Characterization of a New Laser Isotopologue Hygrometer for Measurements of Isotopes in Cloud Water

Bryan Rainwater [1*], Adriana Bailey[2], Lance E. Christensen[3], Robert L. Herman[3], Darin W. Toohey [1]

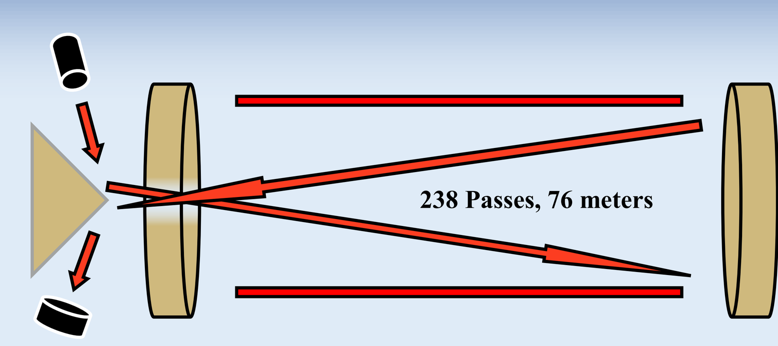
1. University of Colorado Boulder
2. National Center for Atmospheric Research
3. Jet Propulsion Laboratory

Observations of water isotopologues in clouds can play an important role in studies of cloud microphysical and dynamical processes that are important in the hydrological cycle, including elucidation of various aspects of the aerosol indirect effect. Among the challenges for obtaining observations in clouds are representative in-situ measurements of $HD^{16}O$, $H_2{}^{18}O$, and $H_2{}^{16}O$ with precision and accuracy that can both (1) track important changes, and (2) remain stable throughout the observation period over a wide range of atmospheric conditions. To address some of these observational challenges, we are developing a new laser isotopologue hygrometer suitable for in-situ aircraft measurements with provisions to reduce measurement drift, including during warm-up periods and cloud encounters. We have also developed new algorithms for fitting spectra obtained by lasers that measure pairs of water isotopologues simultaneously, thus improving measurement precision when water concentrations are changing rapidly during short-duration cloud penetrations. The instrument will be small, lightweight, and autonomous to allow for broad deployment on a variety of platforms. This presentation will focus on characterization of the precision of laboratory measurements of $H_2{}^{18}O/H_2{}^{16}O$ and $HD^{16}O/H_2{}^{16}O$ ratios at water mixing ratios expected in clouds, stability of the optics under realistic environmental conditions, and intercomparisons with a flight-ready Picarro water isotope analyzer. We will also discuss plans for future tests of an instrument on research aircraft.

$$\delta^a X = \left(\frac{{}^aR_{obs}}{{}^aR_{std}} - 1\right) * 1000$$

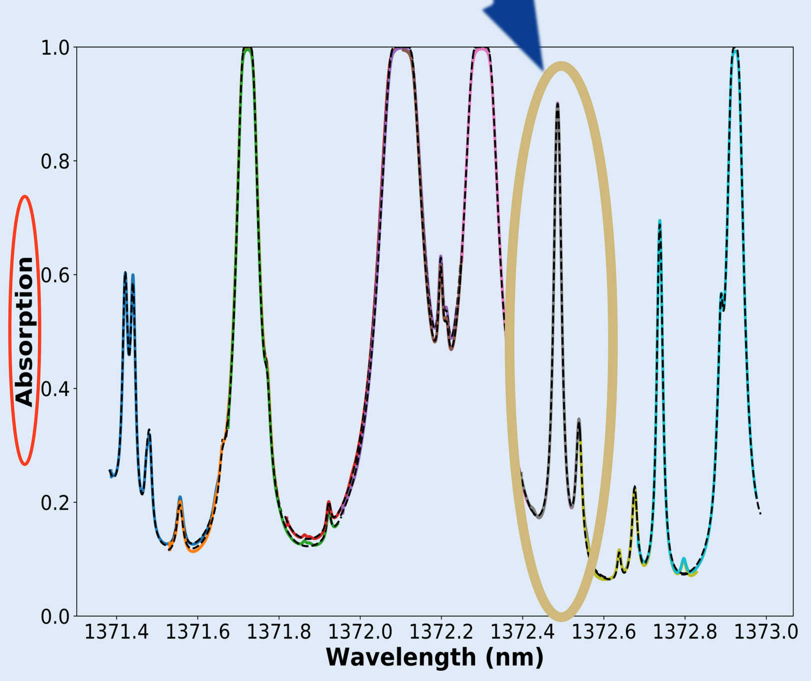
where $\quad {}^aR = \frac{{}^aX}{{}^bX}$

