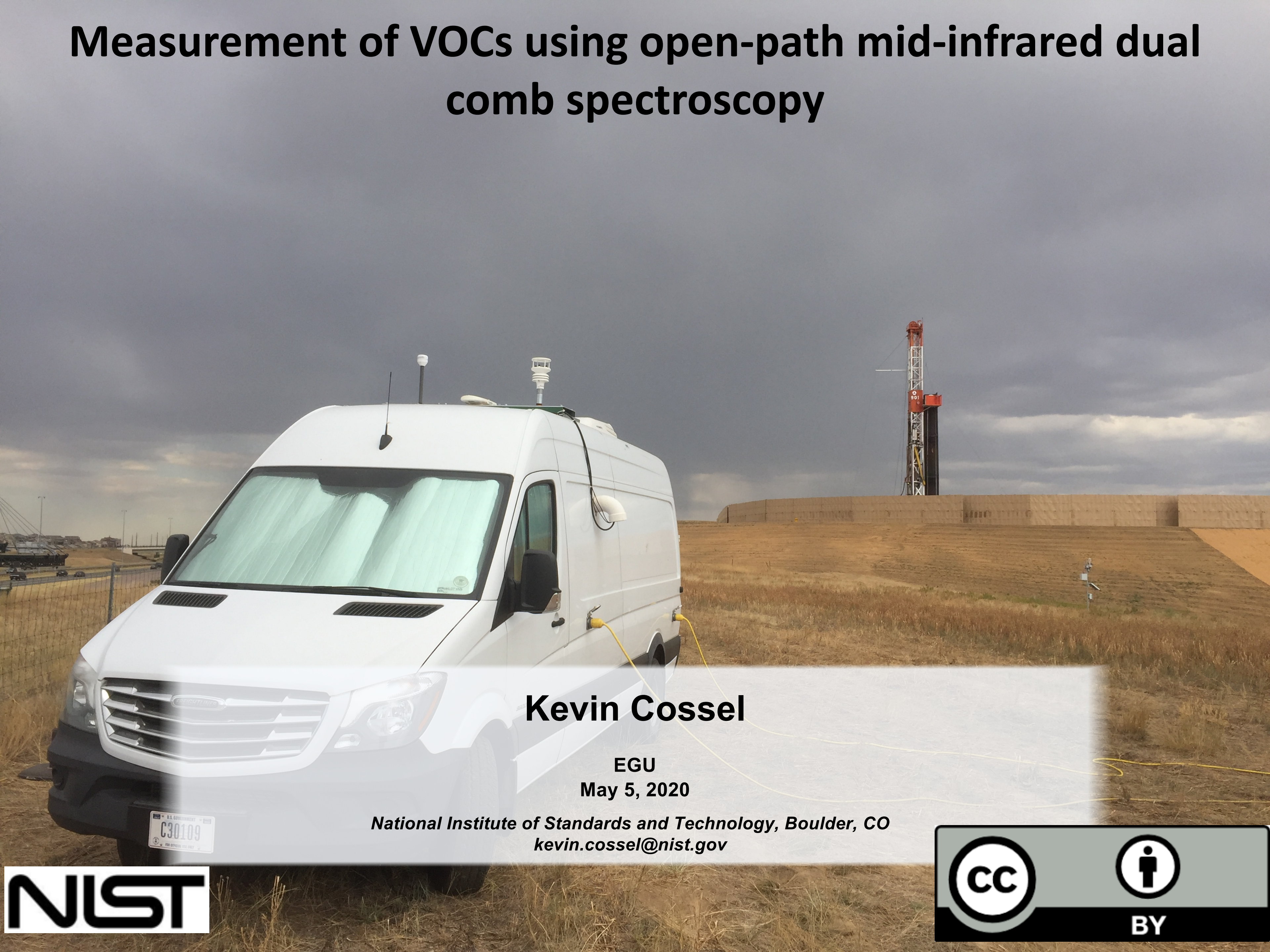

Measurement of VOCs using open-path mid-infrared dual comb spectroscopy

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EGU
May 5, 2020

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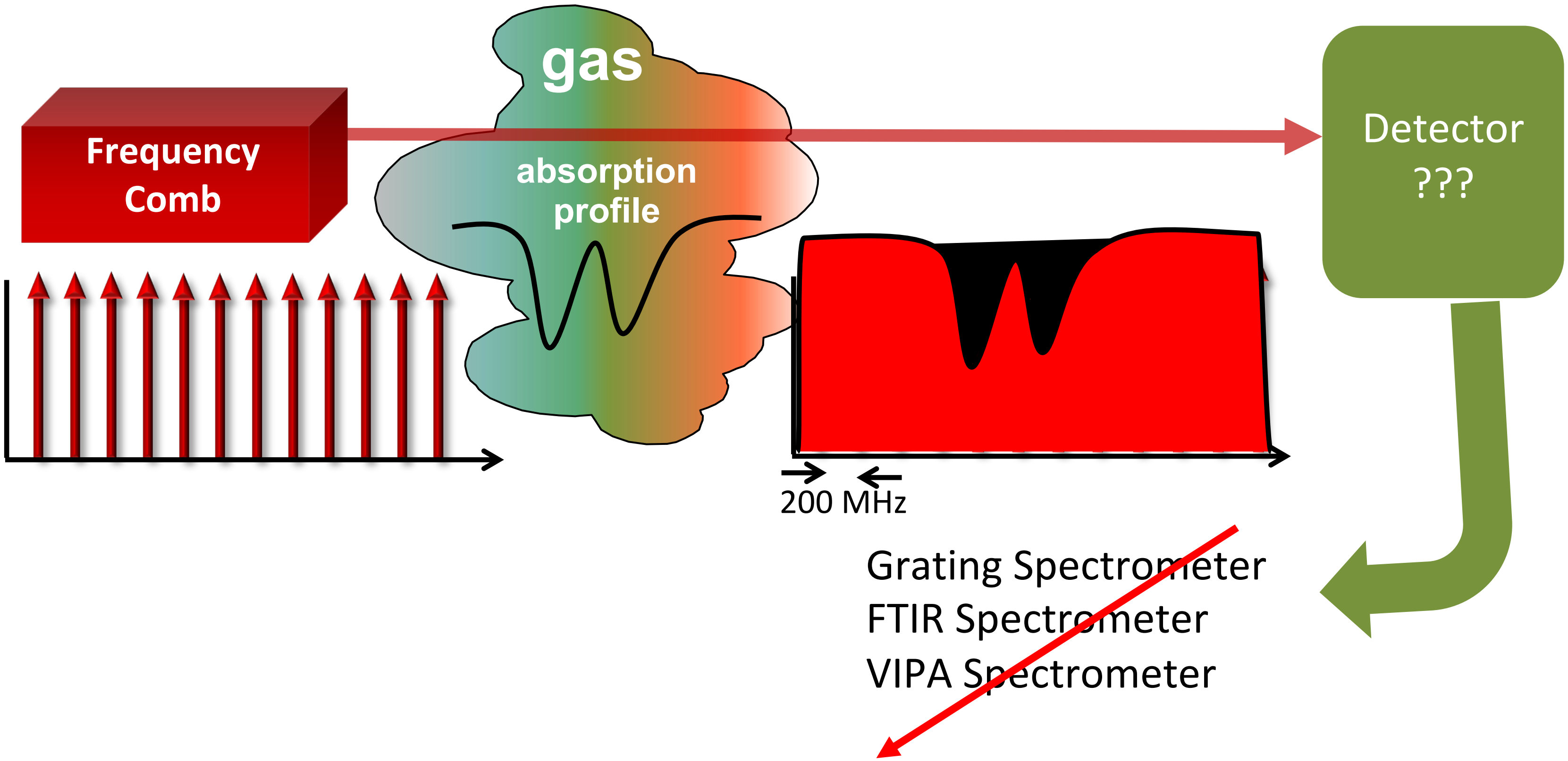
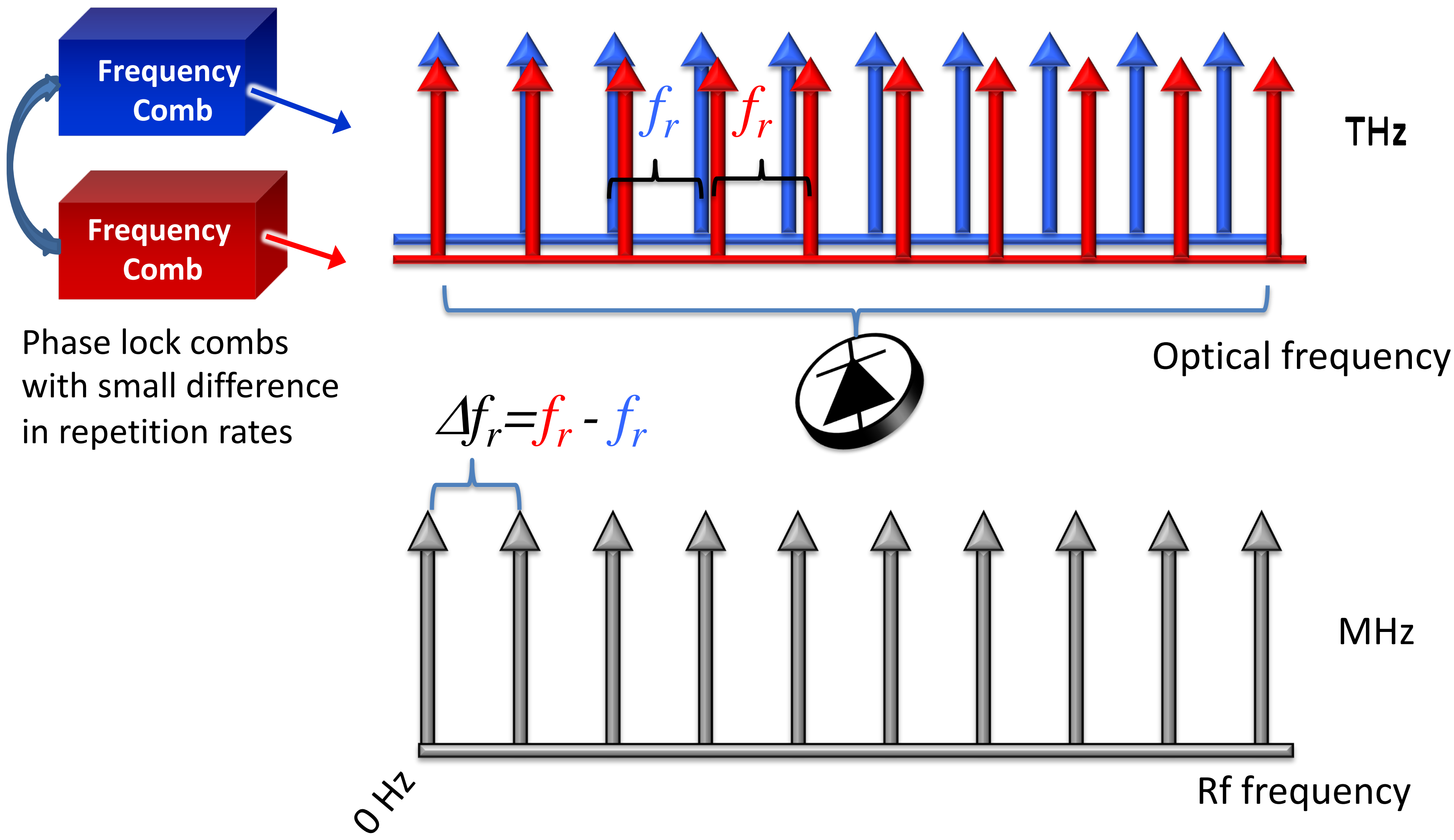
NIST

