

New experimental methods in Terahertz spectroscopy

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ABSTRACT

Spectroscopic studies are useful in a range of areas, from remote sensing and radio astronomy to the medical community. Since spectroscopy can provide information used to identify chemicals, new techniques have been developed for high-resolution measurements of chemical absorption frequencies. These high-resolution measurements not only enhance accuracy of the molecule's energy level transitions, but also allow for environmental information to be gathered through collisional broadening of the spectral lines. High-resolution measurements, made possible by far-infrared lasers coupled with Schottky diodes, were supplemented with data taken by variable pathlength FTIR measurements in the terahertz region. Chemicals investigated include methanol, nitromethane, water and its isotopes.

Keywords: Terahertz, FIR, side-band generation, spectroscopy

1. INTRODUCTION

Spectroscopic studies are useful in a range of areas, from remote sensing and radio astronomy to the medical community. [1-3] From these studies a wealth of information can be gathered and used to identify specific molecules. Techniques such as Fourier transform infrared (FTIR) spectroscopy can provide a wide range of frequency data and allow a broad analysis of the absorption frequencies of a particular molecule at reduced resolution. Although FTIR measurements lack the resolution to clearly separate and identify molecular transitions, they can still help quickly identify the best range of frequencies for higher resolution techniques to study in better detail.

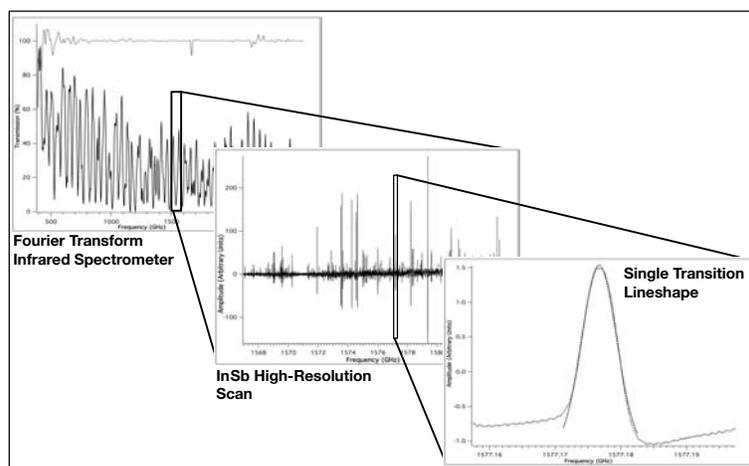


Figure 1: Examples of data collected using the methods outlined in this paper. The top graph is data collected using an FTIR spectrometer, the middle graph shows data collected using an indium antimonide detector, and the bottom graph represents the level of detail that can be achieved using an FIR laser in conjunction with a Schottky diode.

Figure 1 shows the spectral signature of a molecular gas studied using low resolution to high resolution techniques. Absorption frequencies in methanol were measured from 0.3 THz to 3 THz by FTIR with a resolution of 3.6 GHz. Using the information gathered through FTIR measurements as an initial starting point, the absorption frequencies of methanol were remeasured at a higher resolution (100 kHz) using a far-infrared (FIR) laser in conjunction with a Schottky diode mixer. This measurement allows the complex spectra of methanol to be observed in a very fine manner. Figure 1 depicts the different levels of data collected using the methods outlined in this paper and shows the progressive increase in resolution used to observe the different absorption transitions and lineshapes. As we will describe below we were able to generate a tunable THz source by mixing the output of a stable THz laser and a tunable microwave signal in a Schottky diode. This allowed spectral measurements with a resolution equivalent to the laser linewidth and a potential tuning range of hundreds of GHz. This method allows accurate observation of molecular transition frequencies but provides no information regarding the environment of the molecule due to lineshape distortions resulting from the frequency modulation applied to the tunable microwave signal. In order to gather absorption frequencies as well as environmental information from a molecule's spectra a third experiment was constructed to look at individual absorption transitions at a resolution of 25 kHz. To study how the molecule behaves in different environments, the FIR laser and Schottky diode were constructed to look at single absorption transitions and monitor the molecule's pressure broadened lineshape using air from the surrounding laboratory. Collisional broadening measurements are useful to the remote sensing community as any molecule found at atmospheric pressures is subject to collisional broadening.