$H_2{}^{18}O/H_2{}^{16}O$ Line Pair



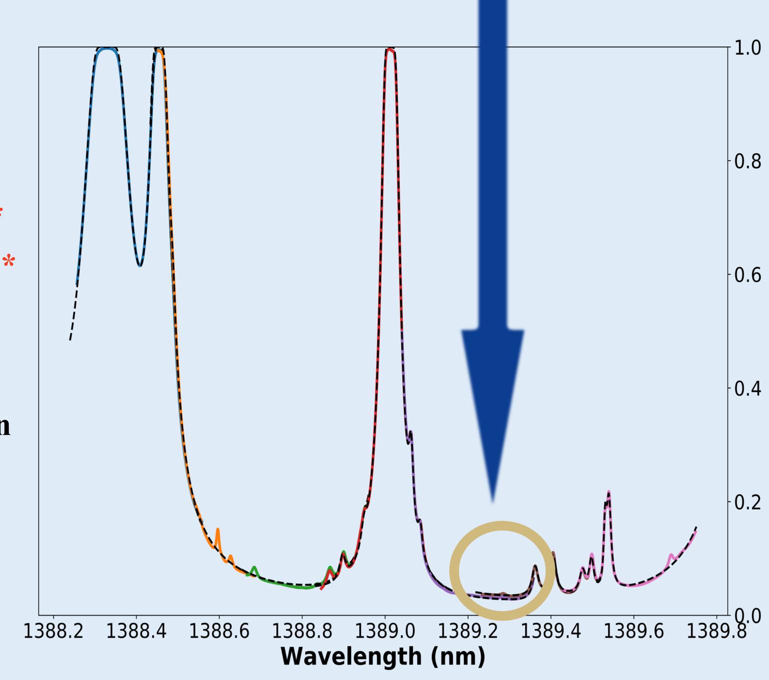
$HD^{16}O/H_2{}^{16}O$ Line Pair

