Detecting Atmospheric DHO with a Spectroscopic THz Sensor

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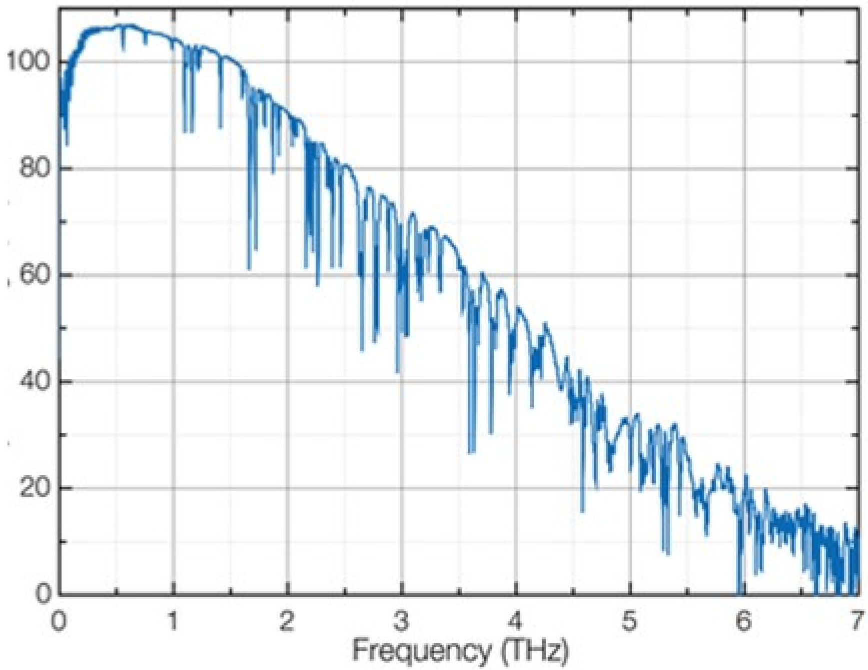
Motivation

- **Terahertz (THz) spectroscopy is a useful tool for gas analysis because robovibrational transitions for a large variety of molecules occur in this frequency domain**
- **The transitions are specific to each molecule and may be used to determine the concentration of different molecules**
- **Isotopologues have a significantly different spectrum**
- **Will allow monitoring, detection and identification of emissions with UAV based in-situ measurements. This includes measuring deviations from the natural DHO/H_2O ratio which may indicate unnatural heavy water production**
- **Finally, DHO is easy to work with. It is easy to obtain, economical, concentrations are easy to adjust because it is soluble in water, it is relatively harmless and the molecular transitions are in a spectroscopic H_2O window**

Problem



- Greater that 1 THz spectral range of interest
- Significant absorption by atmospheric H_2O
- Pressure broadened H_2O absorptions cover up most other gas signatures

In the sub-mm regime remote gas characterization and sensing through the atmosphere isn't a viable option

Point detection is required.