2. PART I - FTIR

2.1 Experiment

In this part of the experiment, the data were collected using a Bruker IFS 66v Fourier transform infrared (FTIR) spectrometer. The system had a variable pathlength gas cell from Pike Technologies mounted in the sample compartment. The FTIR was optimized for different frequency regions by selecting appropriate beamsplitters and bolometer filters. Figure 2 shows the experimental set-up.

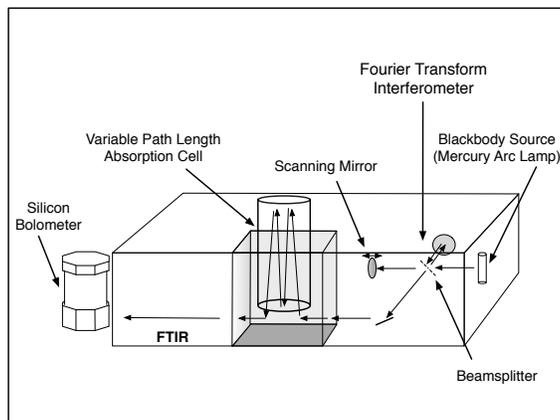


Figure 2: Experimental setup consisting of an FTIR spectrometer with a variable pathlength absorption cell in the sample chamber.

As detailed in a previous report [1], Figure 2 depicts the experimental setup. The alignment of the FTIR spectrometer was optimized to obtain a resolution of 3.6 GHz (0.12 cm^{-1}). The IFS 66v was equipped with a 125 Watt Mercury arc lamp as well as a $23 \mu\text{m}$ mylar beamsplitter for measurements from 400 GHz to 2.6 THz. The variable pathlength gas cell has non-wedged Z-cut quartz windows, 0.157 inches thick, to enable radiation below 6 THz to pass with little attenuation.

The absorption cell features an adjustable folded-path to achieve pathlengths ranging from 2 to 7 meters. The folded-path scheme also allows the base of the cell to fit within the sample chamber of the FTIR. The top of the gas cell extends outside of the FTIR. Therefore to remove the effect of absorption of the light beams moving

through the rest of the interferometer, we created an airtight seal between the gas cell and the interferometer interior and purged the beam path outside of the gas cell with dry nitrogen.

There are two additional ports extending from the top of the cell. One port connects to the vacuum pump used to evacuate the absorption cell. The other port is connected to the sample apparatus. The sample in this case was methanol obtained from Fisher Scientific at a purity of > 99%. Two MKS pressure sensors were used to monitor the sample gas pressure inside the cell.

2.2 Results

Preliminary test measurements were taken on methanol as shown in Figure 3, in black. In order to collect this data, 15.5 Torr of methanol was released into the absorption cell and the pathlength was adjusted to 3 meters before collecting the transmission spectra.

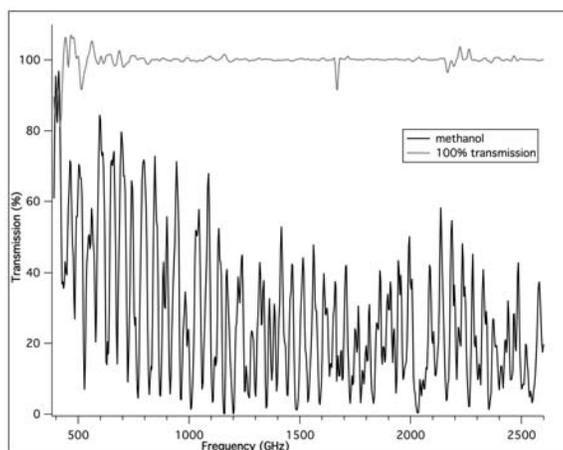


Figure 3: Absorption spectra of 15.5 Torr methanol, in black, measured at a 3 meter pathlength. For comparison purposes the 100% transmission line is shown in grey.