Spectroscopy with a Comb Source



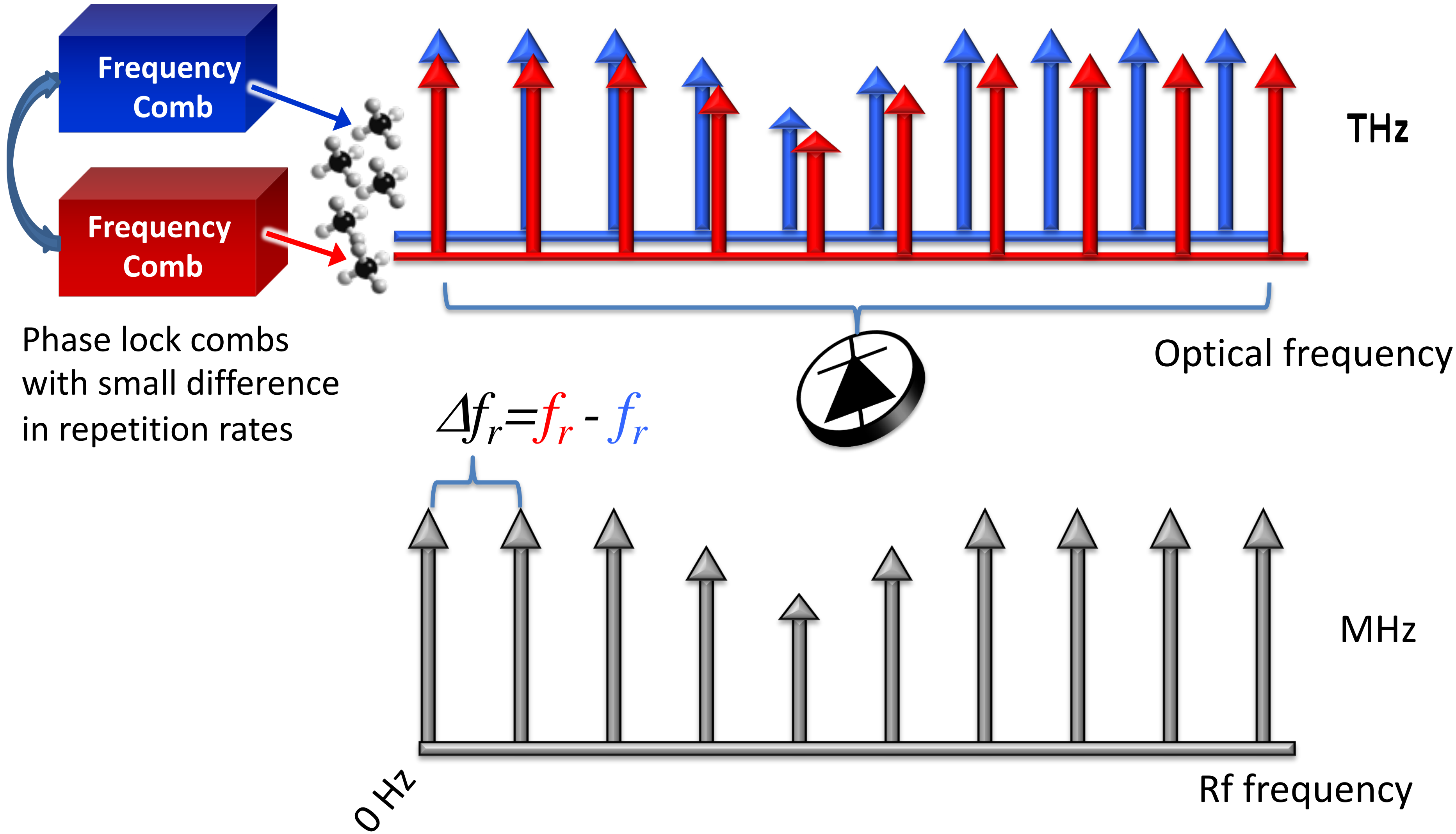
Hard to resolve 200-MHz comb teeth
"Smear out comb" -> Limited by instrument
Might as well use a light bulb!

Dual-comb spectroscopy enables readout with comb-tooth resolution and broad spectral coverage



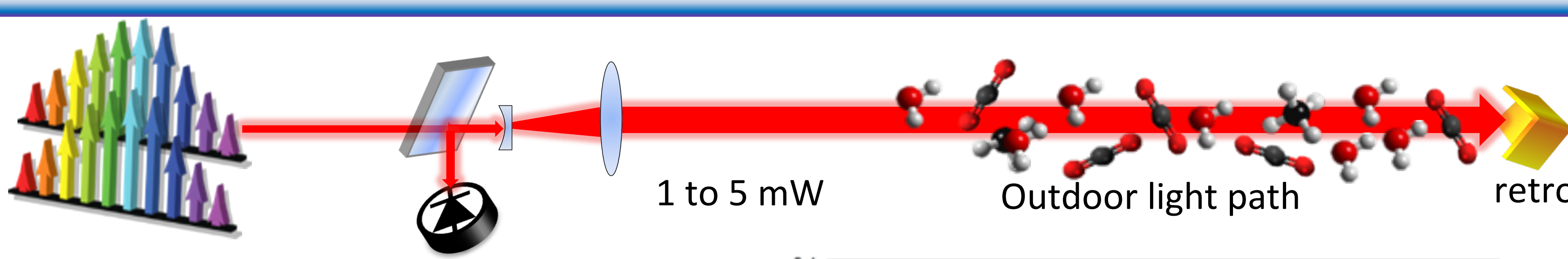
EXACT one-to-one correspondence between optical & rf frequencies

Dual-comb spectroscopy enables readout with comb-tooth resolution and broad spectral coverage



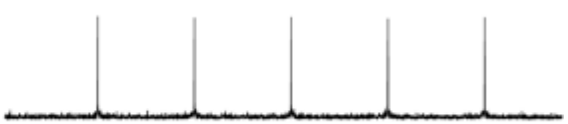
EXACT one-to-one correspondence between optical & rf frequencies

Dual Comb Spectroscopy for Open Path Sensing

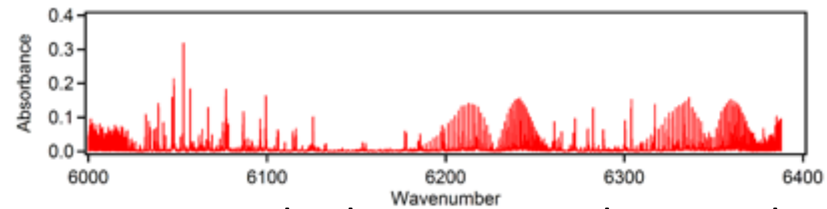


Broad spectrum

Coherent & bright



Accurate frequency scale



Measure multiple gases simultaneously

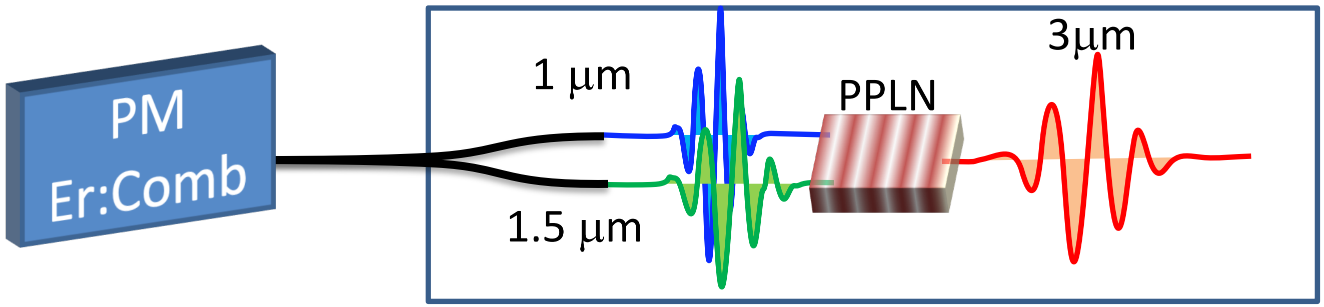
Multi-km open-air paths achievable (good match to models, less likely to miss plume)