Our Solution

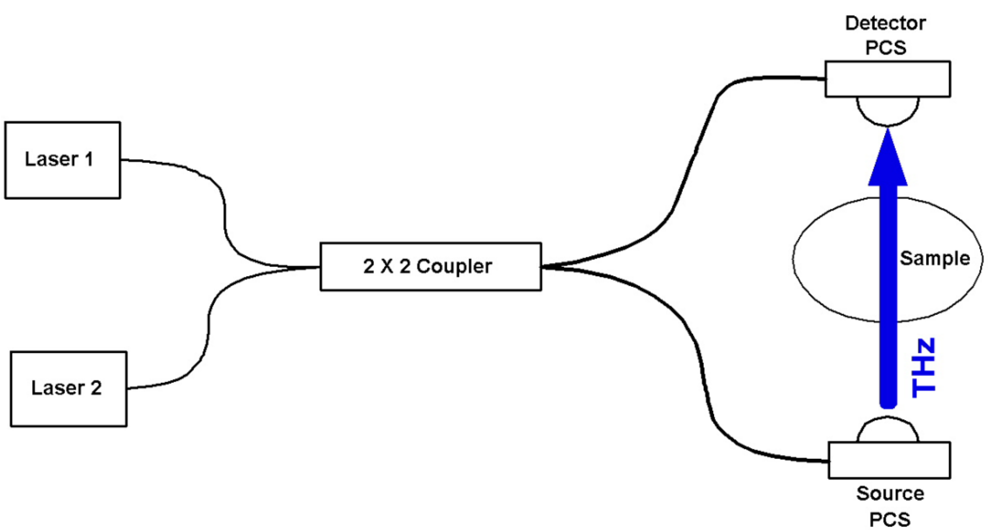
Perform the measurements *in situ*

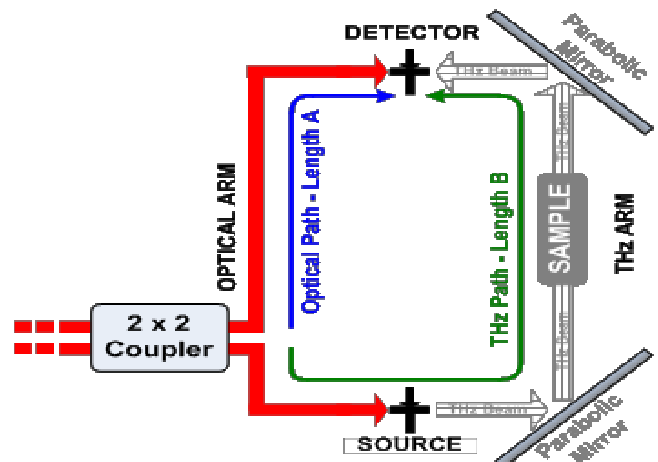
- Portable THz spectrometer weighing 3.5 kg with battery
- Attached to a consumer or commercial UAV
- No sample cell – 10 cm path-length of atmosphere

Stop by **Booth 243** to see our demonstration system flown over Paramount Ranch July 5th 2016 to measure water vapor concentrations

1st Generation Spectrometer

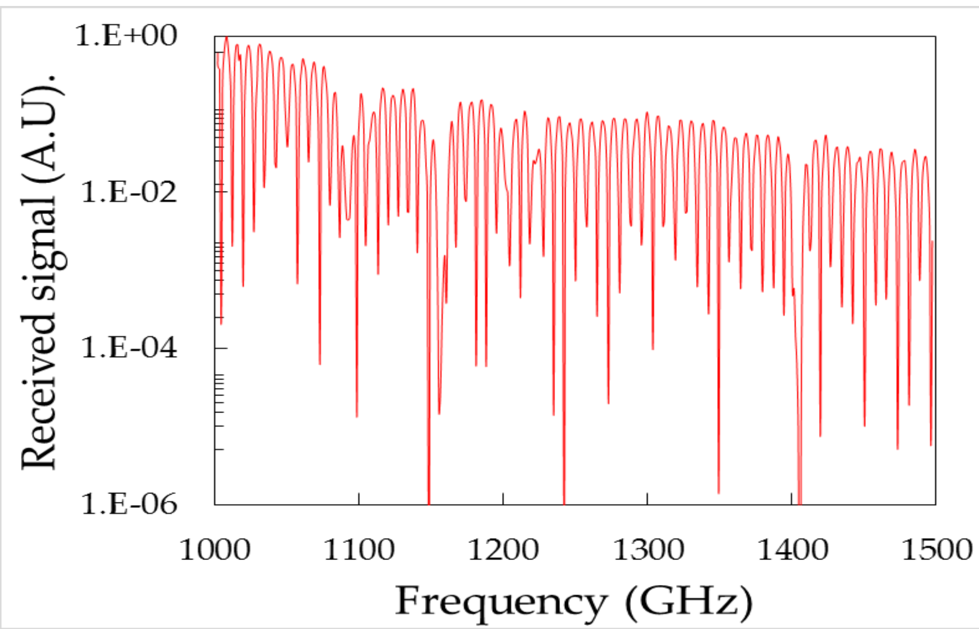
- Heterodyned semiconductor DFB lasers (780, 855 or 1550 nm).
- Photomixer conductivity is modulated at the difference frequency of the two lasers.
- Source photomixer antenna bias is chopped at 6 kHz.
- Chopped THz signal is detected on the receiver photomixer.
- Instrument is actually an interferometer with two path lengths.



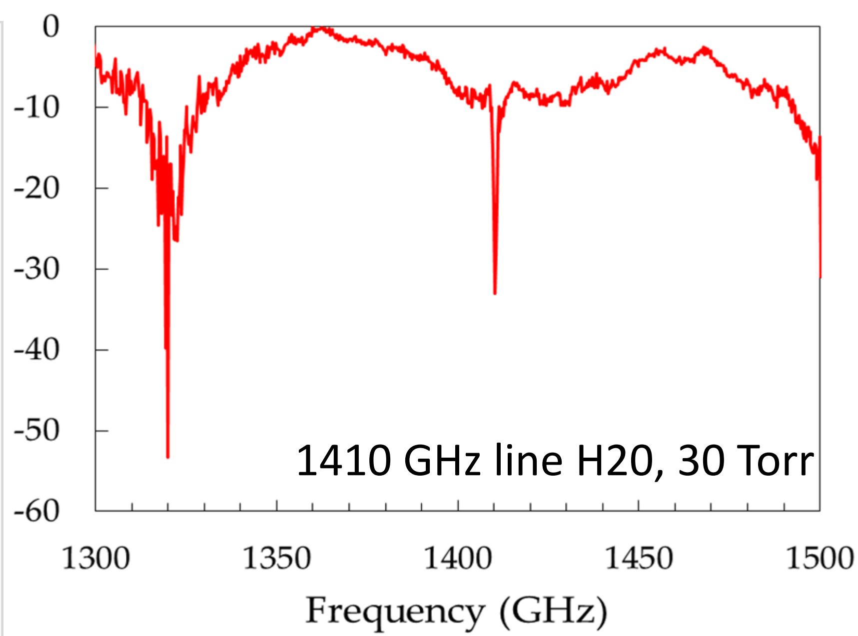


The Fringe

- **The path lengths can be adjusted to change the fringe spacing**
- **Source and detector moved apart or fiber lengths changed**
- **Pressure and temperature will also alter fringe spacing**