Figure 3 shows the periodic nature of the methanol spectra, though individual absorption lines cannot be resolved due to the limited resolution of the FTIR. For comparison, a 100% transmission spectra is shown in grey along with the methanol spectra. A 100% transmission spectra is produced when a background scan and a transmission scan are taken in succession without changing any parameters. The variations/rippling in the 100% transmission line are a product of low throughput signal wherein after taking a background scan and a transmission scan the small number is divided by another small number. Any variation between scans at these points results in a noticeable ripple of the 100% transmission line. Since some of the absorption lines measured were completely absorbing, such as those absorption frequencies at 1.156 THz, 1.2 THz and 2 THz, it was determined that subsequent measurements be performed at a reduced pressure.

Nitromethane was studied in a similar manner. Transmission spectra were measured every meter between 2 and 6 meters. Using data from measurements like those in Figure 3, the absorption coefficient of nitromethane was calculated at each data point using

$$T = I_o \exp^{-\alpha * L} \quad (1)$$

where T represents the normalized transmission from the FTIR at a specific pathlength, α is the absorption coefficient and L represents the pathlength. By using Eq. 1 to solve for α through a least squares fit, the absorption coefficient is determined for that wavenumber [4]. The absorption coefficients are graphed as a function of wavenumber as seen in Figure 4.

While the FTIR data cannot give detailed information about specific absorption lines due to the limited resolution, it does provide an indicator of where absorption lines lie for a given molecule. From this information it is possible to design an experiment at the appropriate frequencies to accurately measure a molecule's absorption lines.

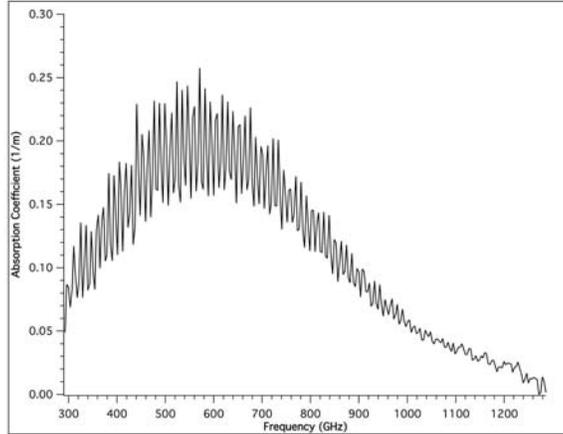


Figure 4: Absorption coefficient of 520 mTorr of nitromethane

3. PART II - SIDEBAND GENERATION

3.1 Experiment

Using the data collected from the FTIR spectrometer to determine general locations of methanol absorption frequencies, an experiment was designed to accurately measure the frequencies of individual absorption lines of methanol around 1.5 THz with a resolution of 100 kHz using the experimental setup shown in Figure 5. A grating tunable CO₂ laser with less than ± 0.5 MHz drift for days at a time [5] was used to optically pump the far-infrared (FIR) laser in order to produce the local oscillator (LO) frequency. Once the FIR laser has reached thermal equilibrium its drift is similar to the CO₂ laser's drift. The CO₂ laser was tuned to the 10R10 line in order to efficiently couple with the methanol (CH₃OH) lasing medium contained in the FIR laser. The methanol laser line has been measured to high accuracy, to within 100 kHz, and can be tuned around that frequency. A hole output coupler and a 6.72 mm inner diameter glass waveguide were used with the FIR laser [6-7].