Wavelength calibration unnecessary

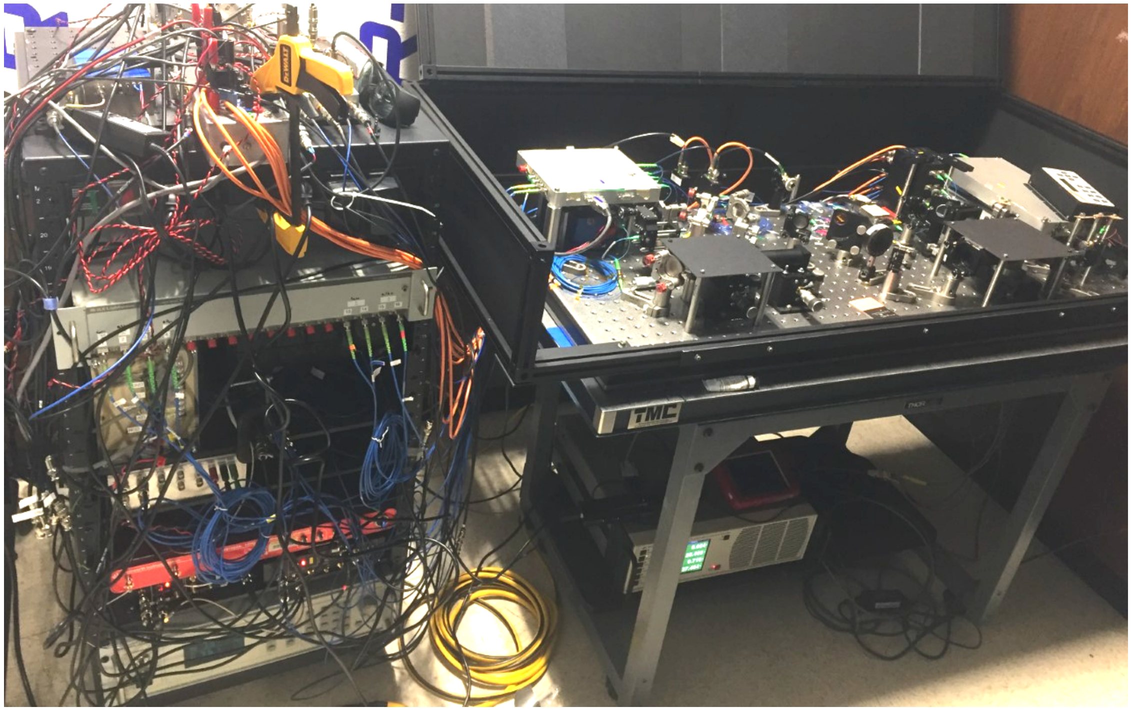
Eye safe, accurate, continuous, automated measurements

Mid-Infrared comb from difference frequency generation

Ycas et al, Nat. Photonics **12**, 202 (2018)
Ycan et al, Optics Express (2020)



Full mid-IR DCS system

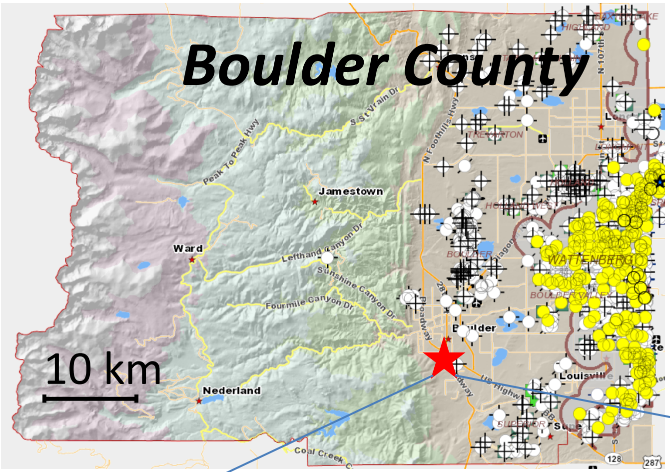


- Broad spectral coverage (500 nm instantaneous coverage)
- ~5 mW mid-IR power

Outline

1. Test measurements of VOCs in 3 μm region
2. Field deployment
3. Test measurements in 4.5 μm region

Open-path measurements across 1 km path

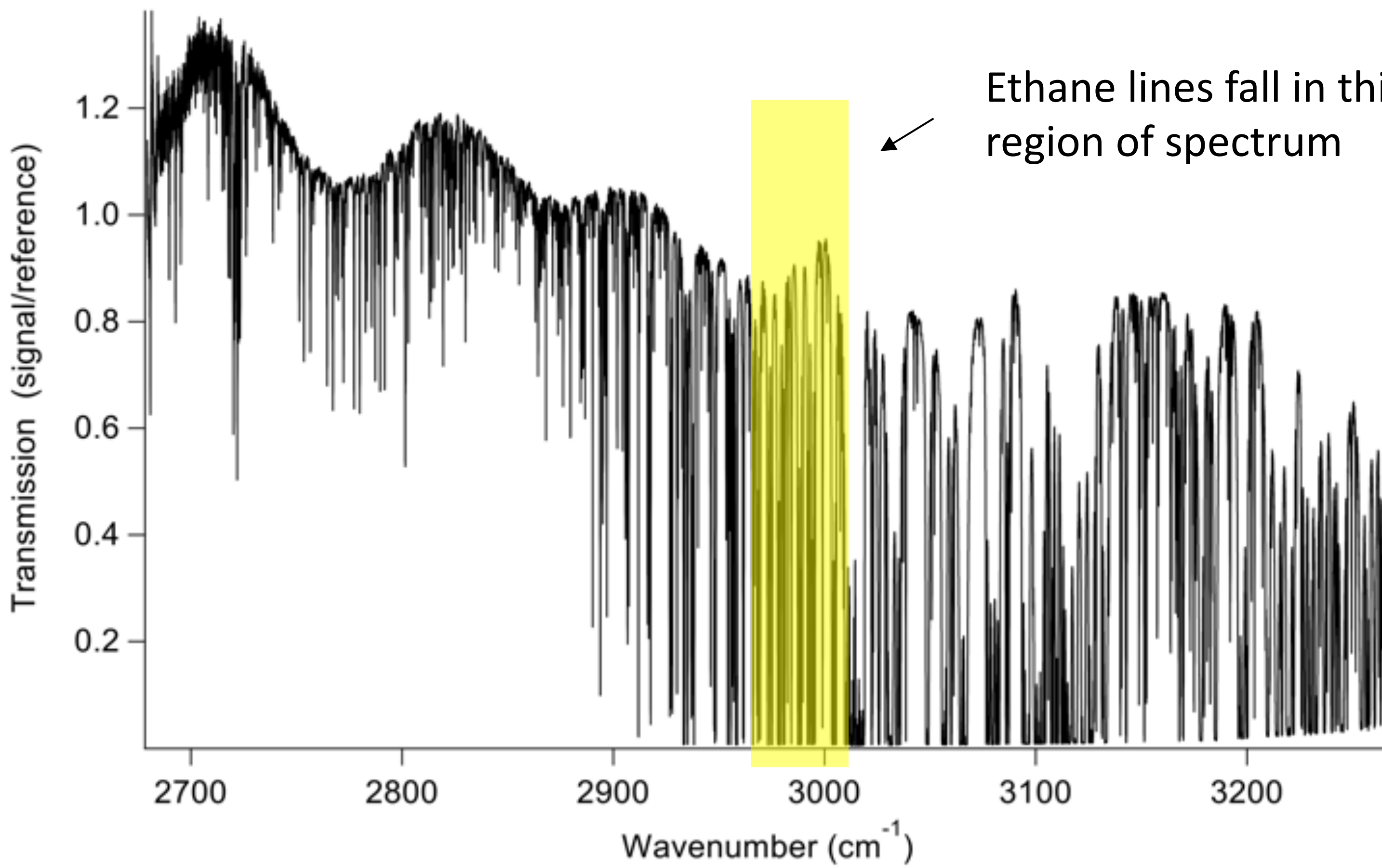


To Denver-Julesburg oil and gas basin

N
W E
S

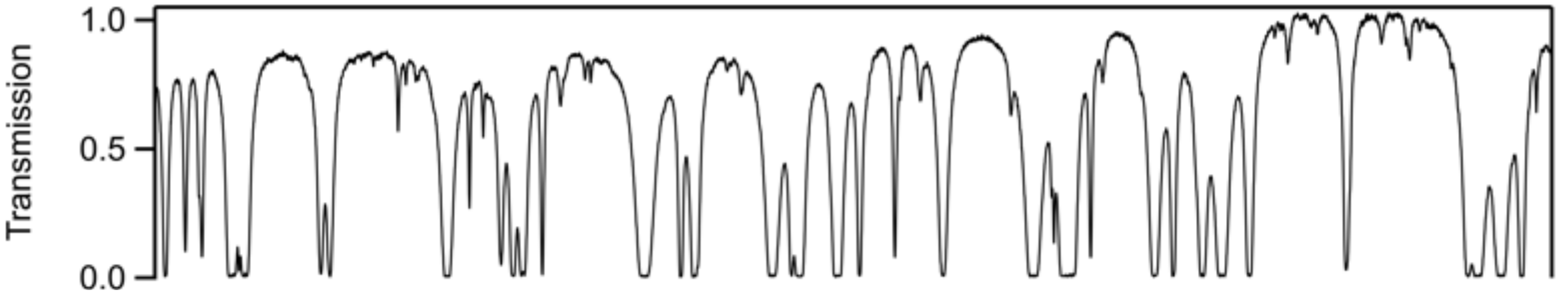
- Producing well
- Plugged & abandoned well
- ★ NIST Boulder

