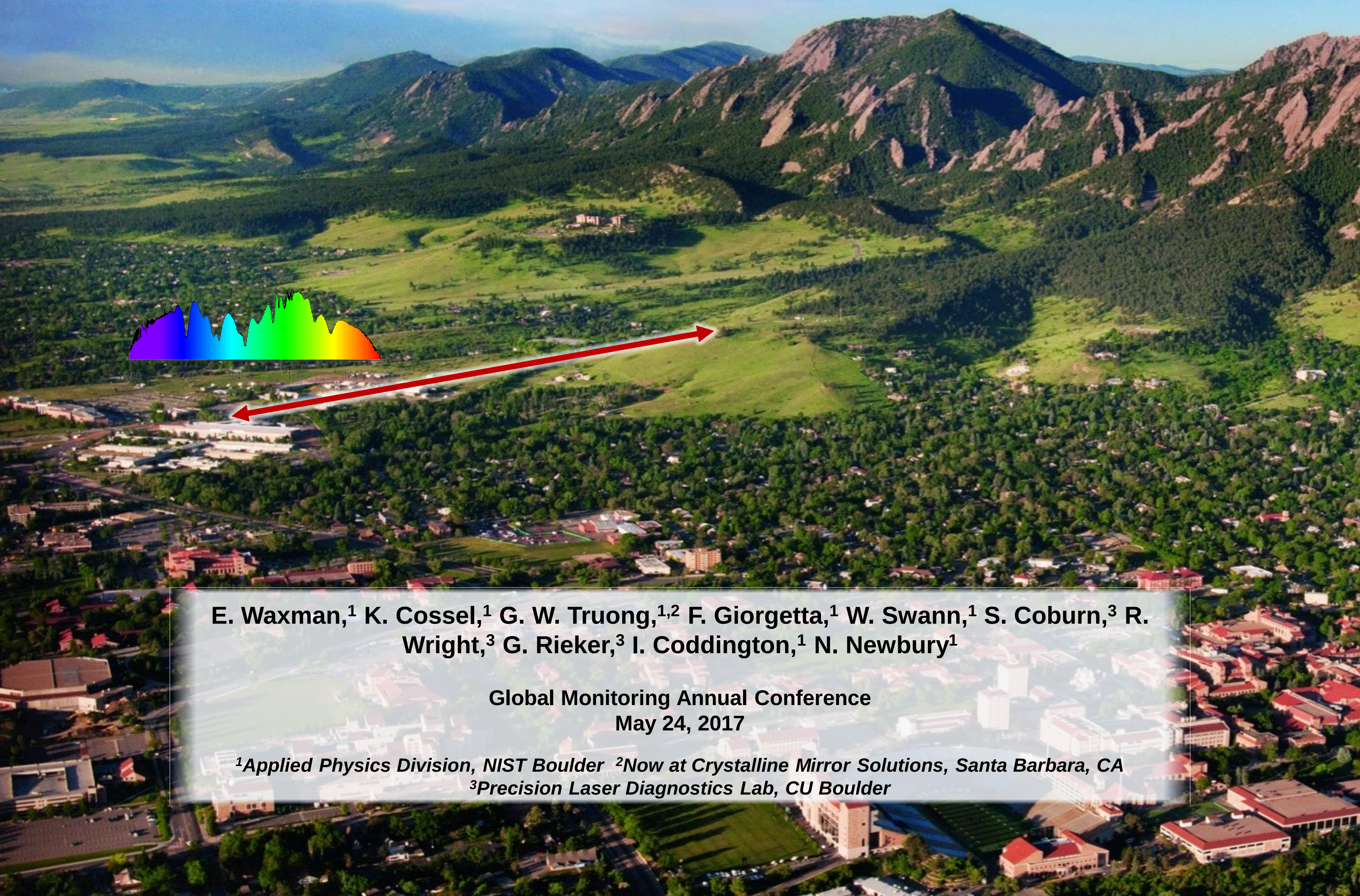
Dual Frequency Comb Measurements of Greenhouse Gases Over Boulder



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Global Monitoring Annual Conference
May 24, 2017

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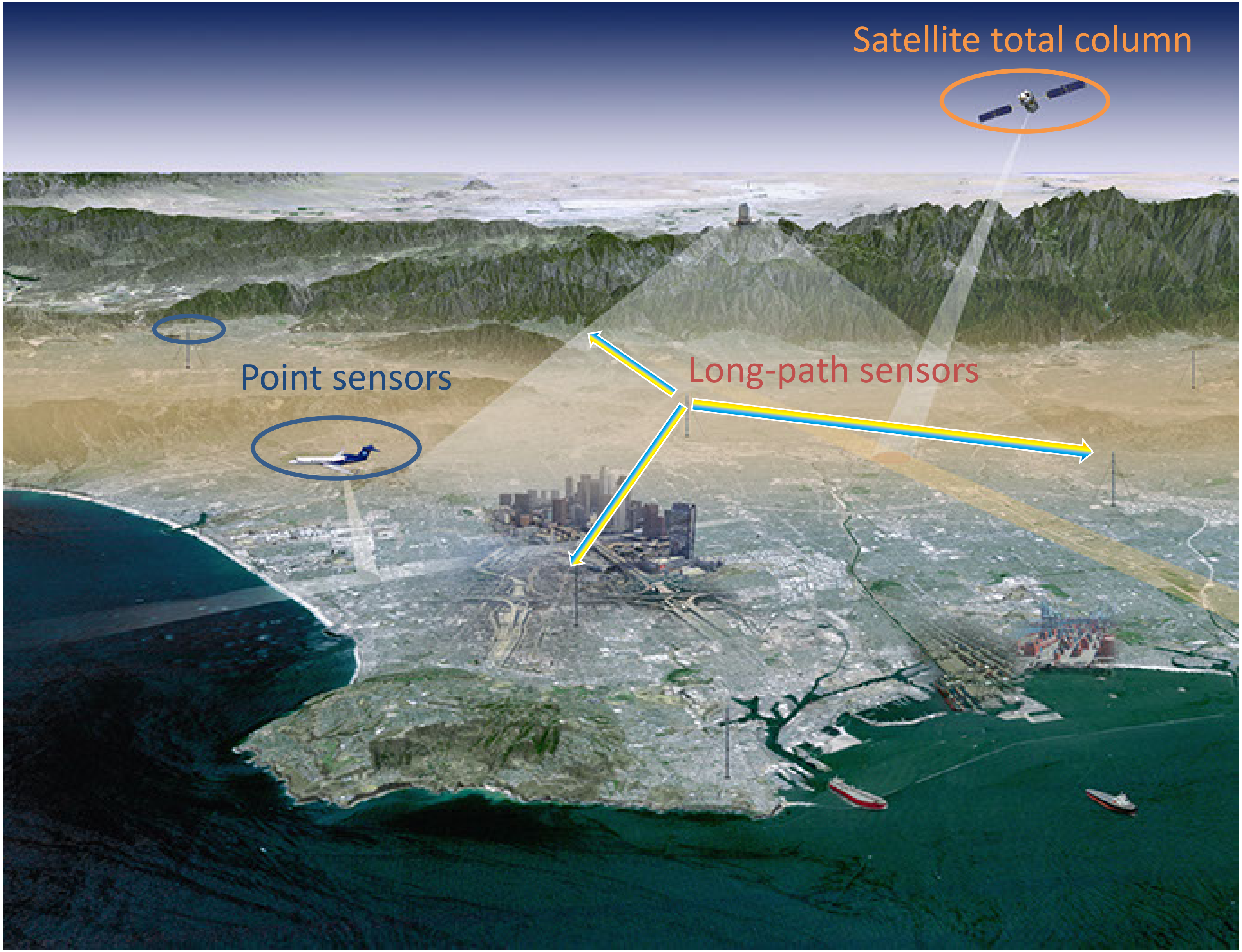
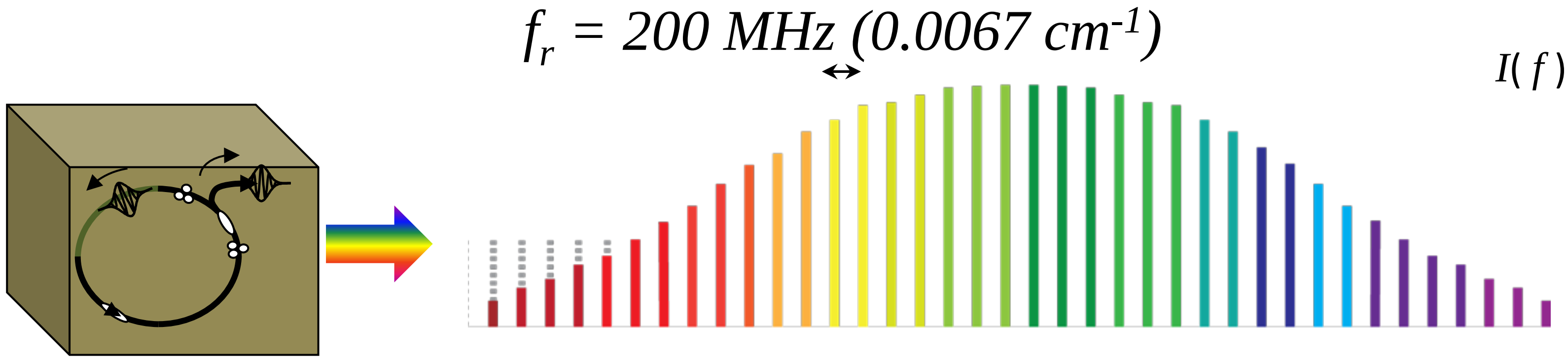
Motivation: Tiered observing system for urban measurements