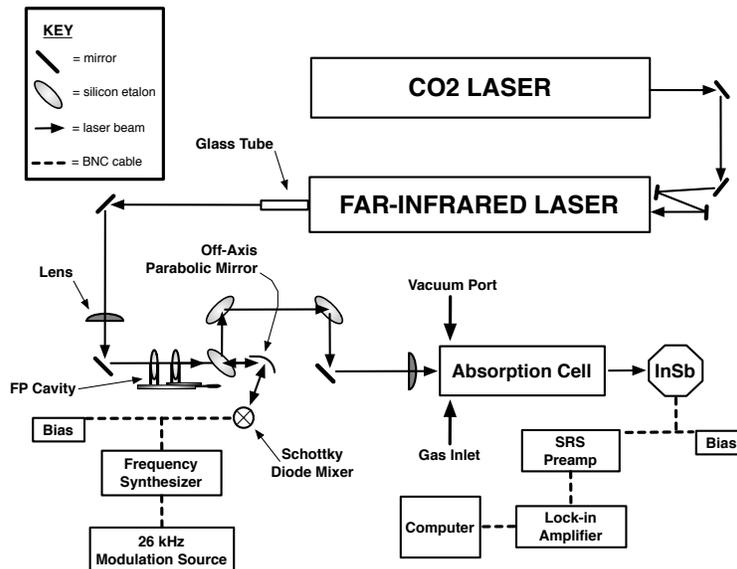


Figure 5: Diagram of experimental set-up for measurements of methanol absorption frequencies

The FIR laser beam was focused onto a corner-cube mounted, whisker contact, Schottky diode using an off-axis parabolic mirror. The Schottky diode acted as a frequency multiplier by harmonically multiplying the signal generated by the frequency synthesizer and combining this frequency comb with the FIR laser frequency

thus generating sideband frequencies [8-9].

$$\nu_{sideband} = \nu_{laser} + n\nu_{synth} \quad \text{where } n = \text{harmonic number} = \pm 1, \pm 2, \pm 3, \dots \quad (2)$$

With the frequency synthesizer it was possible to sweep through a range of frequencies. The linewidth of the microwave harmonics is small compared to the laser linewidth, therefore the sideband linewidth (and hence the spectral resolution) is limited by the linewidth of the laser (130 kHz). A 26 kHz frequency modulation was applied to the signal from the frequency synthesizer to filter out noise sources.

Silicon etalons were employed to separate the desired sideband frequencies from the unshifted laser frequency. The sideband frequencies were focused into a 1m long absorption cell to probe the methanol gas sample and the intensity was measured using an indium antimonide (InSb) detector.

The cryogenically cooled InSb detector was connected to a Stanford Research System (SRS) preamp, and the amplified signal was sent to the lock-in amplifier. The lock-in amplifier used the 26 kHz modulation as reference and was programmed to detect at twice the modulation frequency. By detecting at twice the modulation frequency the second derivative of the lineshape of the molecular absorption line was captured. The measured lineshape appeared to be Lorentzian.

3.2 Results

The spectra seen in Figure 6a is the result of many contiguous frequency scans each approximately 0.139 GHz wide with 1600 data points per scan. The scans overlapped in order to obtain uniform coverage over the 17 GHz