Let’s look for ethane



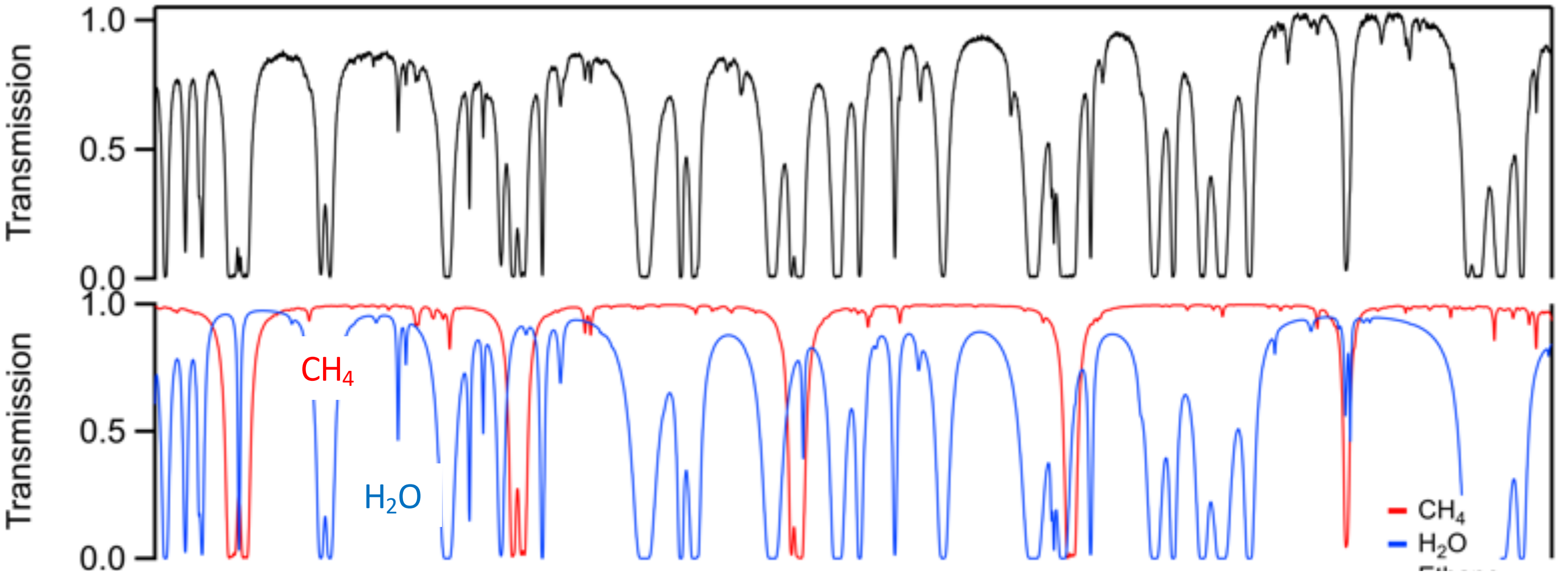
Ethane lines fall in this region of spectrum