NASA/JPL Megacities project

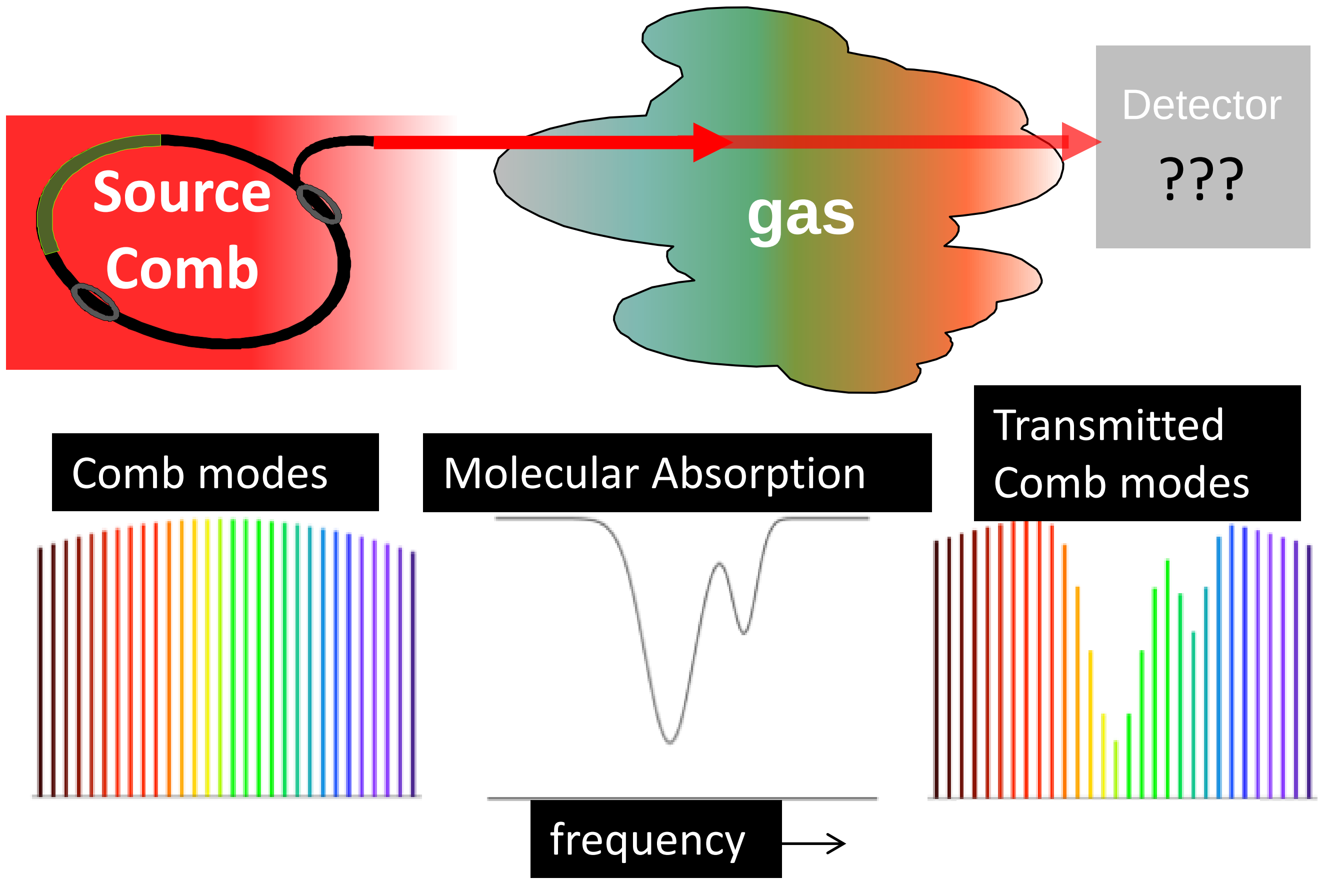
Frequency Comb: Stabilized Mode-Locked Laser



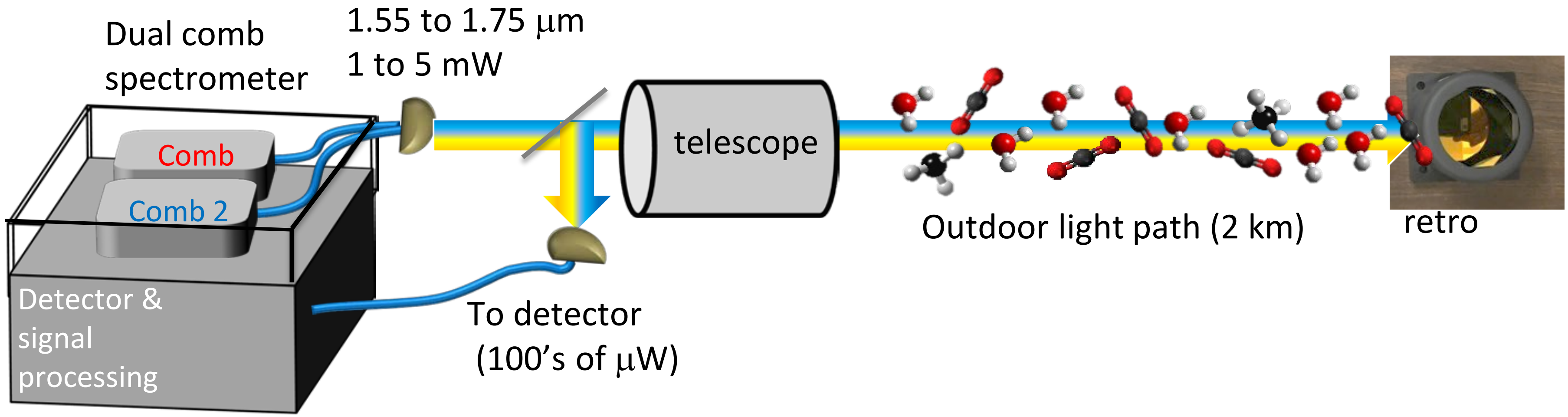
Broadband light source with:

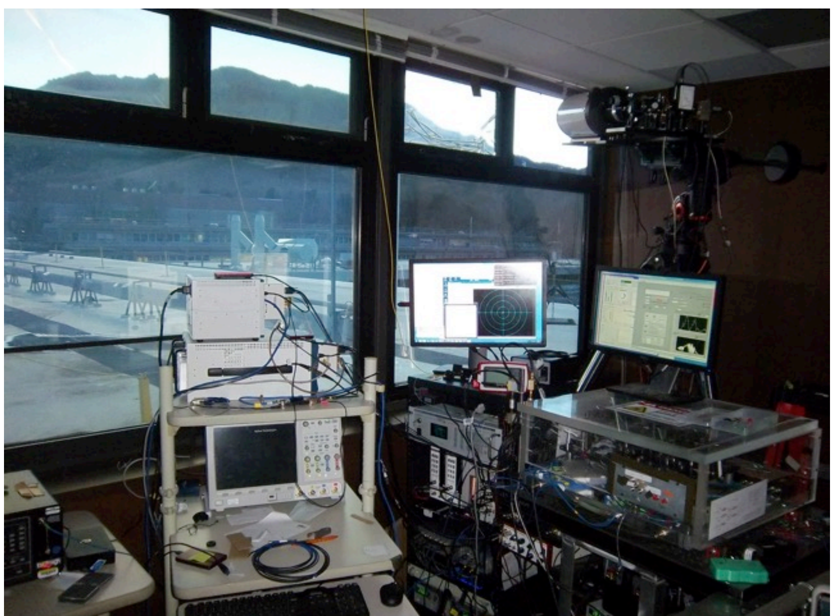
- **Specific, individual frequencies**
- **No moving parts**
- **~0.0067 cm^{-1} point spacing**
- **<0.001 cm^{-1} instrument line shape**
- **Rapid scanning (~2 ms per spectrum)**
- **Calibration-free**
- **Collimated (can send long distances)**