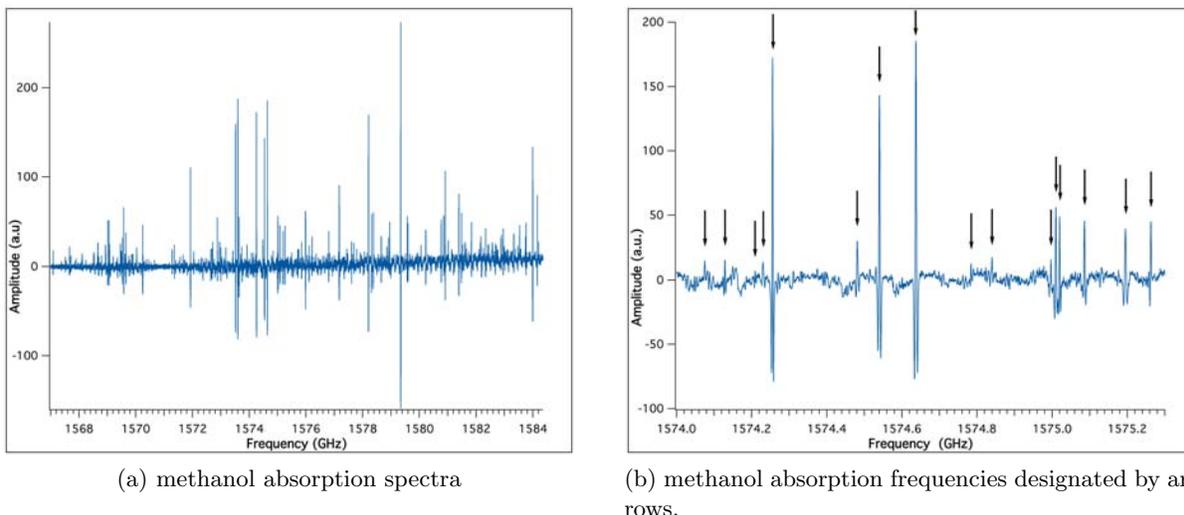


Figure 6: Absorption spectra of methanol measured using an InSb detector and sideband generation.

frequency range and resulted in a resolution of 87 kHz which is smaller than the spectral line width. Figure 6b is an expanded portion of the data shown in Figure 6a and demonstrates the density of the spectral lines collected in this measurement. The arrows seen in Figure 6b point to the methanol absorption frequencies.

A consequence of using this measurement technique is that multiple sideband harmonics are passed through the absorption cell. Therefore a difference technique must be applied in order to determine which harmonic, and therefore sideband frequency, an absorption line corresponds to. A small change in the microwave signal frequency, x , would result in a frequency difference of nx as a consequence of equation 2.

4. PART III - PRESSURE BROADENING

4.1 Experiment

While measurements from the experiment in Part II were able to accurately determine the absorption frequencies of methanol, they do not provide any information about the change in lineshape due to environmental factors,

such as pressure broadening. For this, the self and pressure broadening parameters must be determined in order to accurately measure the behavior of spectral lines under different conditions.

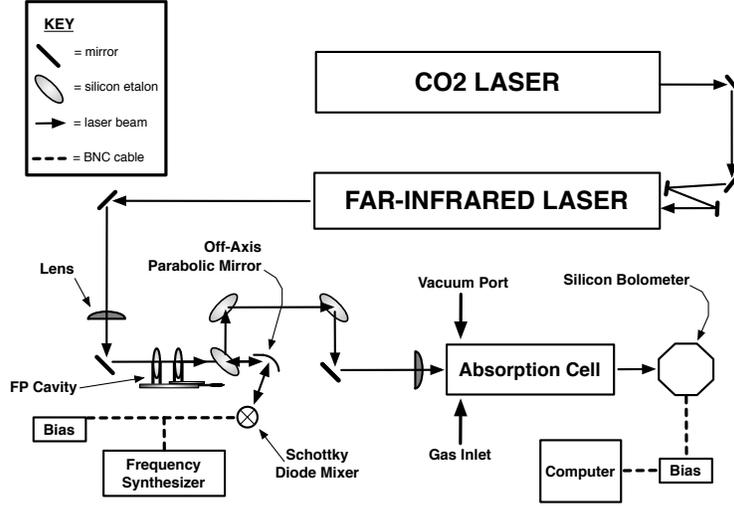


Figure 7: A diagram of the experiment used to measure the absorption frequencies of water and its isotopes as well as the pressure broadening coefficient of HDO.

Similar to the experiment outlined in Part II, an FIR laser was used to produce the local oscillator (LO) frequency. The CO₂ laser was tuned to the 9P22 line in order to efficiently couple with the difluoromethane (CH₂F₂) lasing medium contained in the FIR laser. Since difluoromethane can produce two different frequencies when pumped by the 9P22 CO₂ pump line, the FIR laser was equipped with a frequency selective uniform output coupler to suppress any competing laser transitions [7]. Initial measurements of the FIR laser frequency were carried out using a Fabry-Perot (FP) cavity. Figure 7 shows a diagram of the experimental set-up.

While the majority of this set-up is identical to the system shown in Figure 5, there are significant differences between the two. For example, no modulation was used in conjunction with the signal from the frequency synthesizer in order to preserve the undistorted lineshape. In the previous experiment a 26 kHz frequency modulation was employed to suppress baseline fluctuations in the detected signal. The detector used for this experiment was a cryogenically cooled silicon bolometer instead of an InSb detector due to the bolometer's increased sensitivity. The sideband frequency was then separated from the laser frequency using a series of silicon etalons and ultimately propagated through the absorption cell containing the sample gas. A resolution of 25 kHz was obtained.