Finding Ethane in the atmosphere



Measured
Transmission spectrum

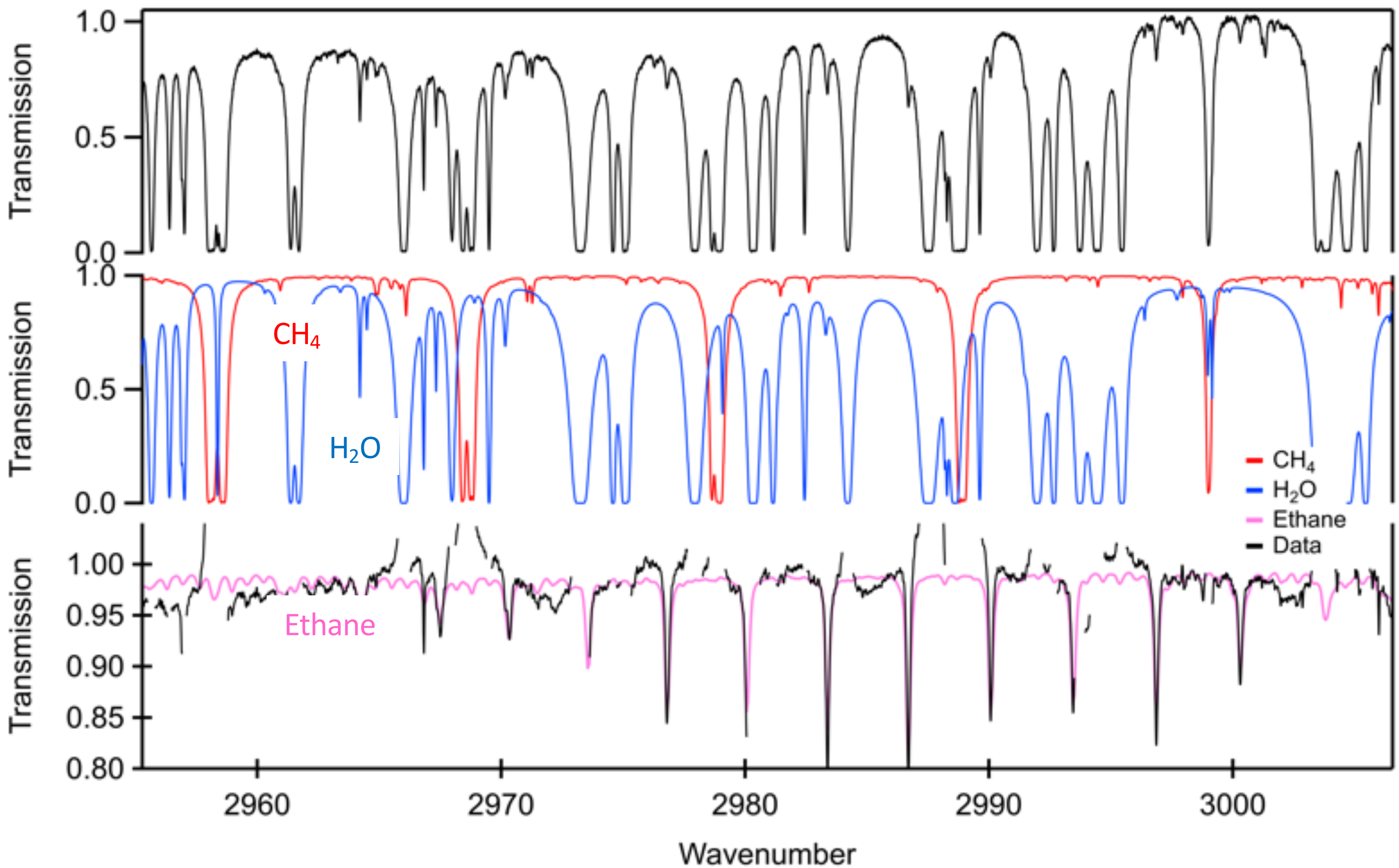
Finding Ethane in the atmosphere



Measured
Transmission spectrum

“Clutter” model for
H_2O and CH_4

Finding Ethane in the atmosphere

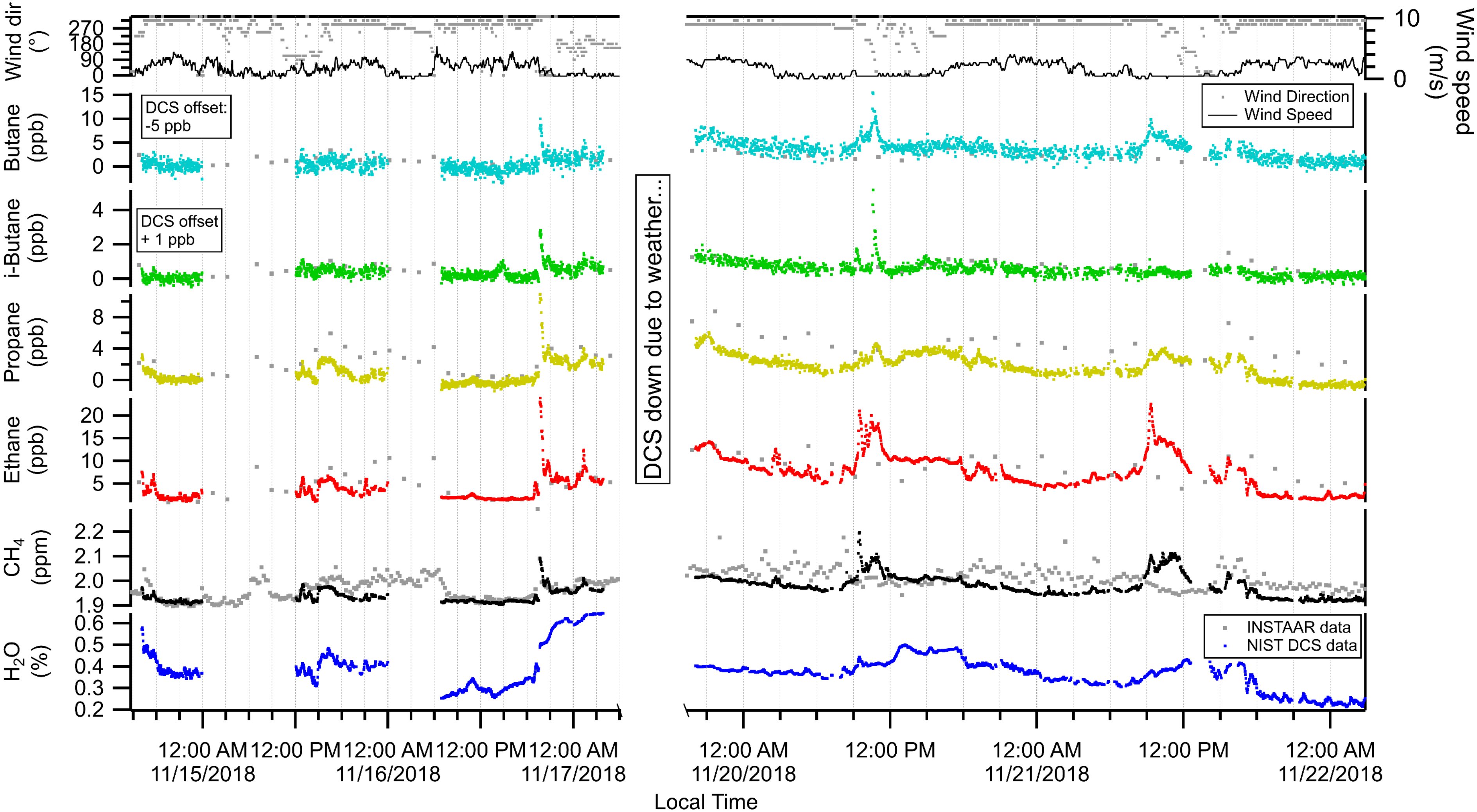


Measured Transmission spectrum

"Clutter" model for H_2O and CH_4

"Decluttered" spectra Ethane (PNNL) model shown

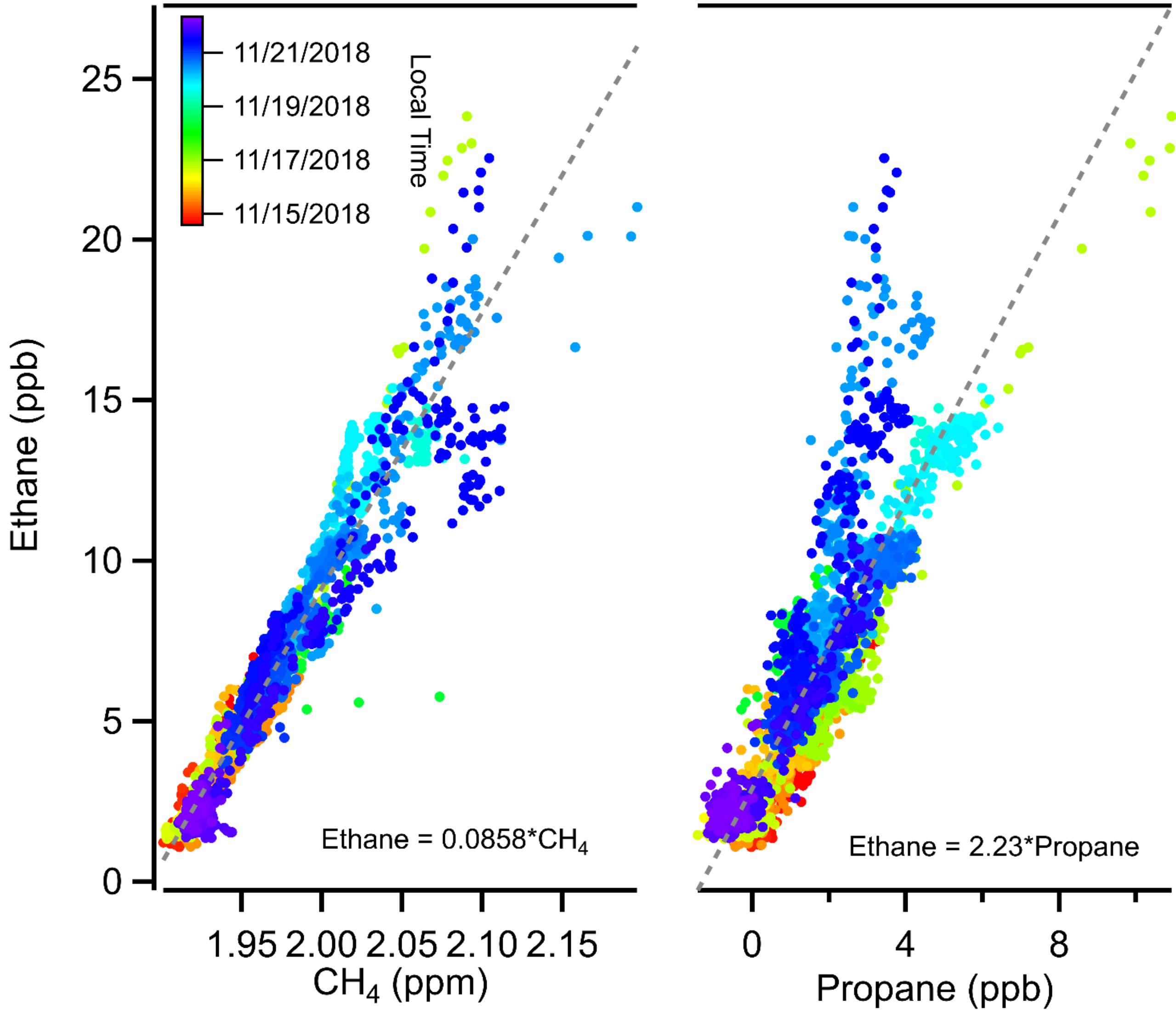
One-week time series of hydrocarbons



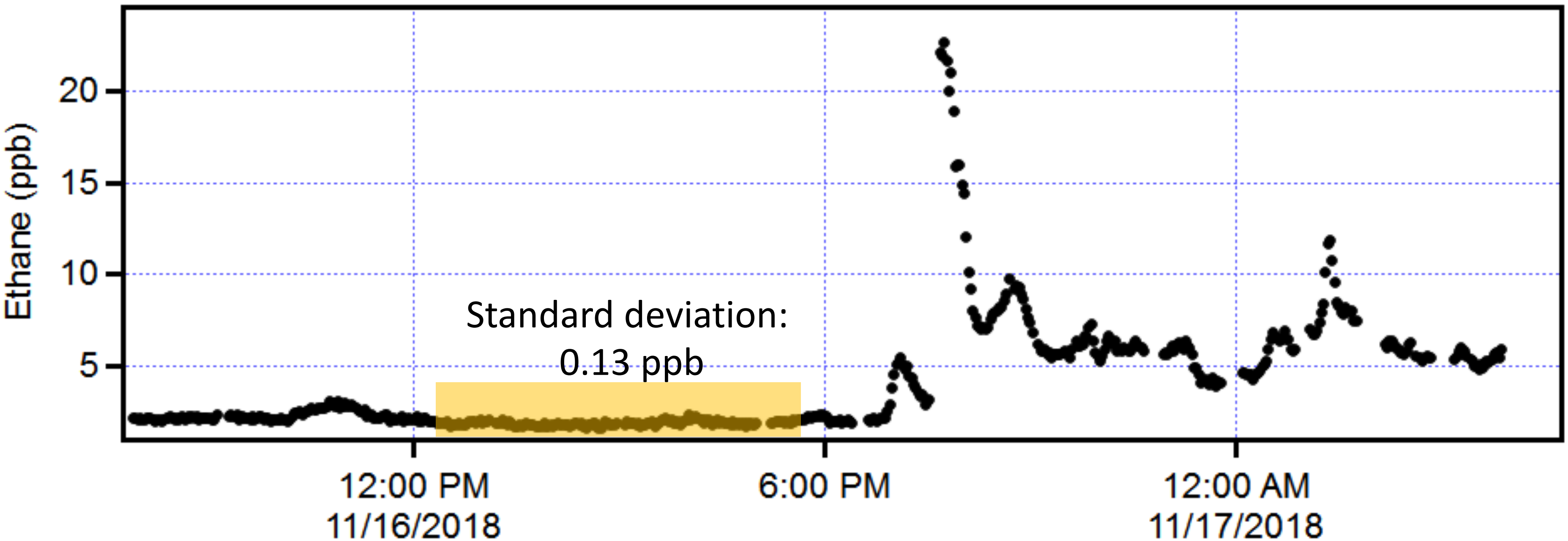
INSTAAR: Point sensor (GC-FID) located ~15 km across Boulder

