Advances in Spectroscopic Methods for Gas Sensing

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CCQM-GAWG Workshop 2016
Standards and Measurements for Clean Air
Instituto Português da Qualidade (IPQ)
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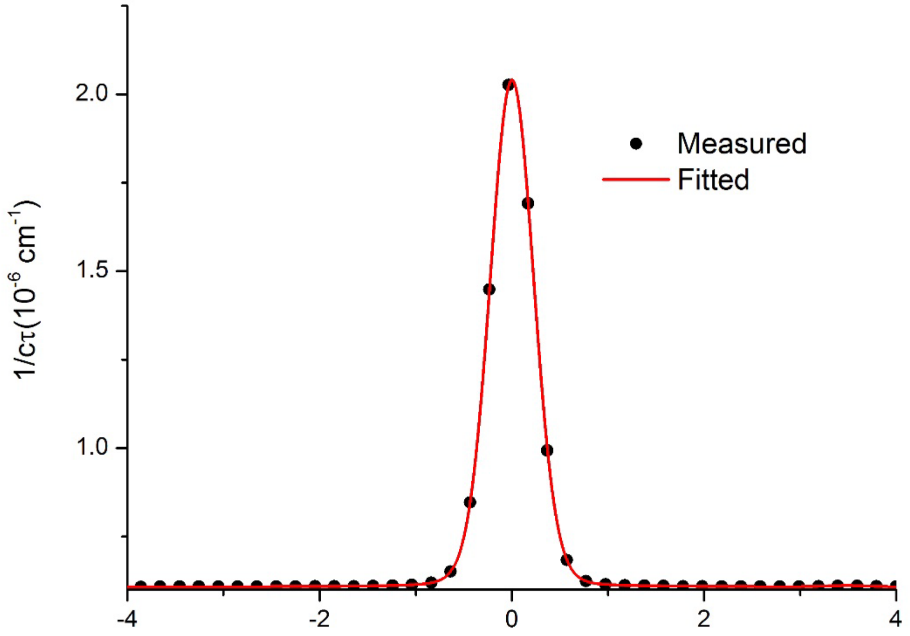
14 October 2016



GHG and Carbon Flux Monitoring

Total Carbon Column Observation Network (TCCON)

Ambitious, high cost, high profile satellites require an unprecedented level of precision (≈0.1%) for reference data to fulfill mission goals

OCO-2 and GOSAT

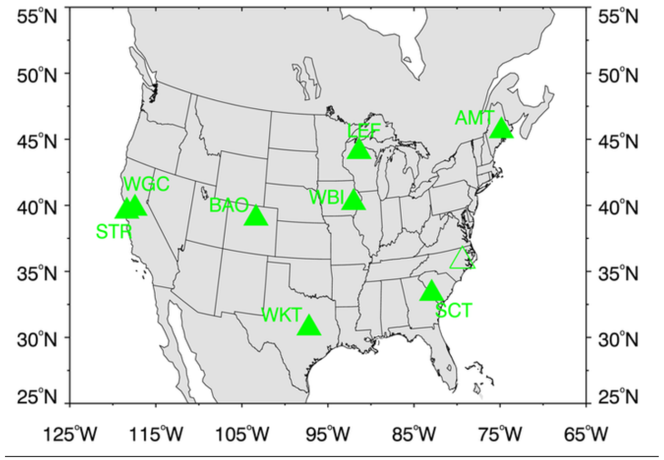
O_2 is evenly mixed in Earth's atmosphere

Used to characterize systematic fluctuations and drifts occurring during atmospheric retrievals of CO_2 and CH_4

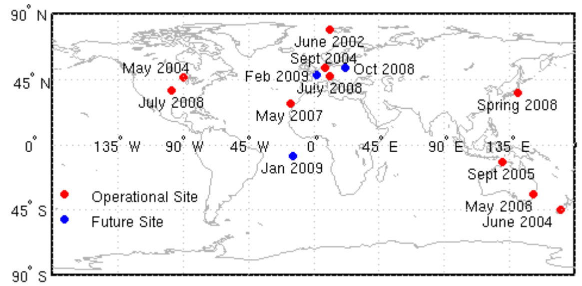
R.A. Washenfelder et al., *J.Geophys. Res.* **111**, D22305 (2006)
NASA, *The Earth Observer*, August 2014, Volume 26, Issue 4