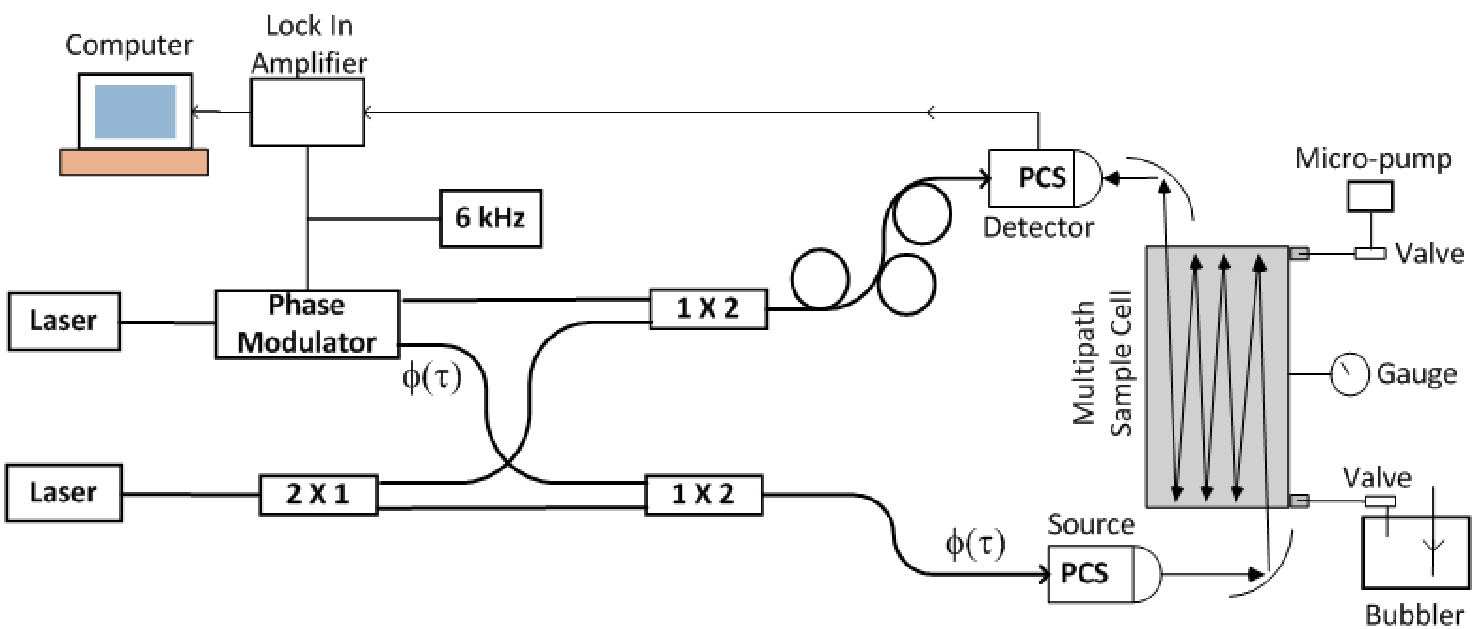


~ 14 fringes per 100 GHz



~2 fringes per 175 GHz

2^{nd} Generation Spectrometer

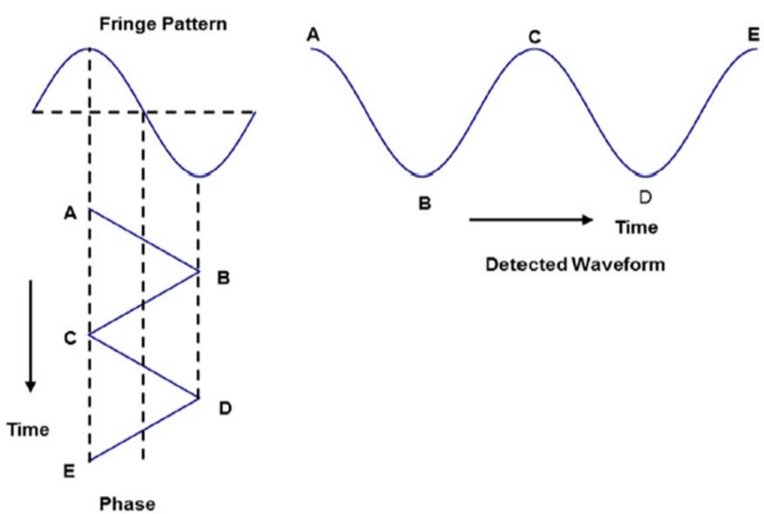


- **A phase modulation is applied to the optical signal feeding the source photomixer**
- **This results in an equivalent phase modulation on the propagating THz radiation**
- **The 1st and 2nd harmonics of the signal are detected when the fringe pattern converts the phase modulation into an amplitude modulation [1]**