Spectroscopy

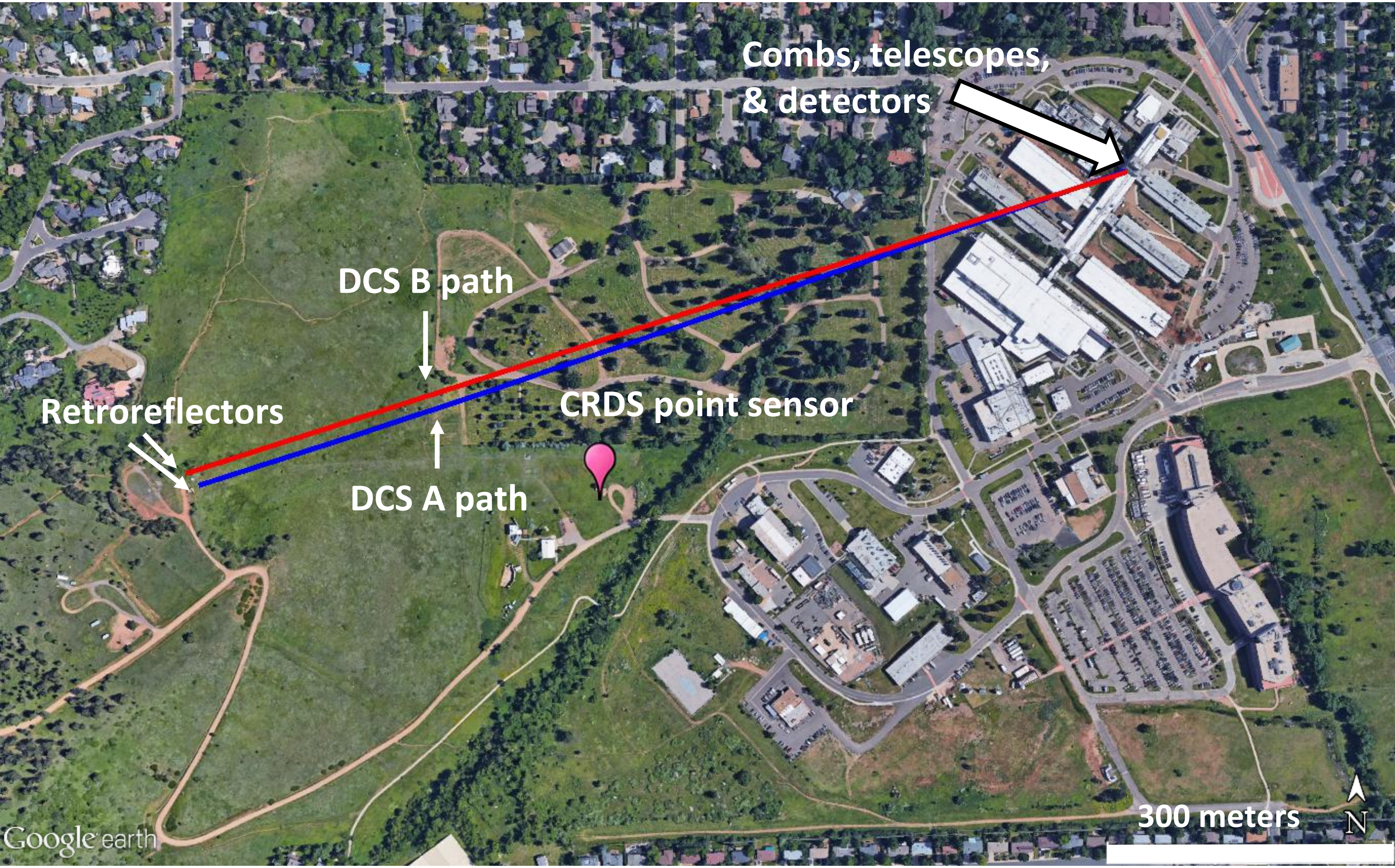


Open-path dual-comb spectroscopy

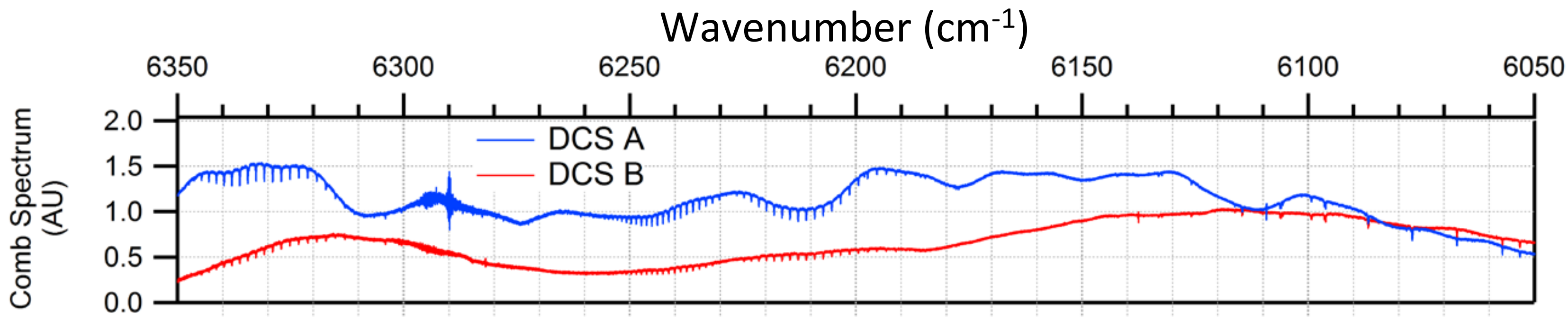




How well does it work?
Dueling DCS



Identical Atmospheric Absorbance Spectra