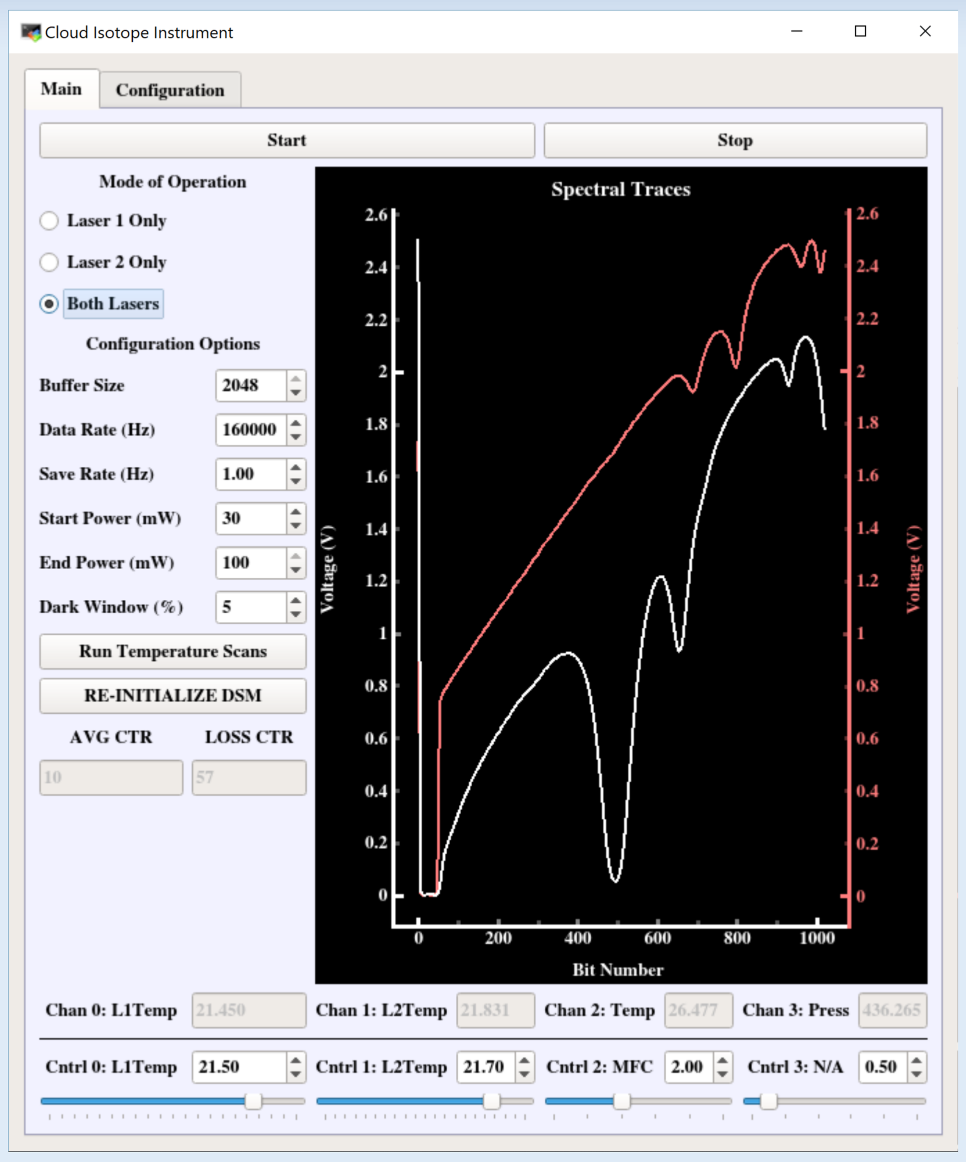
$$Abs = 1 - exp\left(-\frac{qPx}{kT}\sigma_v\right)$$