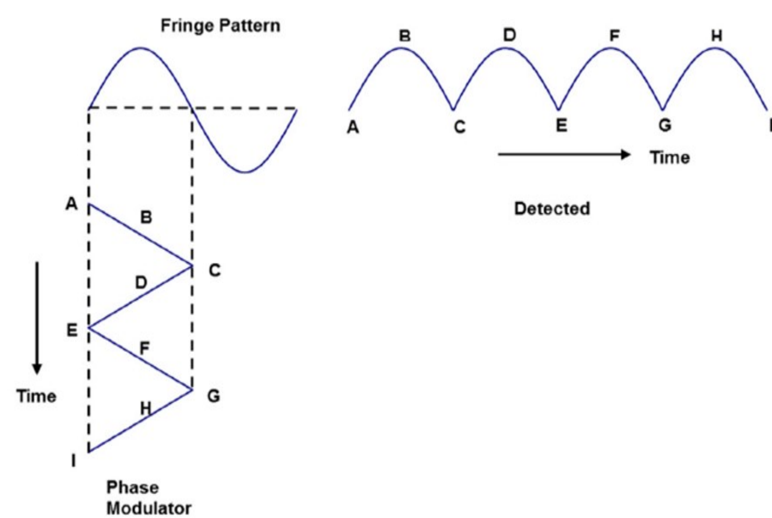
[1] Demers J R, Kasper B, and Daughton D R, "Simultaneous measurement of the 1st and 2nd harmonics of a phase-modulated coherent frequency-domain THz spectrometer," IRMMW-THz 2014, DOI: 10.1109/IRMMW-THz.2014.6956079.

Phase Modulation Illustrated

- **Applying a constant 6 kHz triangle wave to the phase modulator**
- **Freq with 90° phase difference at detector - 1st harmonic is max**
- **Freq with 0° phase difference at detector - 2nd harmonic is max**
- **Can either: record both harmonics and sum *or* apply a bias to continually suppress 2nd harmonic**