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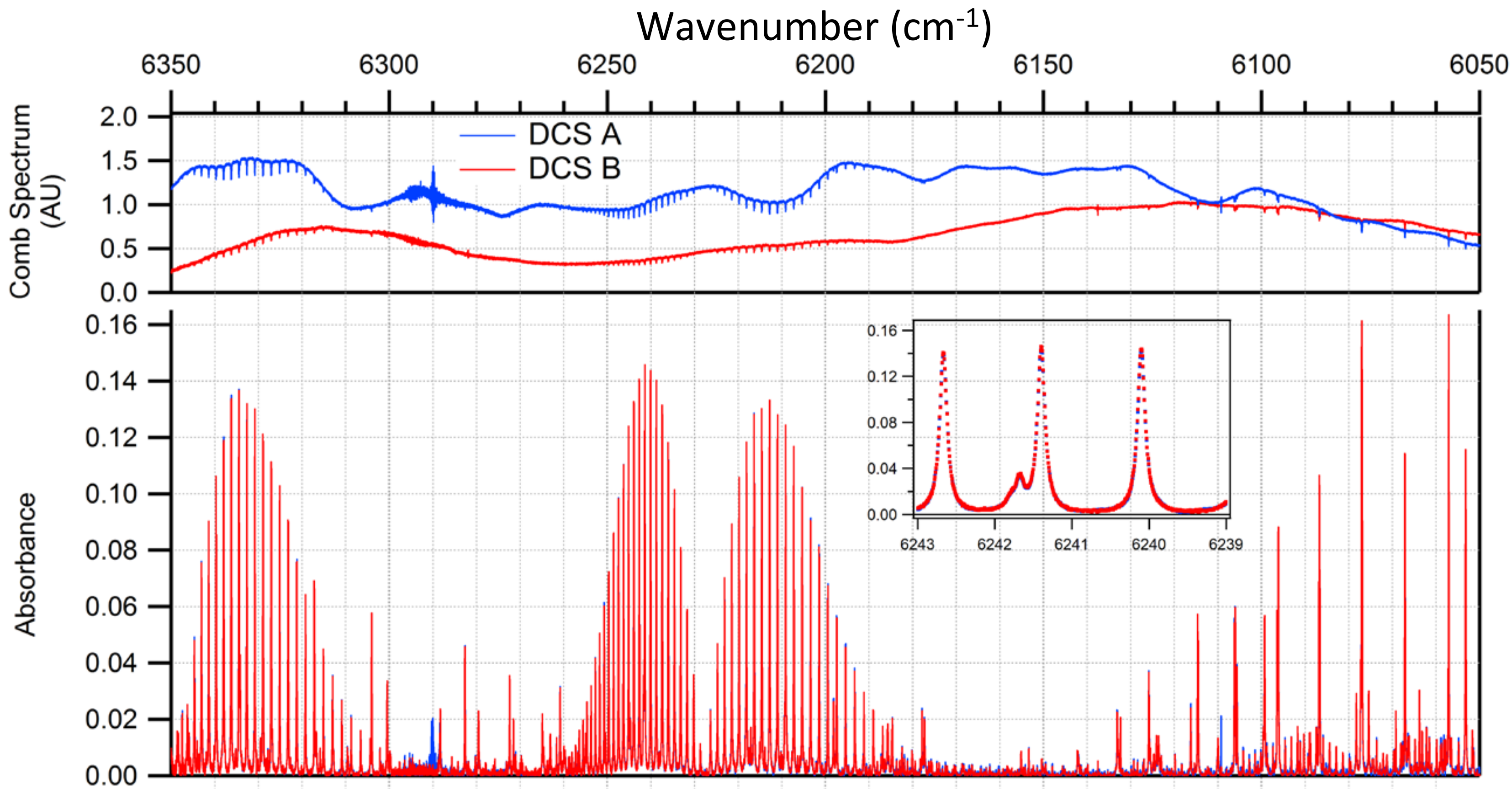
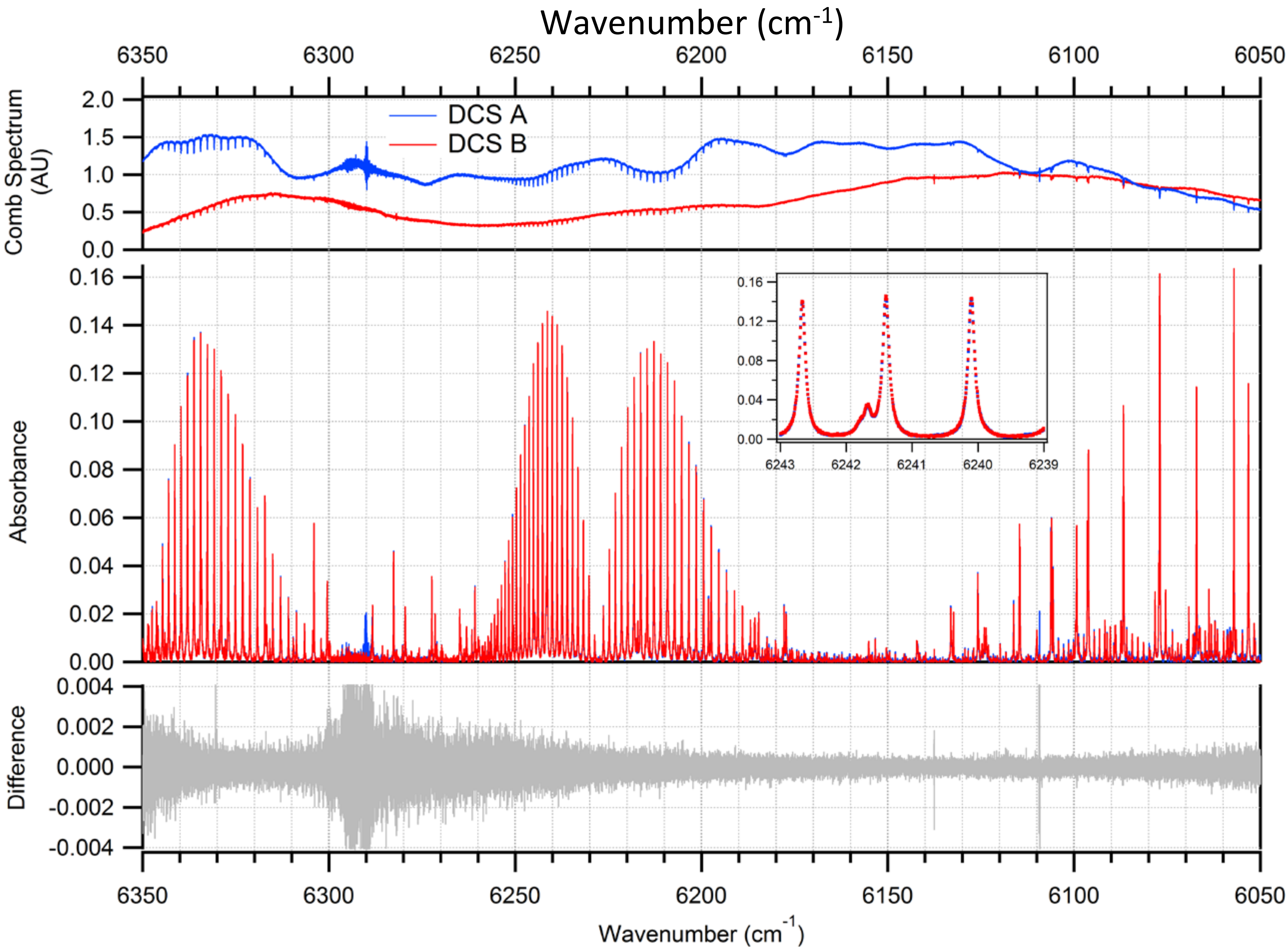
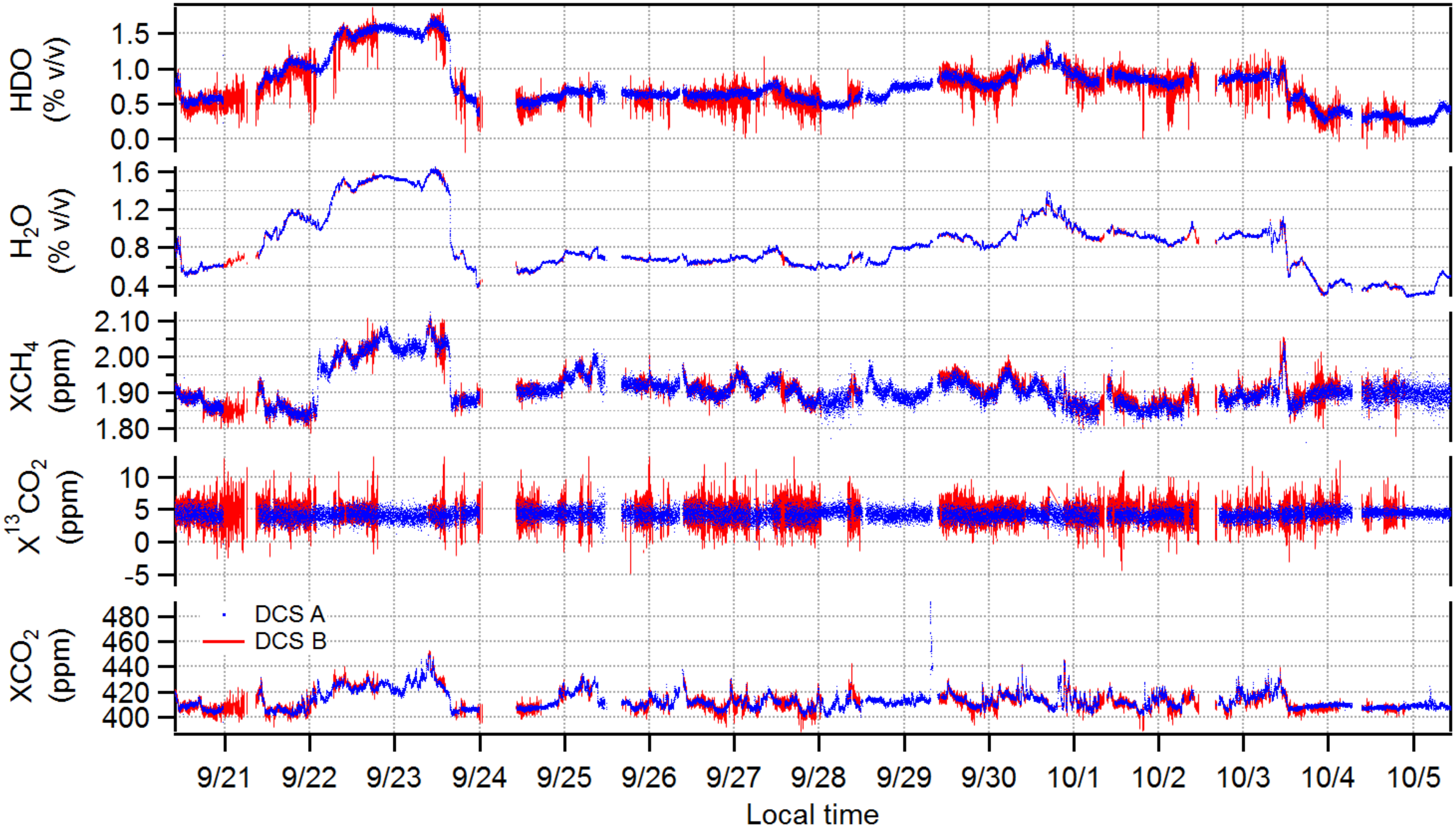