Data courtesy of Detlev Helmig

Ethane/methane and Ethane/propane indicate oil and gas source



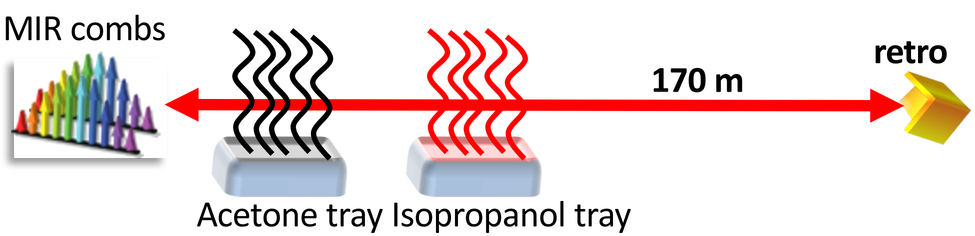
Zoom in on ethane



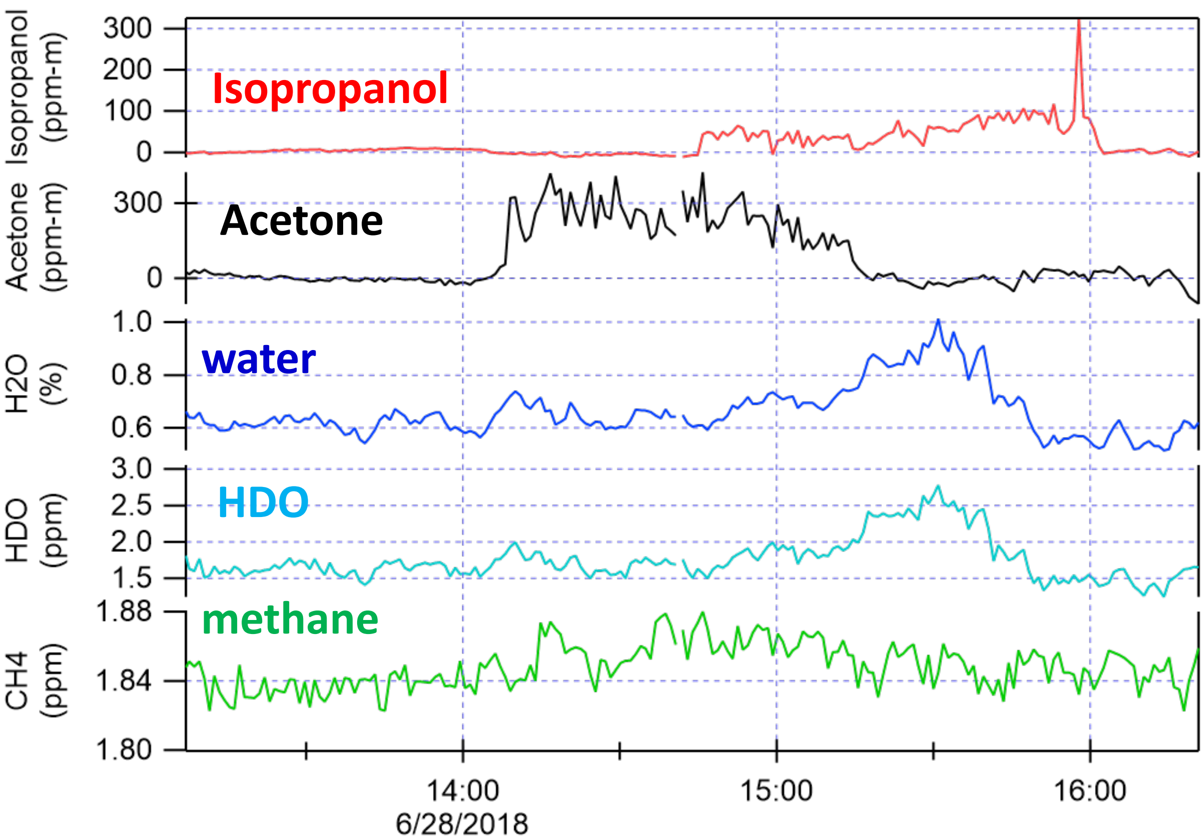
Ethane sensitivity ~100 ppt at 2 minute time resolution (100 ppt-km)

Controlled release of acetone and isopropanol

Ycas et al, Optica **6**, 165 (2019)



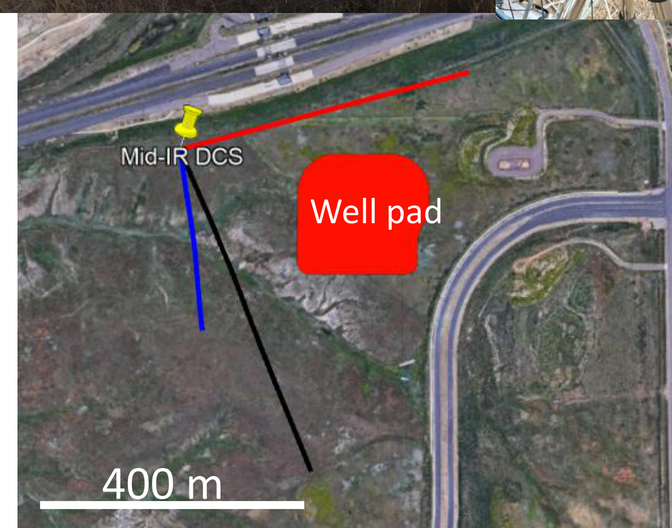
Acetone/ isopropanol tray



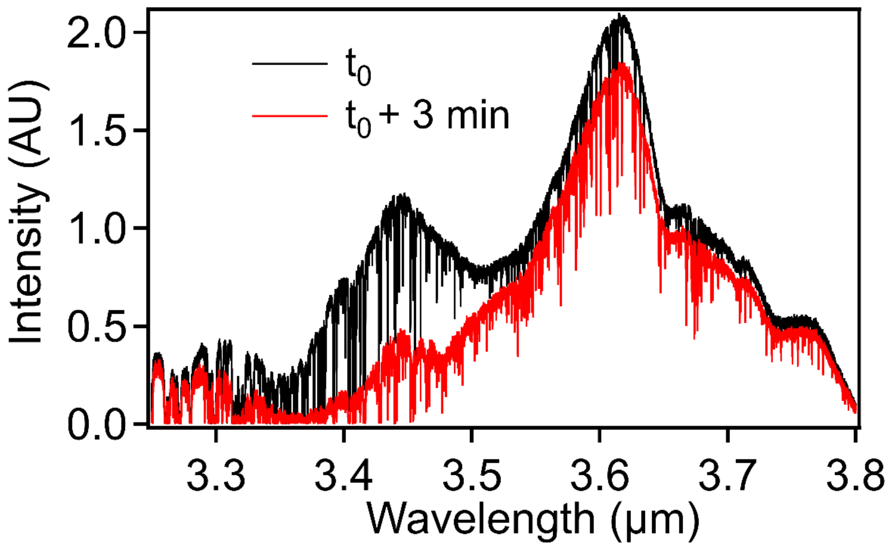
- Change detection
- 3-sigma sensitivities at beginning:
  - Acetone: 30 ppm-m
  - Isopropanol: 5 ppm-m
- Absolute detection of H_2O, HDO, and CH_4

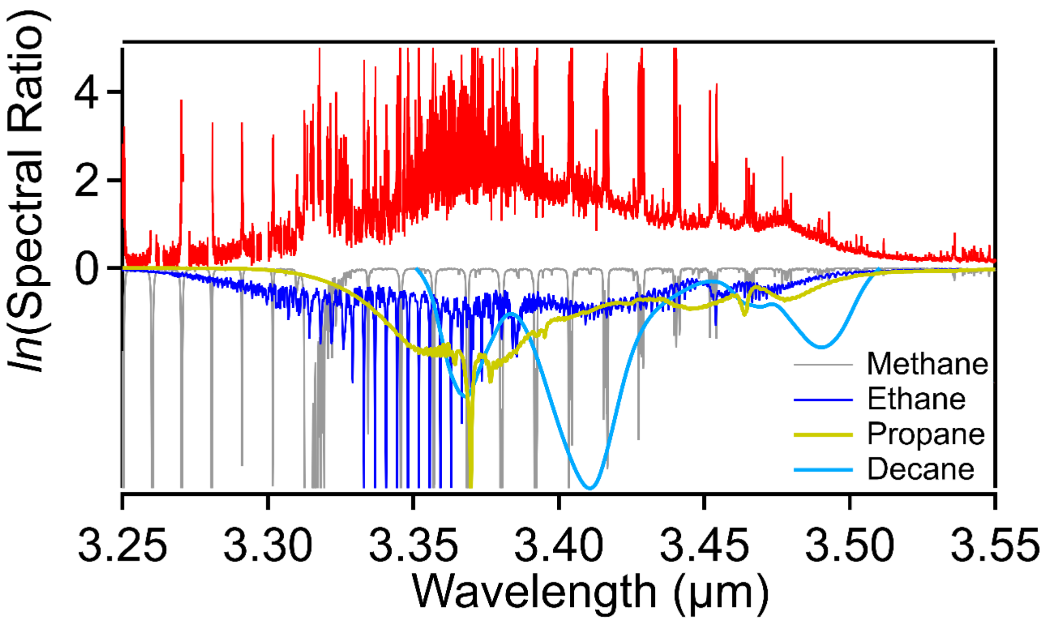
Field deployment to oil and gas drilling operation

- Goal to get emission rate for VOCs
- Hydraulic fracturing operation
- Deployment co-located with Colorado Department of Public Health and Environment mobile lab (CAMML)
- Multiple beam paths
- Deployed for drilling, fracturing, and production
- ~8 weeks of data