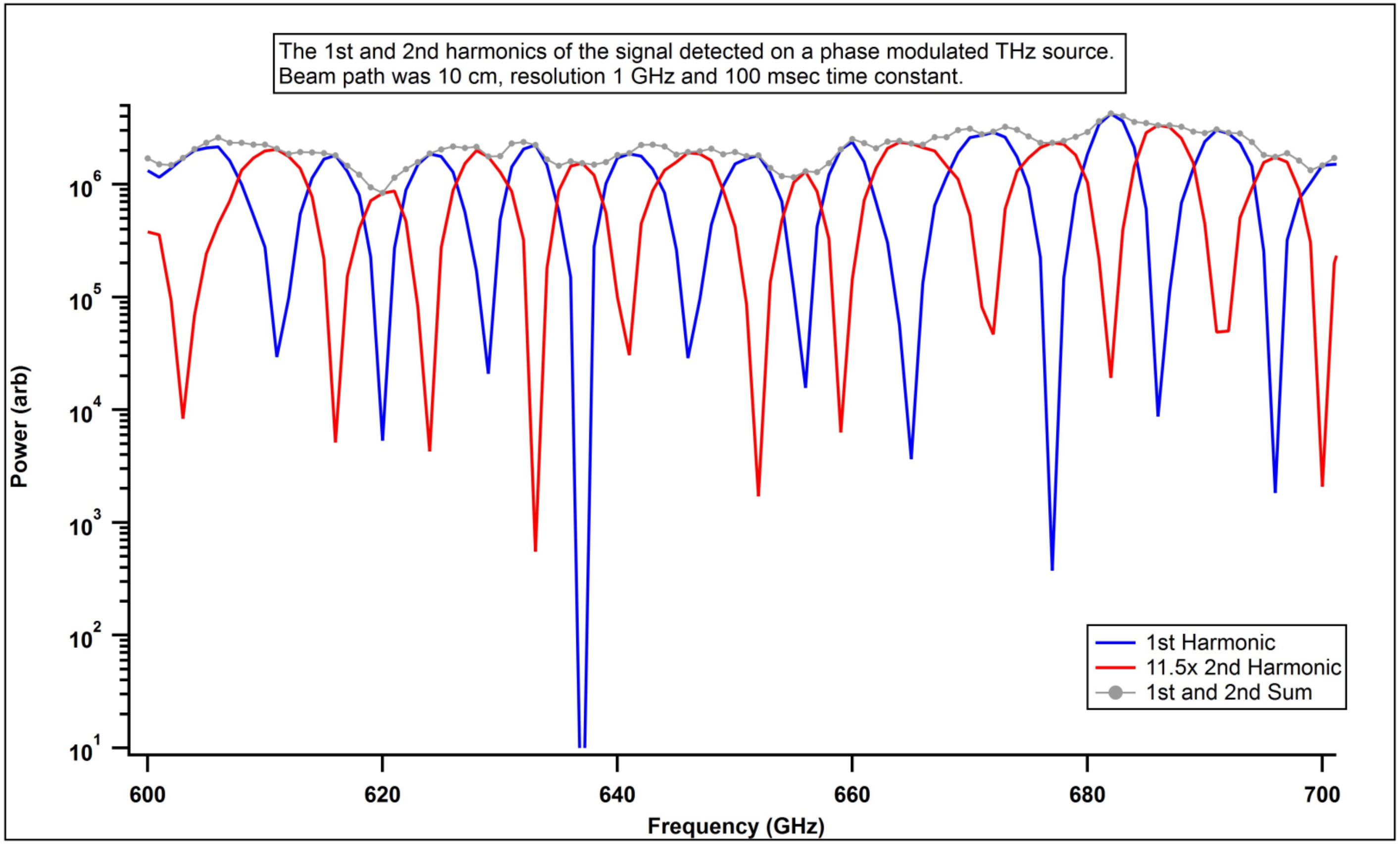


At 3dB point of fringe



At peak or null of fringe

PM Illustration



- **Each channel requires relative normalization**
- **2nd harmonic is lower by 11.5x (firmware issue)**

Multi-pass Sample Cell

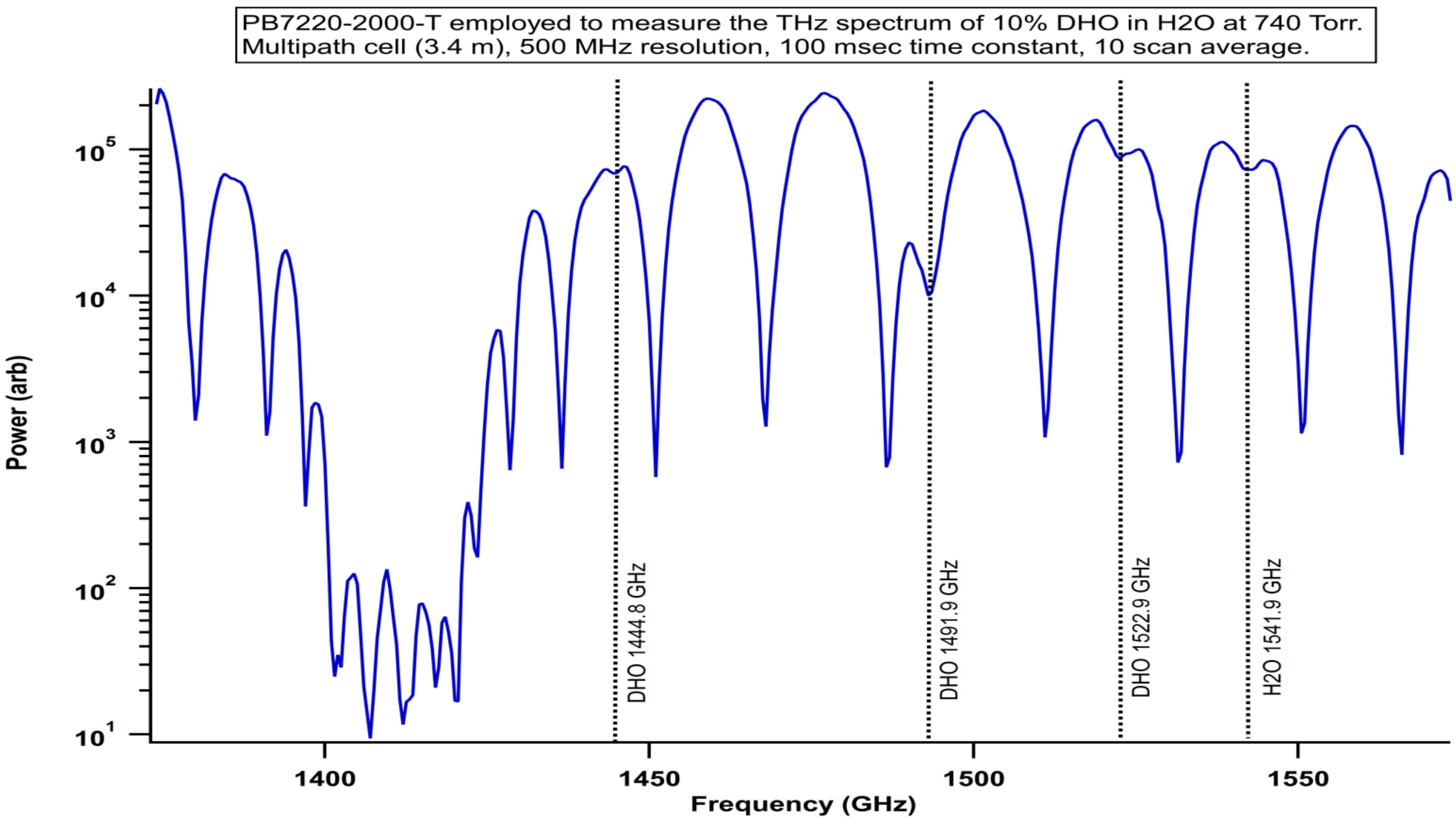
- **Simplest way to increase sensitivity is to increase sample path-length**
- **First article prototype:**
  - Dimensions: 36 cm x 20 cm x 8 cm
  - Mass: 4 kg including scroll vacuum pump
  - Pump vacuum limit: ~ 4 Torr
  - Maximum path-length: 500 cm
  - Too many screws!
- **Designed for more than 5 m path length - currently operating at 3.4 m**
- **Lowest pressure obtained was 100 Torr due to leaks.**