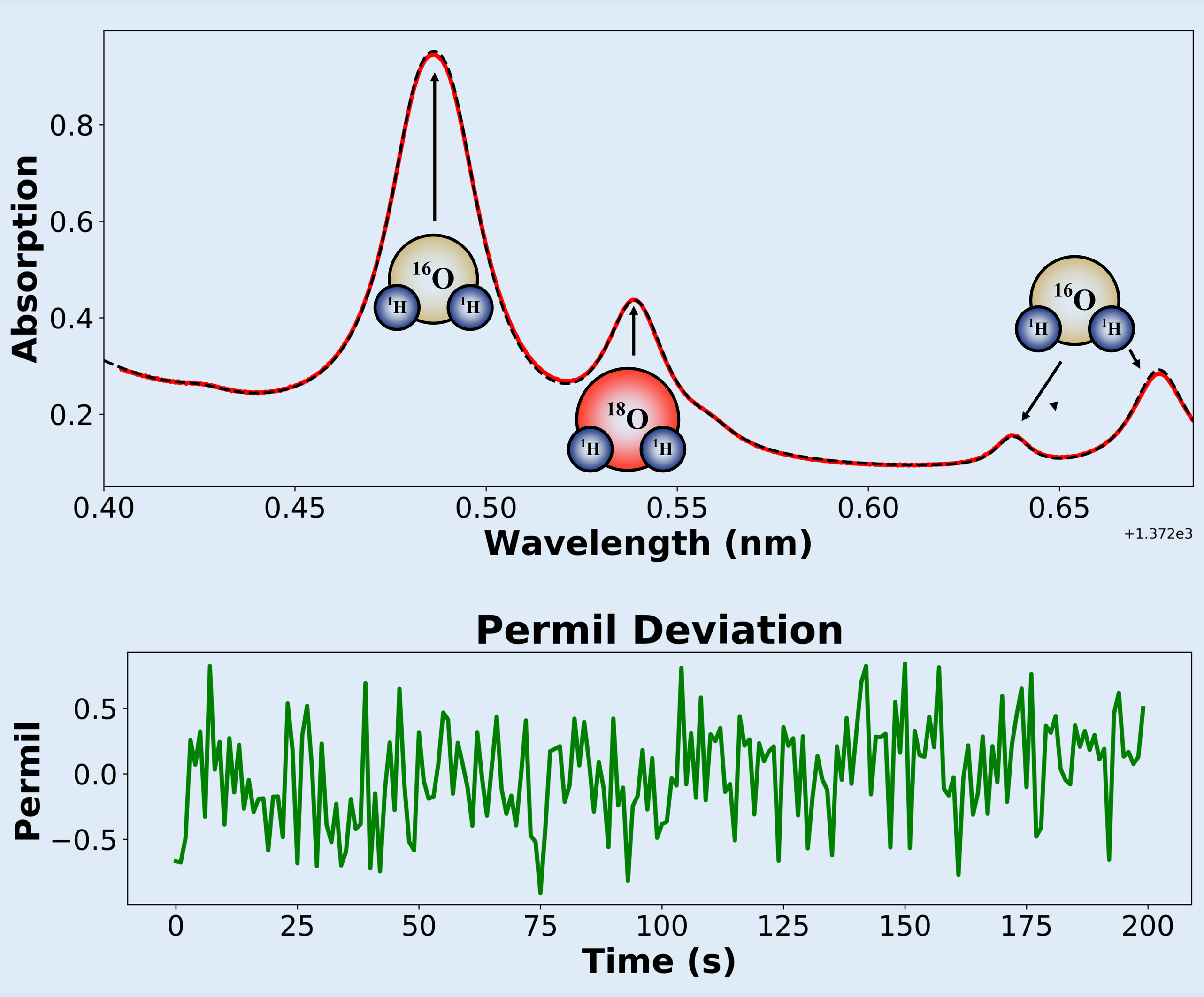
where
q = Mixing Ratio
P = Pressure*
x = Path Length*
T = Temperature*
k = Boltzmann's Constant*
σ = Absorption Cross Section