4.2 Results

As a simple example, an H₂O absorption line was measured and is shown in Figure 8. This H₂O line was analyzed using the polynomial Lorentzian line profile equation:

$$f(\nu) = I_o \frac{\Delta\nu}{(\nu_o - \nu)^2 + \Delta\nu^2} + A + B\nu + C\nu^2 + D\nu^3 + E\nu^4 + F\nu^5. \quad (3)$$

From Eq. 3 the center frequency and full width at half maximum (FWHM) were extracted. Baseline fluctuations in the data, due to multiple cell reflections, required the use of the power series.

Prior to measuring the H₂O absorption line a well-known HDO absorption line (1.5771775638 THz) was measured and used as a calibration line. By measuring the HDO absorption frequency and adjusting subsequent frequency calculations the laser's drift can be accounted for. The H₂O absorption line was 815 kHz higher than the frequency predicted by the Hamiltonian governing an asymmetric rotor [10]. This discrepancy can be attributed to the rotational distortion of the molecule, which is not in the Hamiltonian. The difference in

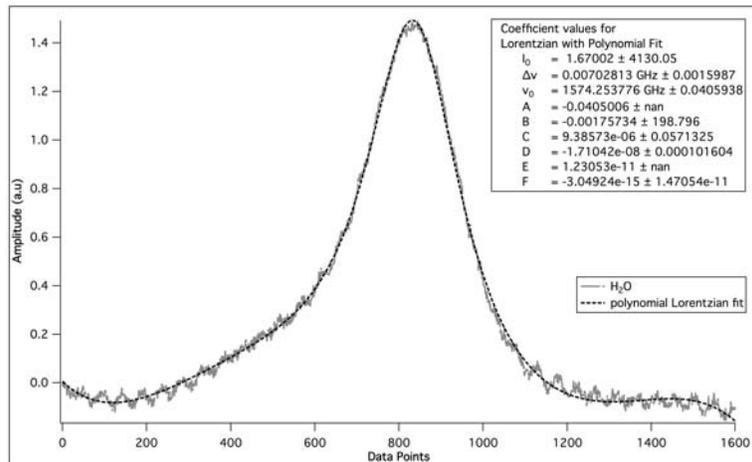


Figure 8: An H₂O absorption transition measured at 25 kHz resolution over a 40 MHz frequency sweep. A polynomial Lorentzian line profile equation was used to fit the absorption lineshape and obtain parameters such as absorption frequency and FWHM.

calculated and measured center frequency is 16 times the predicted calculated uncertainty of 50 kHz [11]. The FWHM of the H₂O absorption line was calculated to be 7 MHz.

Similar results were found in the measuring of the D₂O center absorption frequency. The D₂O absorption frequency was found to have a difference of 880 kHz from the predicted absorption frequency of 1547.931323 GHz [11]. This result is approximately 17 times the predicted calculated uncertainty of 50 kHz. Table 1 lists the predicted absorption frequencies from the JPL database [11] along with the absorption frequencies measured in this experiment.

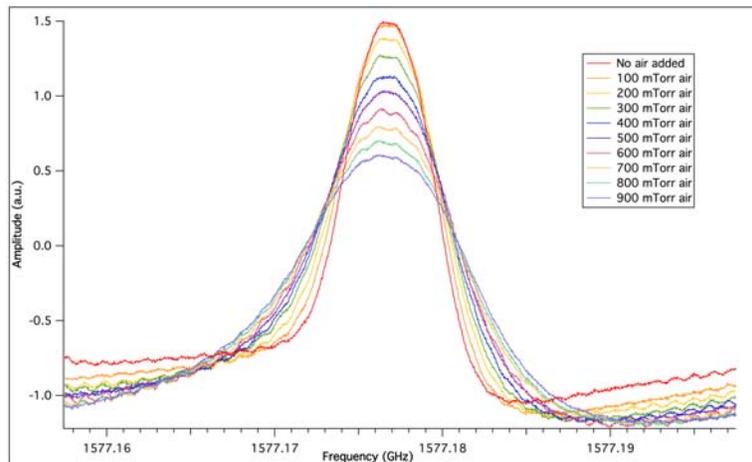


Figure 9: An HDO absorption transition measured with increasing amounts of air added to the absorption cell. From this data the air broadened half-width can be calculated.