The Experiment

- **Fiber on phase modulator broke and we were forced to use a simple spectrometer with balanced arms**
- **After aligning the optics in the multi-pass cell, different fiber lengths were employed to produce a “good” fringe at STP. Fringe spacing was very sensitive to pressure and therefore we operated around 740 Torr**
- **Different concentrations of D_2O in tap water were created:**
  - **Assume complete dissociation of D_2O into 2 X DHO when mixed w H_2O***
  - **10% concentration DHO (10 ml D_2O with 190 ml H_2O)**
  - **1% concentration DHO (1 ml D_2O with 199 ml H_2O)**
  - **0.1% concentration DHO (10 ml 1% concentration into 90 ml H_2O)**
- **Room air was continually pulled through the bubbler and into the cell**
- **Less than 10 dB of loss coupling through multi-pass cell**

*** Not entirely accurate!**

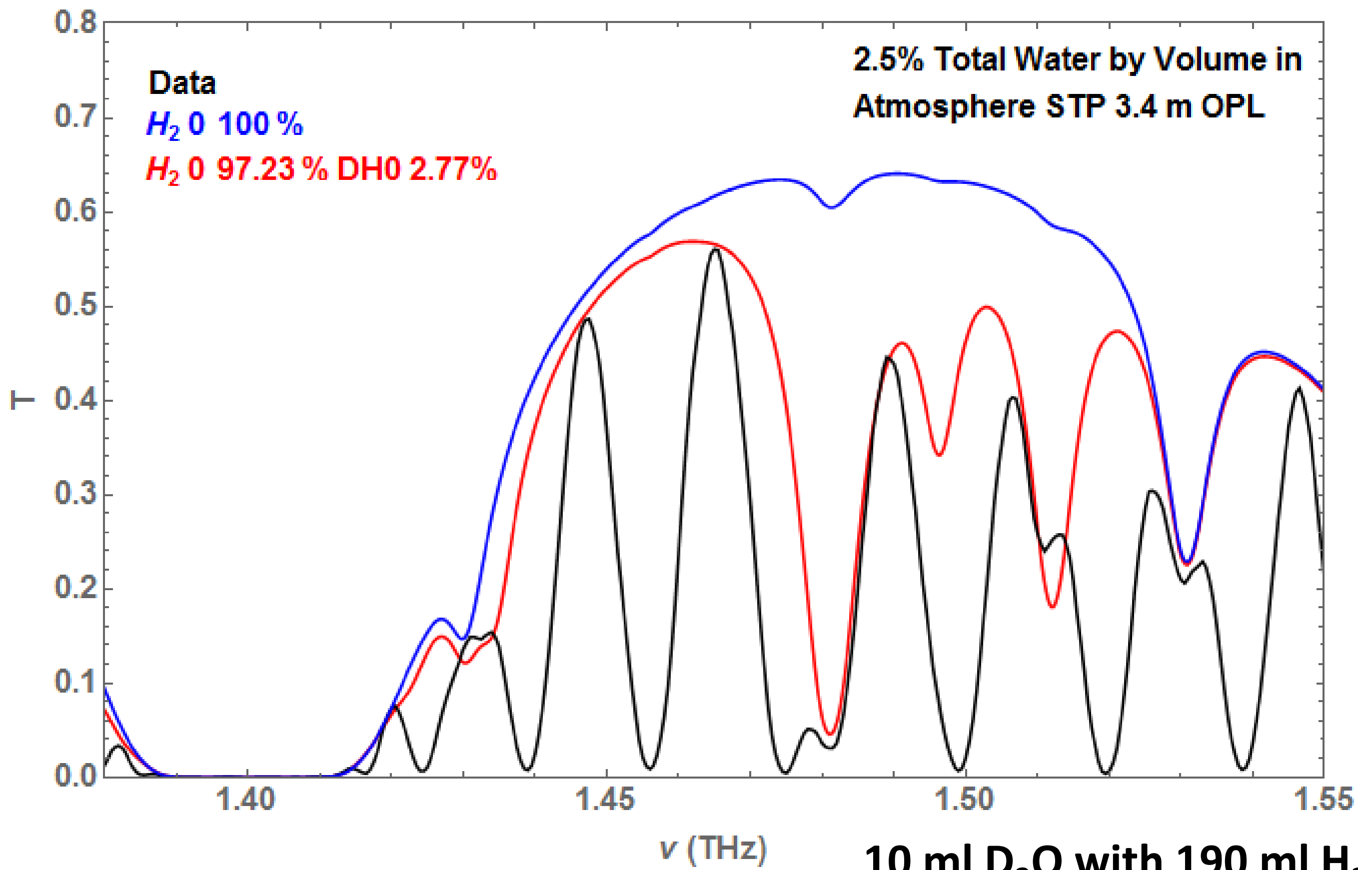
First Scan of 10% DHO



- **Saturated 1410 GHz H_2O absorption makes calibration tough, use 1541.9**
- **Adjusted pressure to "adjust" fringe spacing so DHO lines visible**
- **10 scan average with no smoothing**