*Measured





$H_2{}^{18}O$ Scan

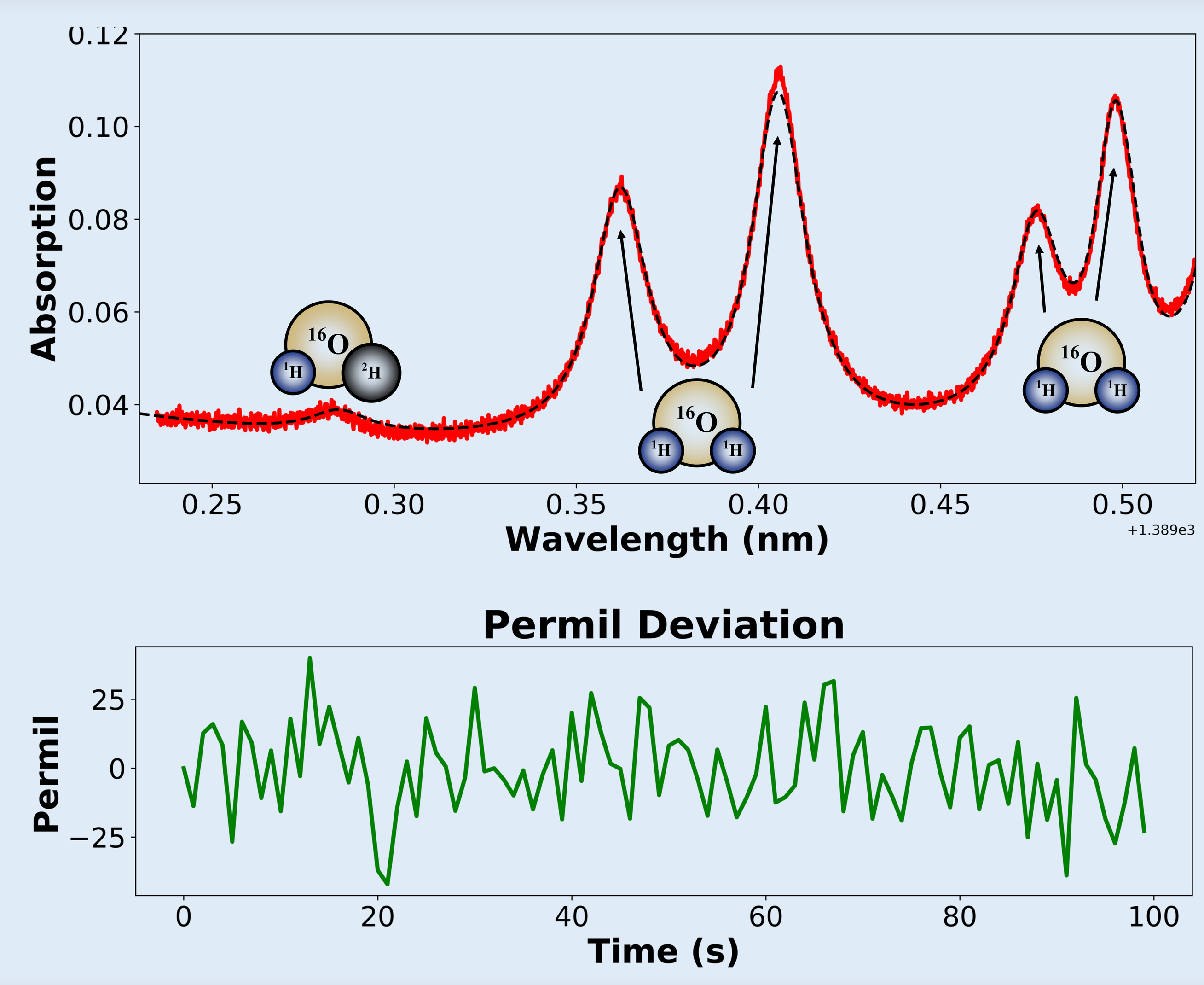


1 Hz Fractionation Precision Inter-comparison

Instrument	δ18	δD
Picarro (from data sheet)	0.15 ‰	0.5 ‰
Old System (HDO using 2.7um)	~0.3 ‰	~2 ‰
New System (1.3um for both)	~0.38 ‰	~16 ‰

*1 sigma standard deviations at approximately 15000 ppm and 400 hPa. Picarro reports 5Hz so precisions have been scaled by 2.25 for 1 Hz estimate.

HDO Scan



Conclusions & References

- New spectral codes are able to characterize the majority of the measurement range of both available lasers; however, mild discrepancies between calibrated measured environmental parameters and fit derived parameters will require further analysis.
- The new computer and electronics prove capable; however, work is necessary to reduce noise on the system to improve sensitivity of the HDO measurement to match previously attained results using the old system lost to hardware failure.
- The move away from 2.7um was based on cost of the lasers and the difficulty with dual laser setups and optics; however, the 2.7um signal strength advantage may justify the requirements.

I.E. Gordon, L.S. Rothman, C. Hill et al., "The HITRAN2016 Molecular Spectroscopic Database", J Quant Spectrosc Radiat Transfer 203, 3-69 (2017).

Future Work & Acknowledgements

- Add real-time fractionation approximation to interface using pseudo-Voigt spectral fitting.
- Complete spectral analysis of laser to reduce fitting degrees of freedom from 8 down to 3.
- Repair inherent artifacts in the new hardware that cause periodic pausing of data acquisition.
- Add temperature control and assess if pressure control will be necessary.
- Calibrate (if necessary) and assemble into flight ready package for sampling on aircraft.

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(970) 459 - 0179
***Bryan.Rainwater@colorado.edu**