Identical Atmospheric Absorbance Spectra



Excellent agreement in measured concentrations between systems



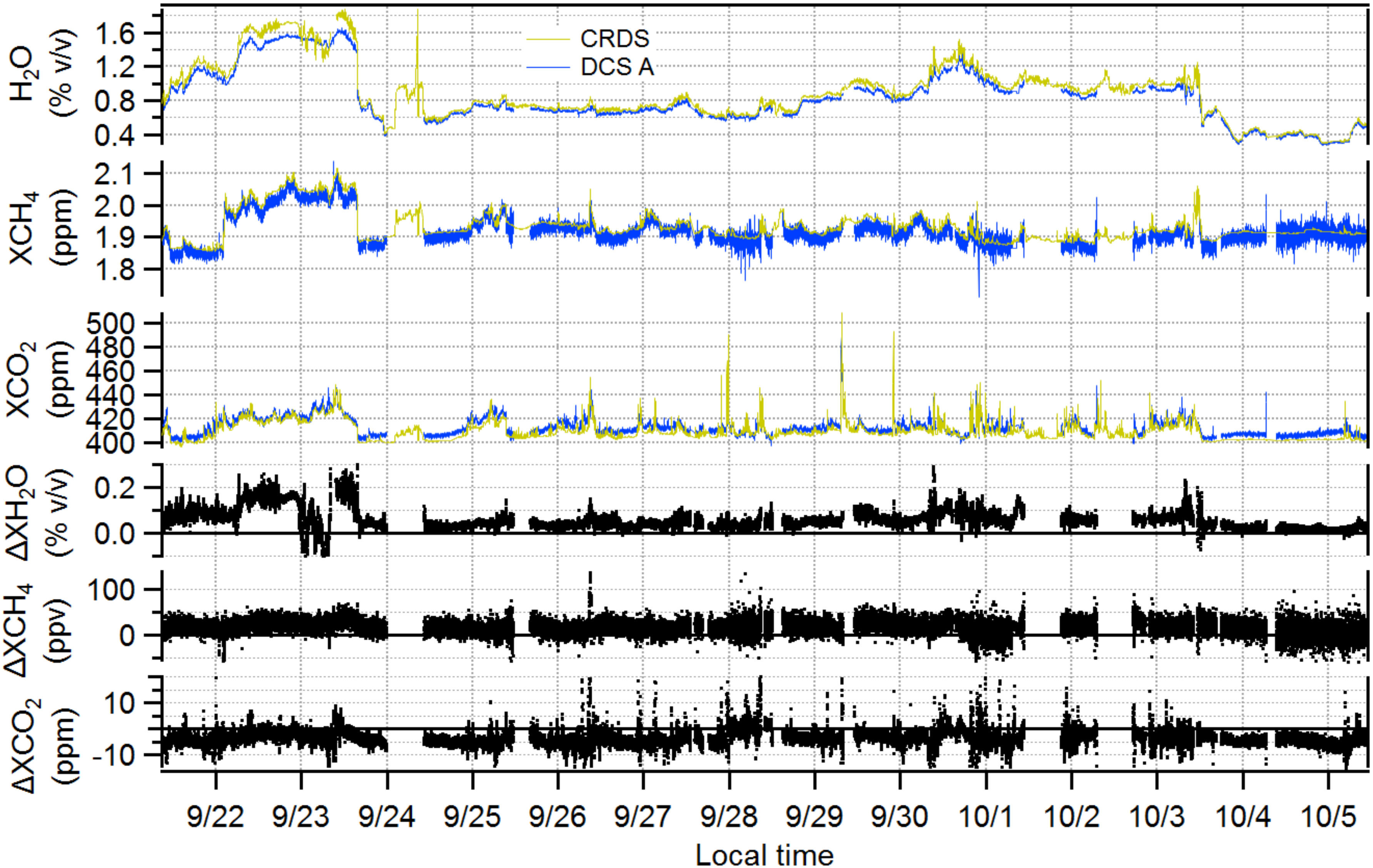
30-second time resolution data.