10% DHO Data and Fit

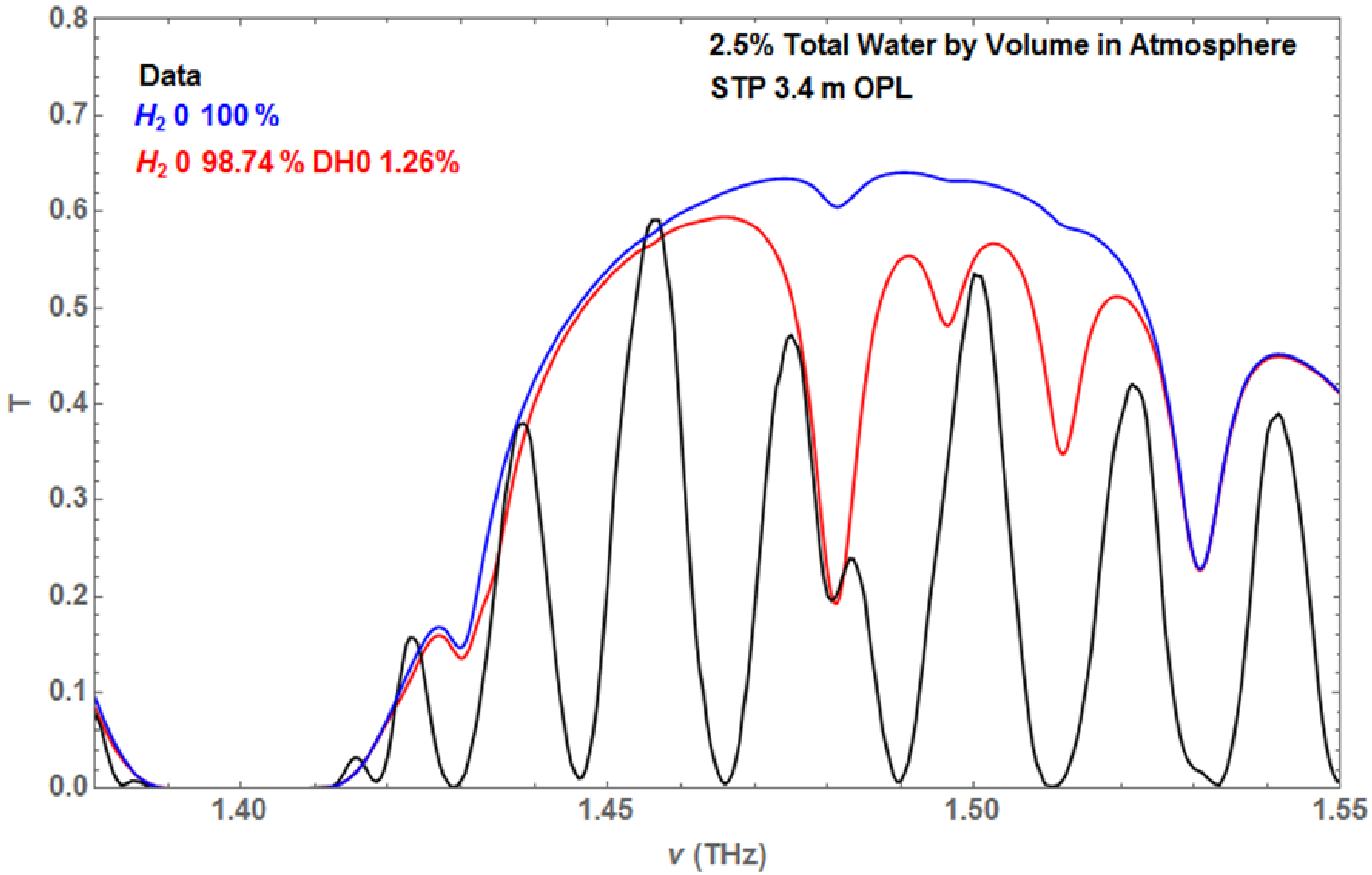
- **Hitran database used for theoretical fit**
- **Atmosphere is H_2O: 2.50%   DHO: 0.03% O_2: 20.00% N_2: 77.47%**
- **Best fit by eye because fringes make sigma calculations all but impossible**
- **Mixture percentages don't match theoretical fits**