Figure 9 shows an HDO absorption line change as 100 mTorr increments of laboratory air were added to the cell. As the pressure increased the linewidth increased while the peak intensity decreased. The linear relationship between the increasing pressure and absorption linewidth can be seen in Figure 10 and was found to increase at

Table 1: Absorption Frequencies and Pressure Broadening Coefficient of Water and its Isotopes

Molecule	Predicted Absorption Frequency [11] (THz)	Measured Absorption Frequency (THz)	Measured - Predicted (kHz)	Pressure Broadening Coefficient (FWHM)
H_2O	1.574232073	1.574232888	815	
HDO	1.5771775638	1.5771775638	0	0.0060682 $\frac{GHz}{Torr}$
D_2O	1.547931323	1.547932203	880	

a rate of 6 MHz (full-width at half-max) per Torr. The pressure broadening parameter

$$\gamma = \frac{v_{avg}\sigma}{2\pi kT} = \frac{\Delta\nu}{P} \quad (4)$$

where v_{avg} is the average particle velocity, σ is the collisional cross section and $\Delta\nu$ is the pressure broadened linewidth [12].

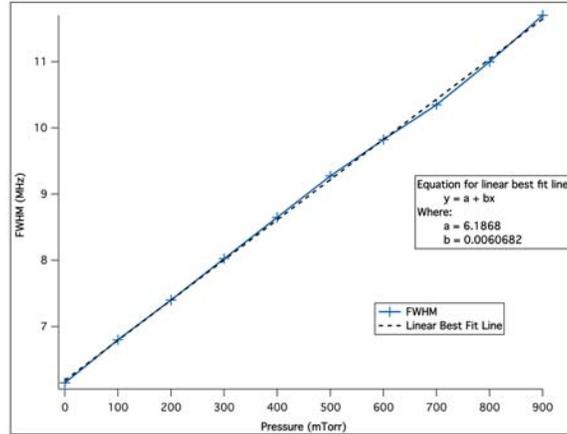


Figure 10: The FWHM data collected from the data shown in Figure 9 graphed against the pressure of air added to the absorption cell. From this, the air broadened half-width can be calculated.

5. DISCUSSION

The measurements from a random sampling of the methanol absorption frequencies presented in Part II have been corroborated with the frequencies listed in the JPL database for spectroscopic lines [11]. Most of the frequencies measured were within 550 kHz of the frequencies listed in the database. However, the absorption frequencies were found to be outside of the listed uncertainties [11]. These differences were only found for lines that had large uncertainties in the predictions. Further analysis is needed to correctly identify the transition frequencies shown in Figure 6a and assign them to the correct transitions by determining which sideband harmonic the transition belongs in.

Results from Part III have been compared with the information provided by the HITRAN database [13]. While the difference between the measured H_2O and D_2O absorption frequencies and those listed in the JPL database have been mentioned, it is of note that the HITRAN theoretical self-broadening parameter for the 1577.17760266578 GHz HDO absorption line is 0.00746 GHz/Torr (FWHM) and the self-broadening parameter presented here is 0.0060682 GHz/Torr (FWHM).

Future work will apply frequency sweeps, such as those employed in Part II, for measuring large numbers of lineshapes for pressure broadening in a single sweep. This change will make measurements of both absorption frequencies and line parameters more efficient as the current technique is to examine each line individually as was described in Part III.

6. CONCLUSION

Spectroscopic studies are useful to a range of applications and each application requires different types of information regarding the spectroscopic lines. Different methods for measuring spectroscopic lines, using an FTIR spectrometer or an FIR laser in conjunction with a Schottky diode mixer, were presented along with representative data collected from these systems. These measurements highlight the benefits of each spectroscopic system along with the type of data that can be collected from them.

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