154,426,415 | 100 | 63,366 | 1,154,366 | 100 | 63,366 |
| 21) | 1,154,161,010 | 50 | 85,075 | 1,154,075 | 50 | 85,075 |
| 22) | 1,154,173,316 | 50 | 85,075 | 1,154,075 | 50 | 85,075 |
Fig. 1. Pressure broadening of CH$_3$OH ground state transition at 999.416.1 MHz (line 2 in Table 1).

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 CH$_3$OH $v_6 = 1$ 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 CH$_3$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-
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 mea-
surement is $5 \times 10^{-7}$. In comparison, we have found
the reproducibility of transversely pumped FIR lasers to be
about $2 \times 10^{-7}$. 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 com-
parison of that laser frequency with the present TuFIR
measured frequency is illustrated in Fig. 6.

The frequencies of methanol of the 119 $\mu$m line cannot
be computed a priori to an accuracy better than the laser
frequency measurement. However, recent measurements
were reported in the excited $v_3$ state of CH$_3$F [17], but in
that case the frequency was lower than 1 THz and the
molecular constants [18] are very precise for that mole-
cule 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 fre-
cuency could also be caused by Raman effects or multi-
mode 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 con-
focal 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 ($^{13}$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 fre-
cuency 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 $\Omega$, typical for this diode [19].
The entire tuning curve could be recorded by means of micro-
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 mea-
surements 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 in-
tracavity 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 re-
ported in [20]. We have repeated the center frequency
measurement under optimized conditions and at a pres-
sure of 30 Pa, obtaining a frequency value of
2 522 782.464 (220) MHz (two standard deviations). Re-
peating the same procedure for different pressures in the
range 11–40 Pa, we observed maximum frequency dif-
fences of about 300 kHz which is consistent with the
TuFIR absorption spectroscopy measurements of the fre-
cuency shifts shown in Fig. 5.

The frequency of the laser output now determined un-
der controlled and optimized conditions of operations is
accurate to $\pm 2 \times 10^{-7}$ and is in agreement with the pre-
cise 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 pump-
ing scheme used in that apparatus; however, it was in
agreement within the reported uncertainty, $\pm 5 \times 10^{-7}$. 

Fig. 6. Comparison of the frequency measurements reported for the
CH$_3$OH transition at 118.8 $\mu$m. The higher accuracy of the present mea-
surement from the laser output mainly originates from the use of a trans-
verse 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$_3$OH 118.8 $\mu$m 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.
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


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