10 ml D_2O with 190 ml H_2O

1% DHO Data and Fit

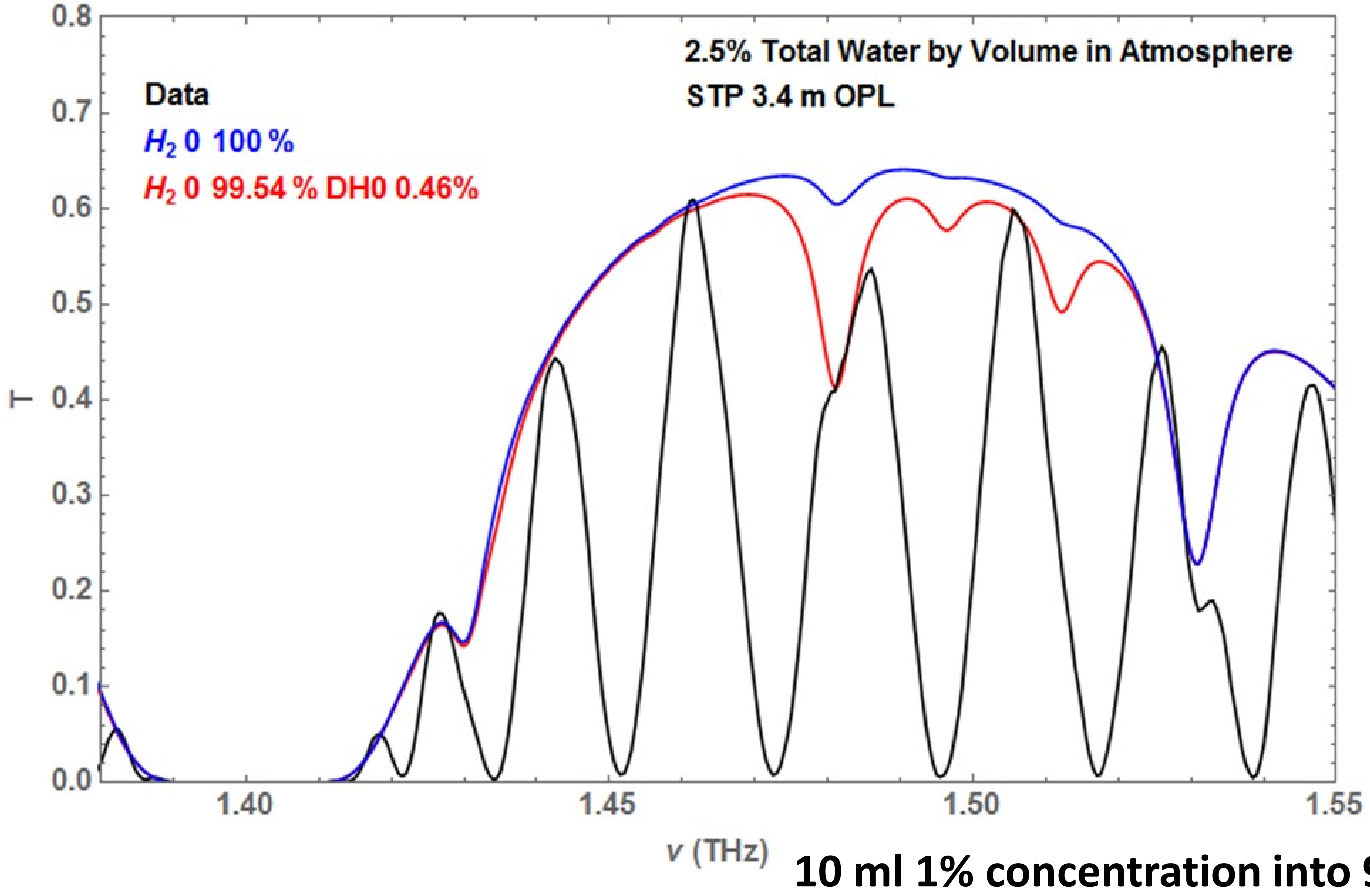
- **Close to mixture concentration**
- **Note the .031% DHO in the H2O theoretical line**



1 ml D_2O with 199 ml H_2O

0.1% DHO Data and Fit

- **Off from mixture concentration by a factor of 5x**
- **Fit is only using a single feature due to fringes**



10 ml 1% concentration into 90 ml H_2O

Conclusions

- We demonstrated a portable THz spectrometer with 3.4 meter multi-pass sample cell and detected 0.5% DHO in H_2O vapor
- From the theoretical plots of H_2O and signal SNR it seems that we should be able to measure 0.031% DHO
- Theoretical and mixture concentrations do not match for reasons that are not clear. Use of atmosphere feed may be to blame.
- Balanced arm approach ok for laboratory but likely not viable for real-world applications (we already knew this)
- Fiber lengths will need to be chosen for operation at a specific pressures
- Total spectrometer mass of 7.5 kg (w/ pump, battery and PC104) but we can do much better than this

Future Plans

- Implementation of phase modulation and 2nd harmonic detection for fringe removal – new phase modulator will arrive May 5th
- Determine if 2nd harmonic detection increases system sensitivity (i.e. improves SNR) and what detection levels are required
- A 3X increase in path length to improve detection sensitivity
- Use a dry nitrogen feed for the bubbler instead of an atmospheric feed. We may convert the bubbler to a lecture bottle of DHO
- Plan to perform measurements on other gases of importance
- Complete the development of the newer, higher speed instrument which is flight ready and has a total mass of under 5 kg (w/ pump and integrated computing)
- Lunch box-sized form factor to fit on much smaller UAVs

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