Systems agree to 0.14% for CO_2 and 0.35% for CH_4 over two weeks with no bias correction

10-100x better than other open-path system intercomparisons

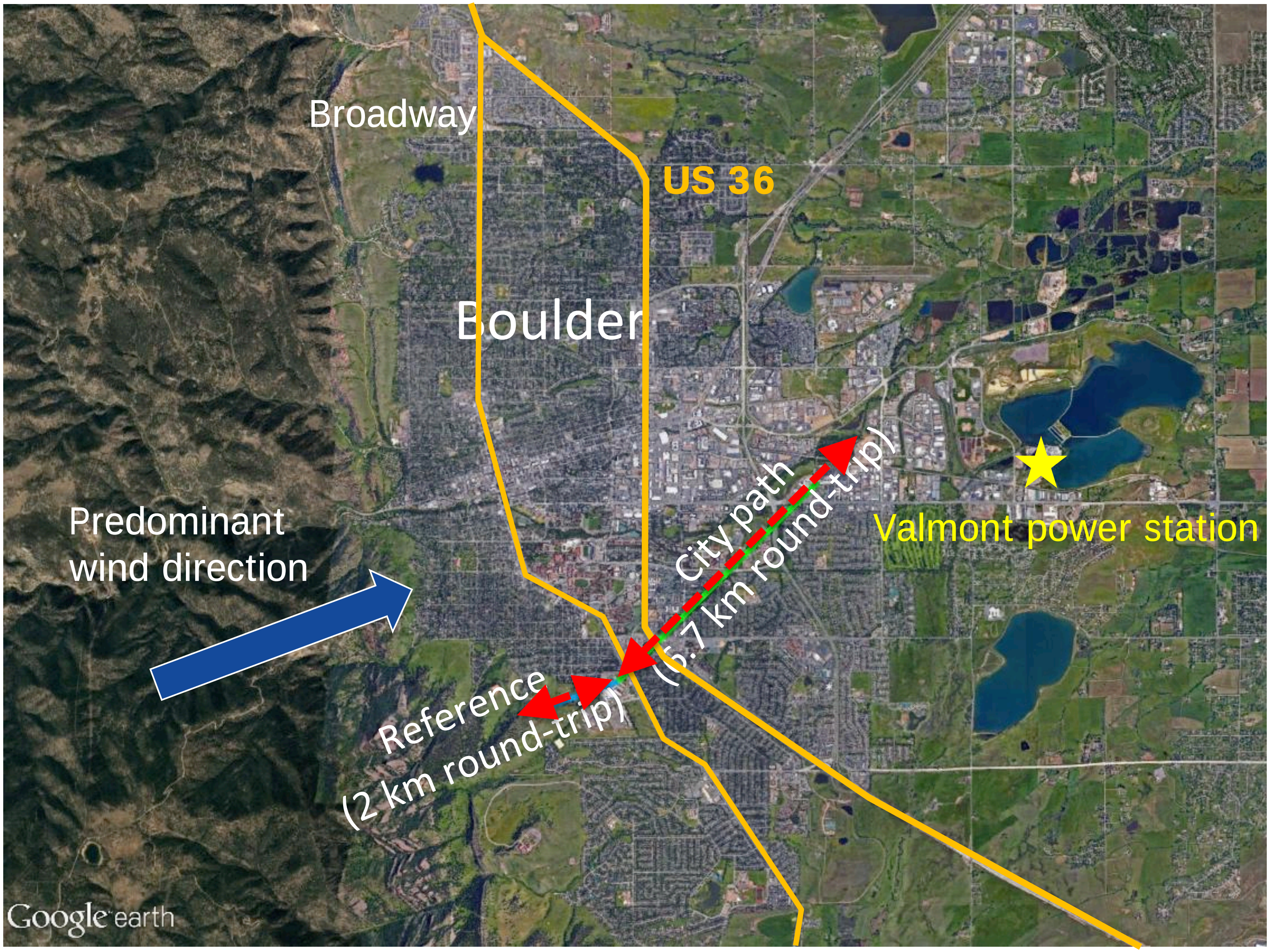
Waxman et al. (2017) AMTD

DCS comparison with CRDS

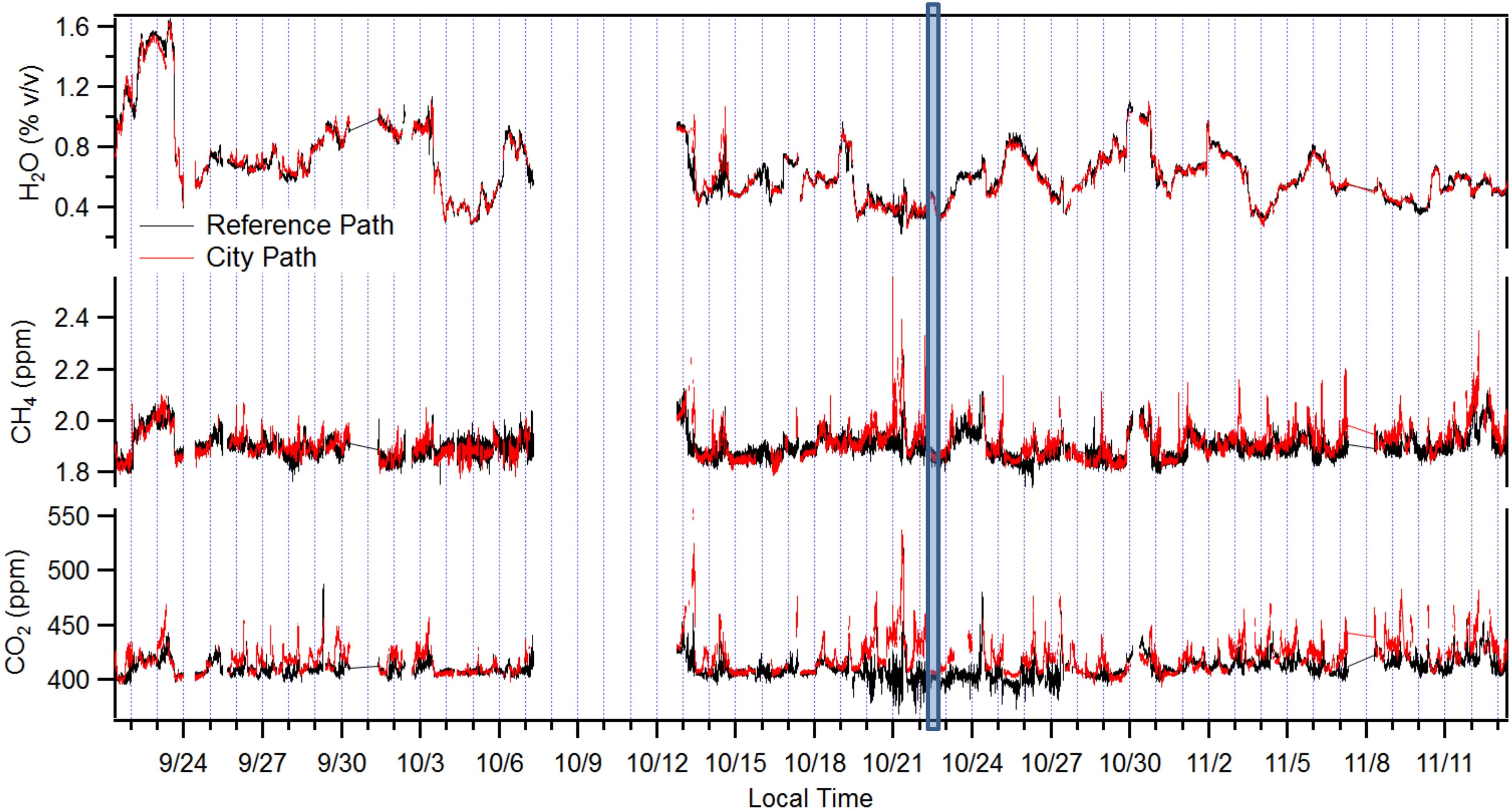


Mean differences: -3.4 ± 3.4 ppm CO_2, 17 ± 15 ppb CH_4, and 580 ± 462 ppm H_2O

Hub and spoke across Boulder

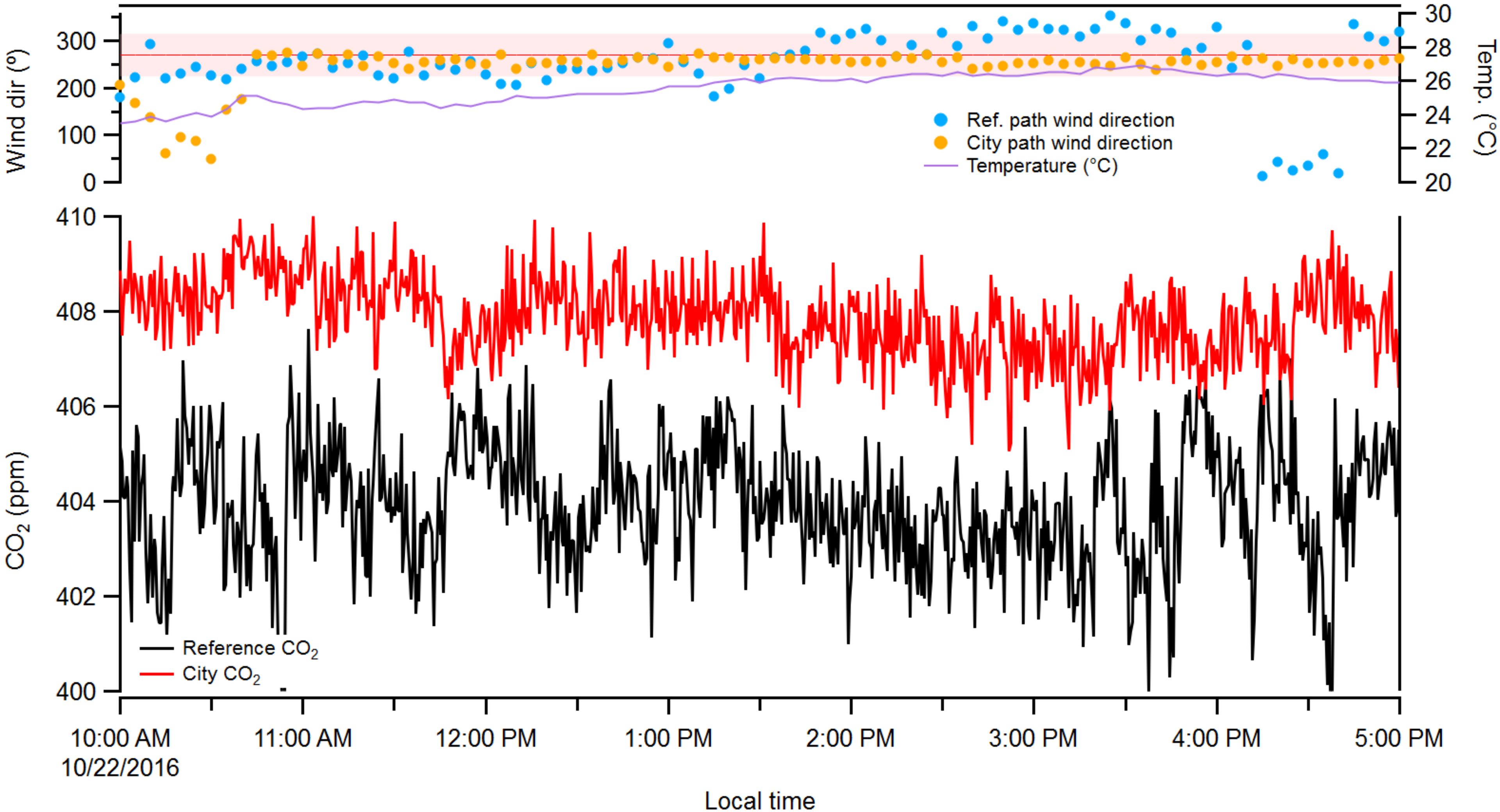


Hub and spoke data for 1.5 months



Goal: understand potential sources, magnitude of city emissions

Case study: Oct. 22 city enhancement



Consistent CO_2 enhancement over the city.

Preliminary estimation of city emissions

$$Q_i = u\Delta y H\left(\frac{c_{CO2,City}(t) - c_{CO2,City}(0)e^{-tu/\Delta x}}{1 - e^{-tu/\Delta x}} - c_{CO2,Ref}(t)\right)$$

Derivation in Seinfeld and Pandis

Q_i = city emissions
u = wind speed
Δy = width of box (perpendicular to wind, 2.7 km)
H = height of box (300 m, estimated from HYSPLIT vertical wind)
Δx = length of box (parallel to wind, 5.5 km)

City transportation emissions: 4.5×10^5 metric tons CO_2 from of vehicle travel annually (2015 inventory)

Assume:

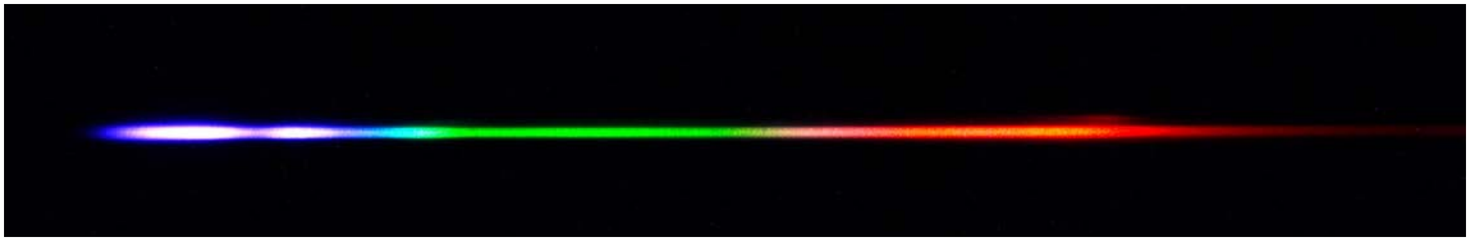
- this covers 25% of the city traffic emissions
- emissions representative of 8 hours/day, 250 days/year (work days)
- → estimate 6.4×10^5 metric tons of CO_2 annually
  - likely includes some contributions from CU and DOC power plants

Conclusions

- DCS measurements are quantitative
  - Spectra are acquired quickly, with high resolution, and are line-shape-free
  - Two DCS systems agree to better than 0.14% for CO_2 and 0.35% for CH_4.
  - Since this work, we may have identified source of discrepancy and improve future work.
- More work needs to be done on CO_2 and CH_4 cross sections
  - Likely source of disagreement between DCS systems and CRDS.
  - Upcoming lab project…
- Using a simple box model calculation, we measure ~150% of the city vehicle emissions inventory.
  - Refinement necessary but reasonable given that:
  - We likely also pick up emissions from the DoC and CU power plants and the NOAA boilers which do not count towards city vehicle emissions.