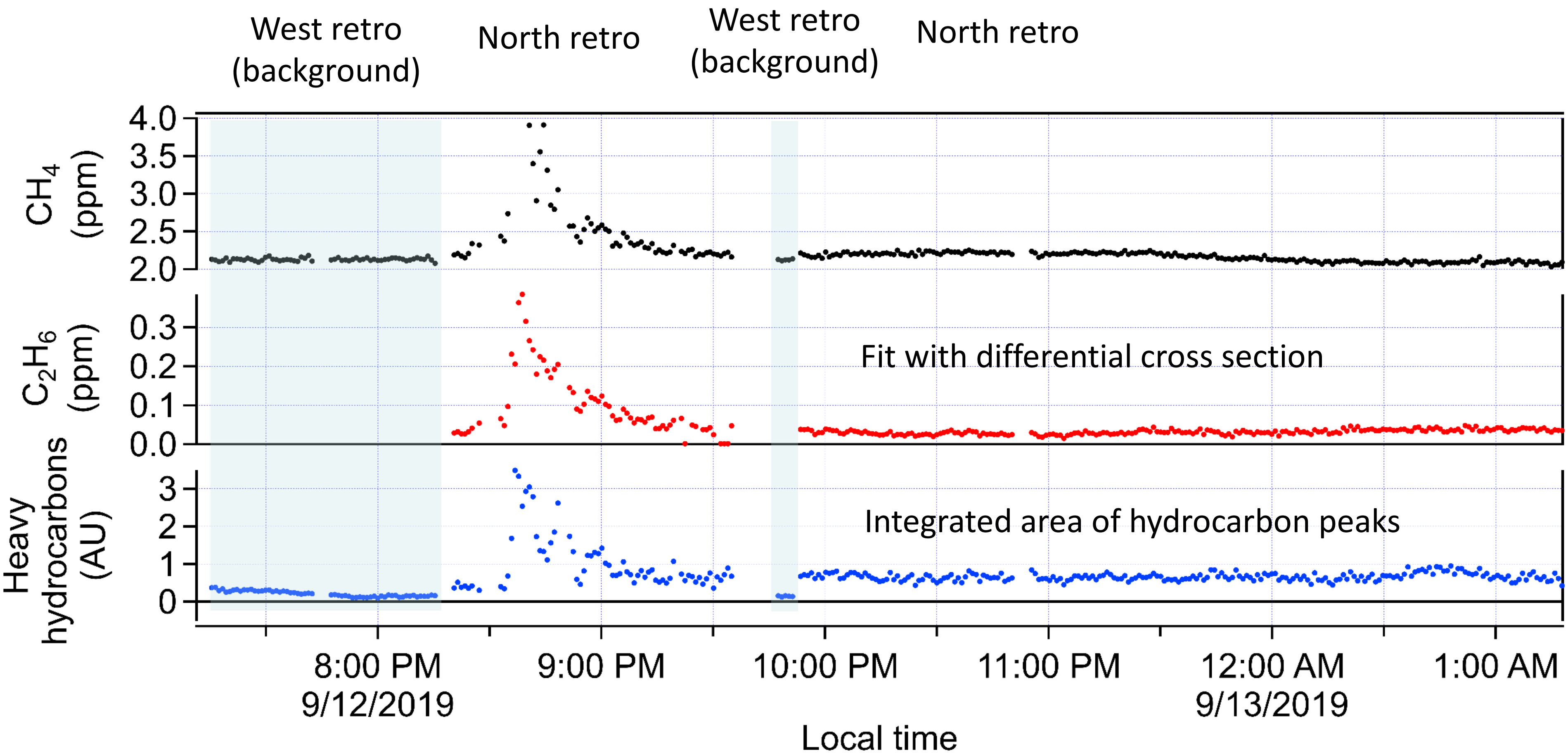


Plumes with large absorption observed





Example methane, ethane, and heavy hydrocarbons

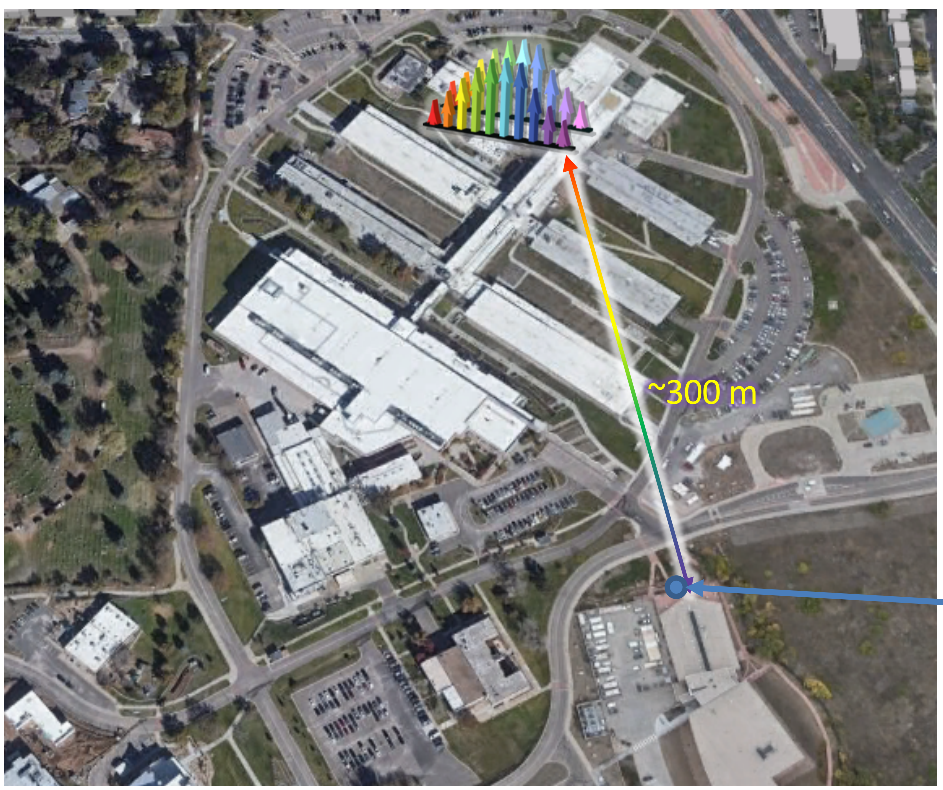


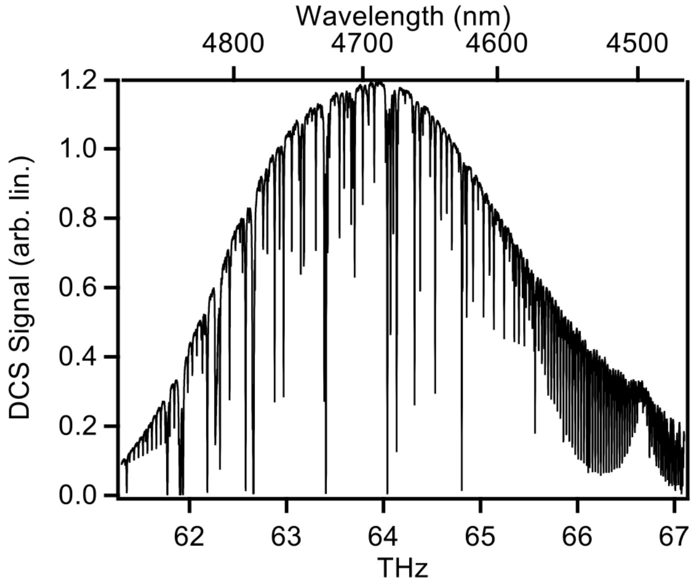
Next steps:

- Test other fitting approaches for improved speciation
- Combine with dispersion model to estimate fluxes
- Compare emissions from different stages: drilling, fracturing, flowback/production

DCS in 4.5-5 µm region

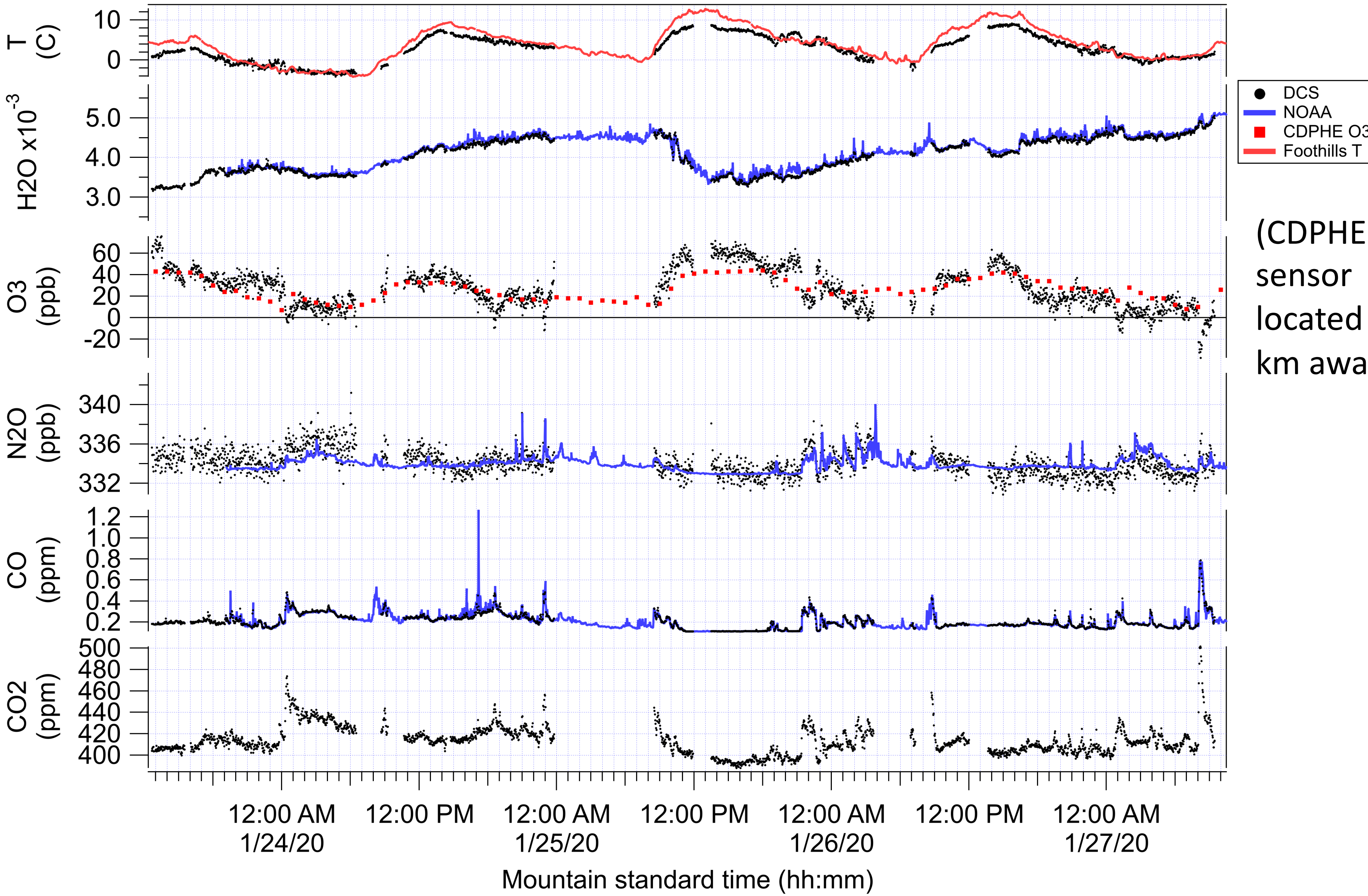
Goal: measure N_2O, CO, H_2O, O_3, and CO_2





NOAA point sensor:
N_2O, CO, H_2O
Averaged to 1 minute time resolution

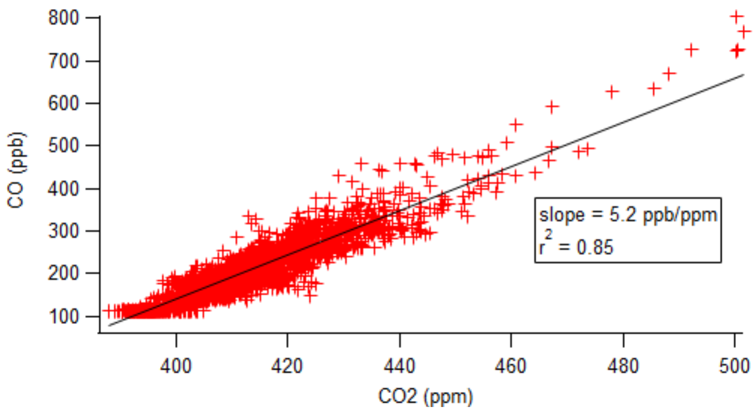
Time series of trace gases and temperature



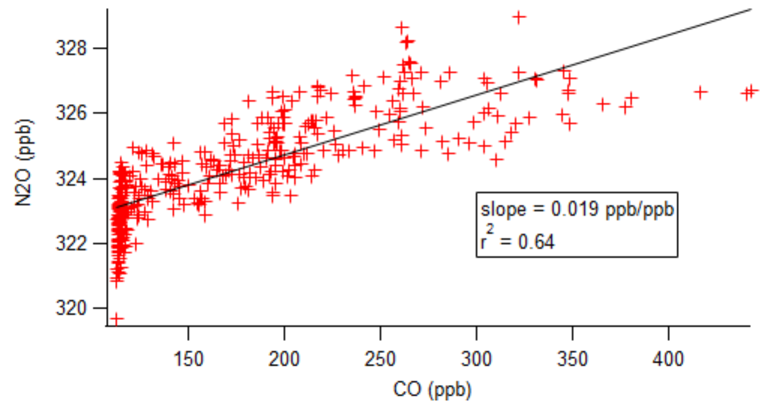
($CDPHE\ O_3$ sensor located ~15 km away)

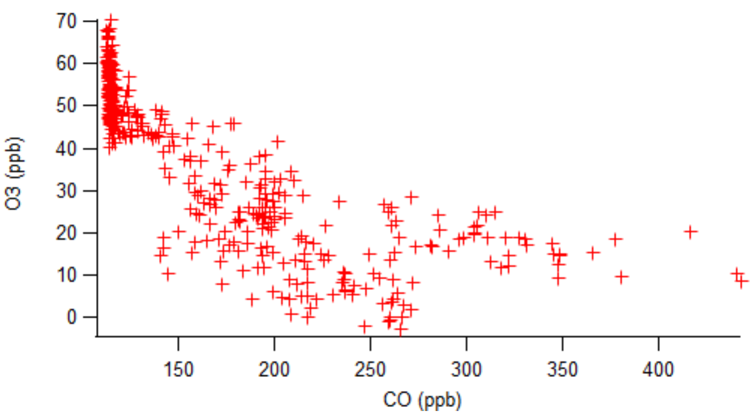
Correlations between species

Strong correlation between CO and CO_2
Indicates CO_2 comes from traffic
(expected ~4-8 ppb/ppm)



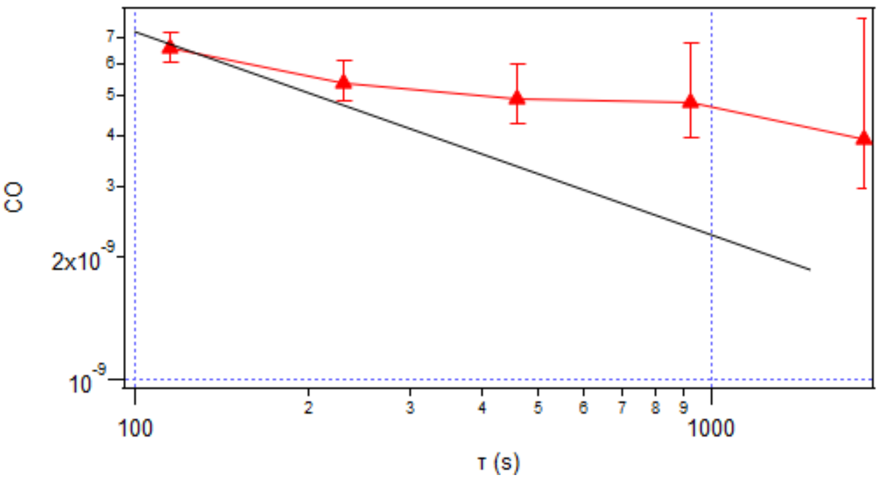
Correlation between N_2O and CO (shown for subset of data)
Indicates N_2O comes from traffic
(expected ~0.02 ppb/ppb)

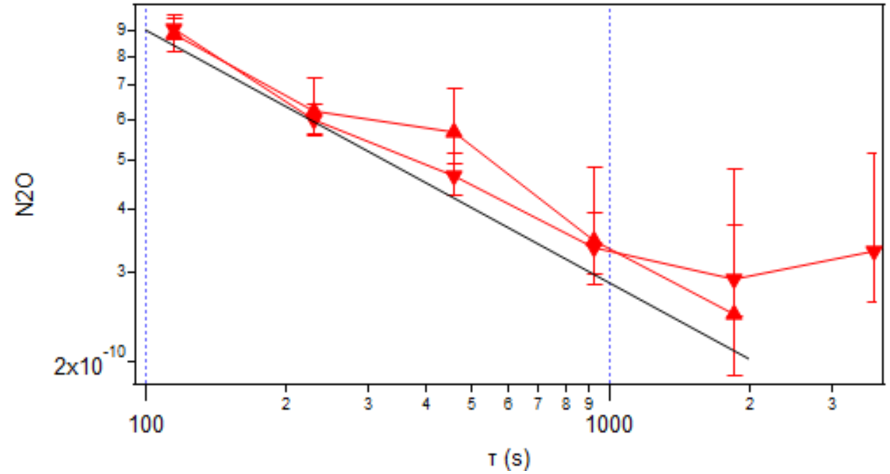


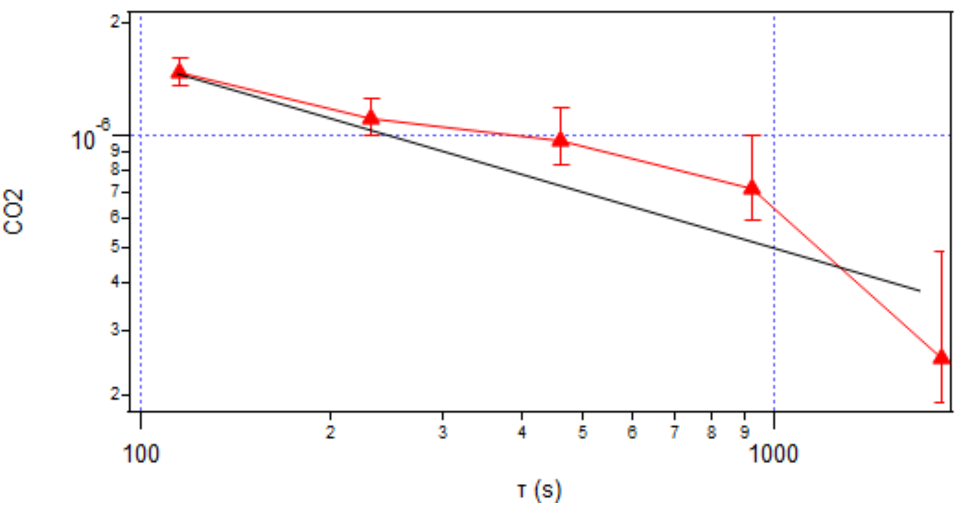


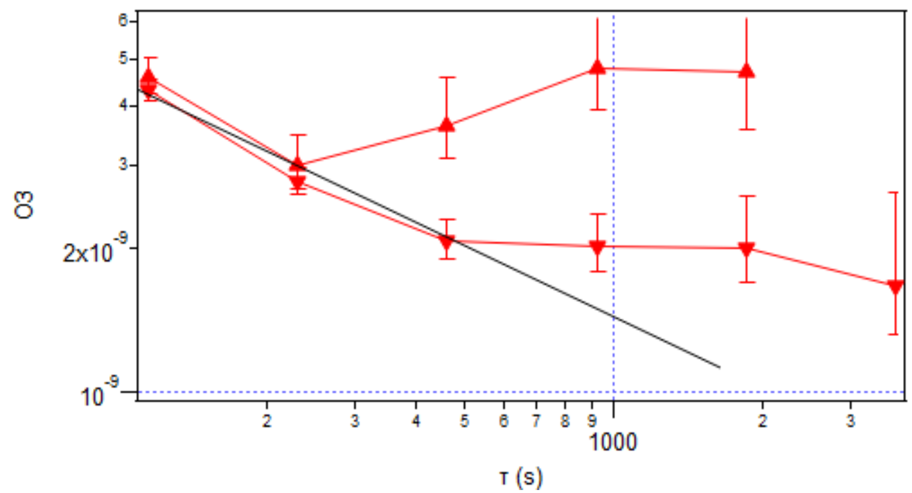
Some correlation between O_3 and CO?
Could be issue with fit
Could potentially be real (O_3 over the city could be lower, especially at night, due to NO + O_3 -> NO_2)

Sensitivity









Conclusions

- Advantages of DCS
  - Simultaneous multi-species detection
  - Accurate
  - Fast measurements
  - Ability to operate over long open-air paths
- 3 µm
  - Measured ambient NMHCs with 0.1 ppb ethane sensitivity in 2 minutes
  - Detected intentionally released VOCs
  - Field deployment to oil and gas drilling site
    - ~8 weeks of data during drilling, fracturing, and production
- 4.5 µm
  - Measured N_2O, CO, H_2O, O_3, and CO_2
  - Applications to urban GHG and air quality, agricultural emissions