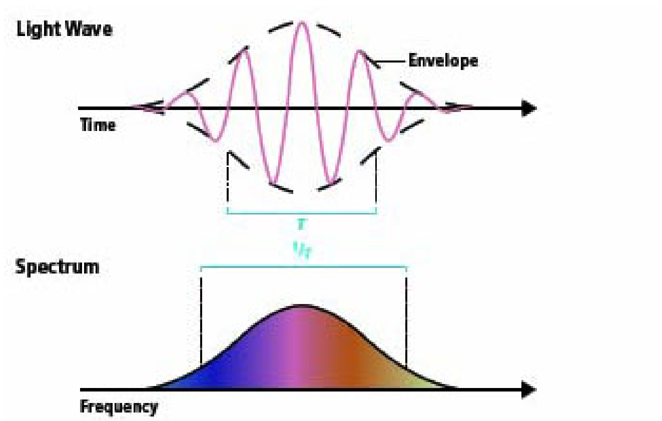
Backup Slides

Stabilized pulsed laser: the frequency comb



Time domain

Single pulse



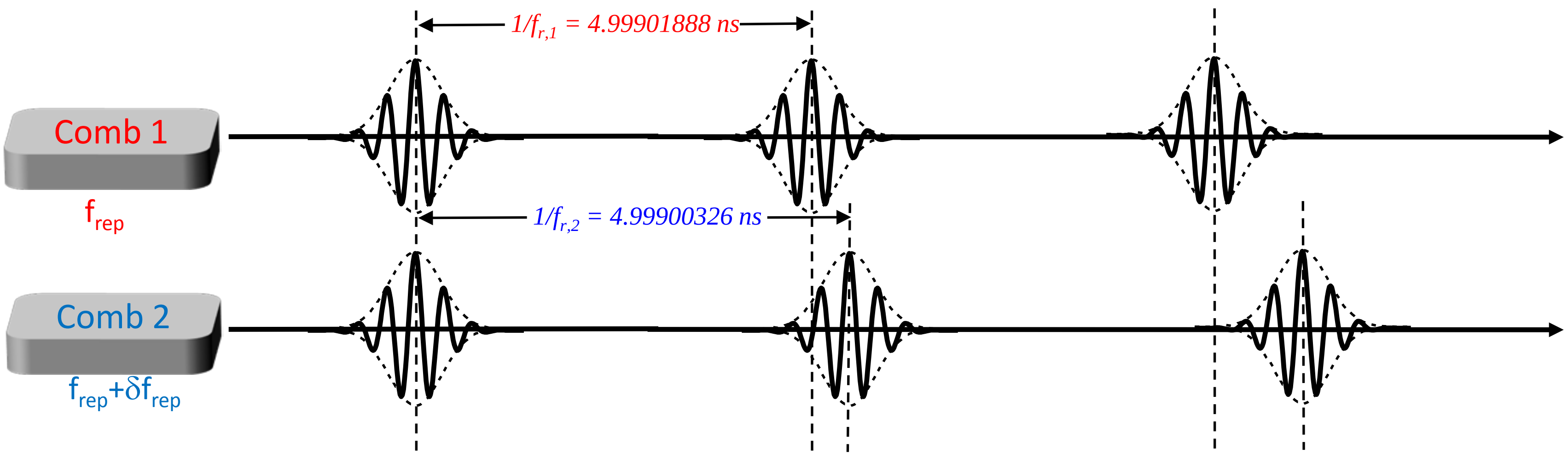
Frequency domain

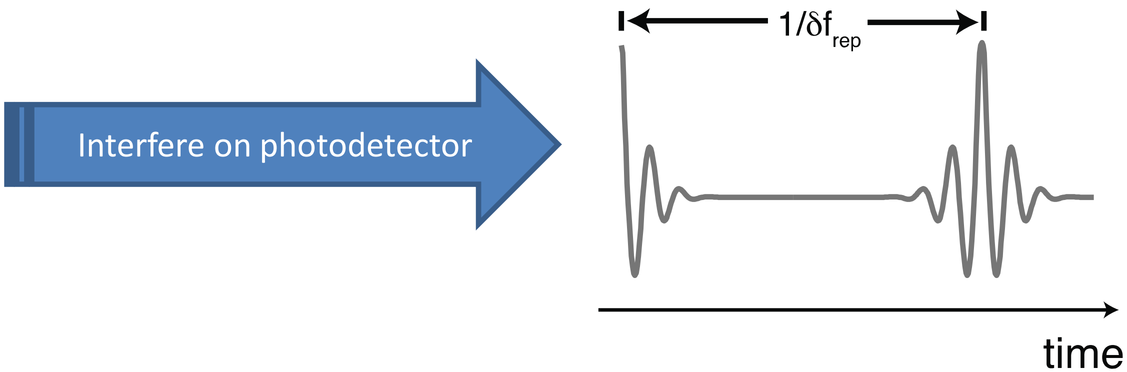
But pulses come every 5 ns → very hard to measure

Hall and Hänsch, 2005 Nobel Prize

S. T. Cundiff, J. Ye, and J. L. Hall, *Scientific American*, April 2008

Two frequency combs: Dual comb spectroscopy



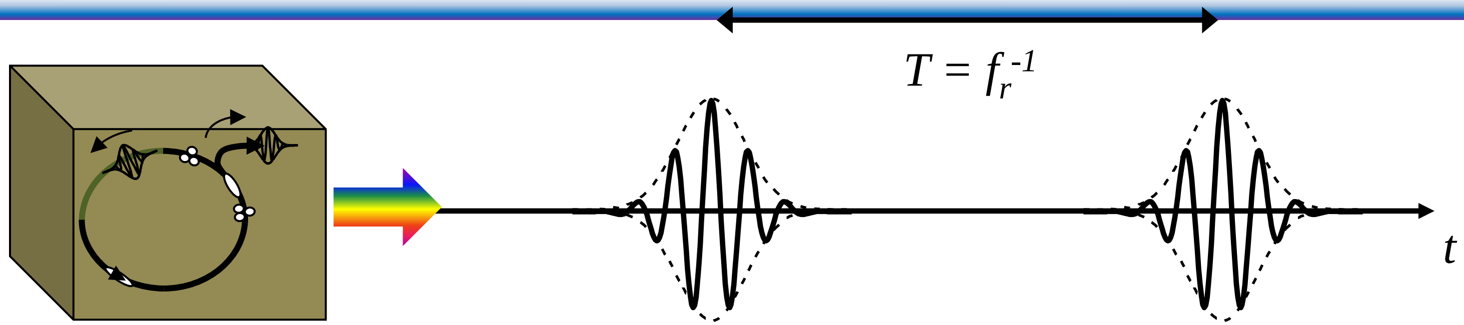


Conceptually similar to FTIR, but:

- **No moving parts**
- **~0.0067 cm^{-1} point spacing**
- **<0.001 cm^{-1} instrument line shape**
- **Rapid scanning (~2 ms per interferogram)**
- **Calibration-free**

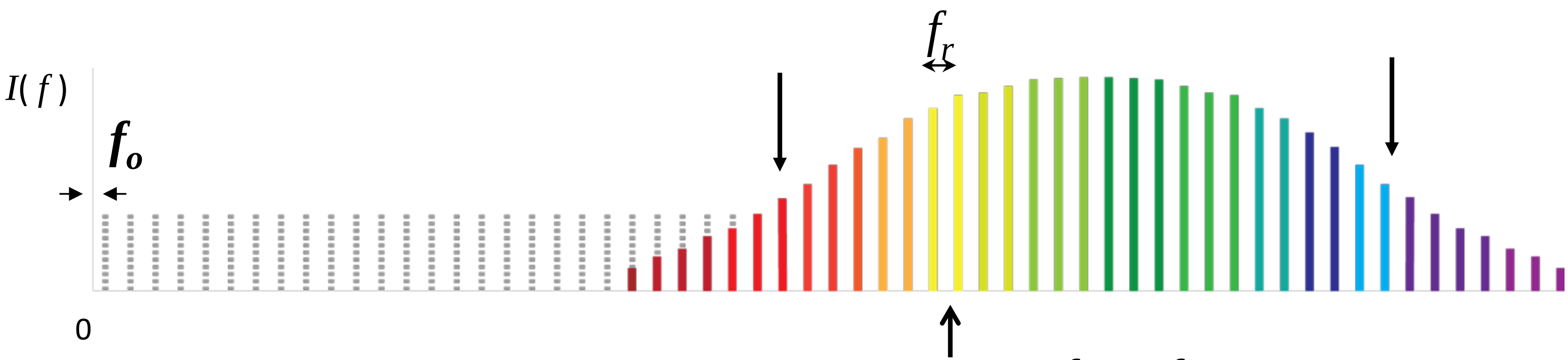
Interferograms arrive every 1.6 ms → much easier to measure

Frequency Comb: Stabilized Mode-Locked Laser



Passively
Modelocked Laser

Frequency comb : Modes stabilized by locking two degrees of freedom



nth comb tooth frequency: $\nu_n = f_o + n f_r$

Each tooth can be 1 Hz wide