GHG and Carbon Flux Monitoring

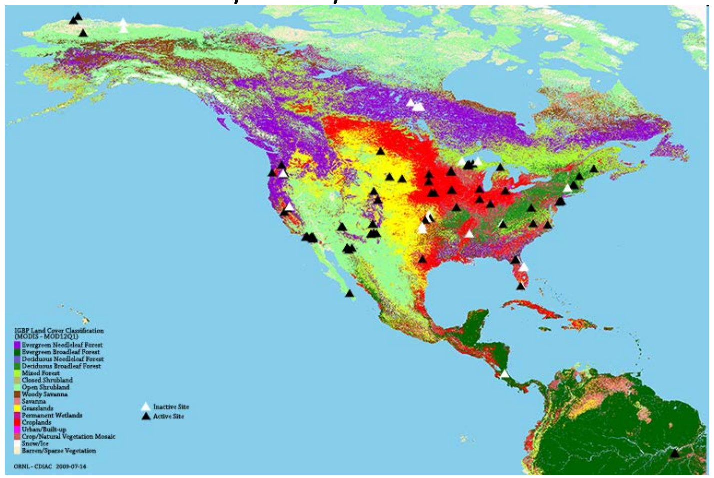
NOAA ESRL Tall Tower Network

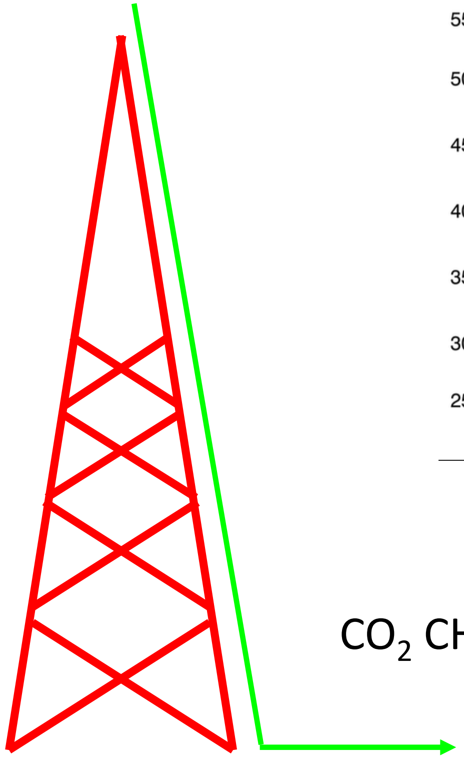


Total Carbon Column Observing Network TCCON



Ameriflux/Fluxnet
DOE/NASA/NSF





CO_2 CH_4 … analyzer

calibration gas
($$$$)

Laboratory Spectroscopy

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GOAL: Link the unique light absorption properties of small molecules to the SI.

DELIVERABLE: Provide standard reference data via high-precision, high-accuracy laser spectroscopy in the laboratory.

FUNDAMENTAL: Evaluate theoretical ab initio models for molecular absorption beyond STP conditions.

Physical Basis for Light Absorption

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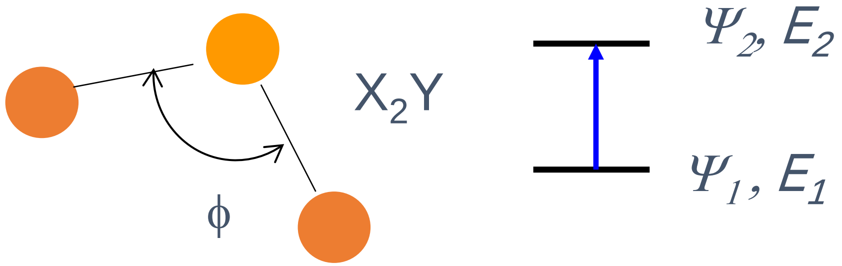
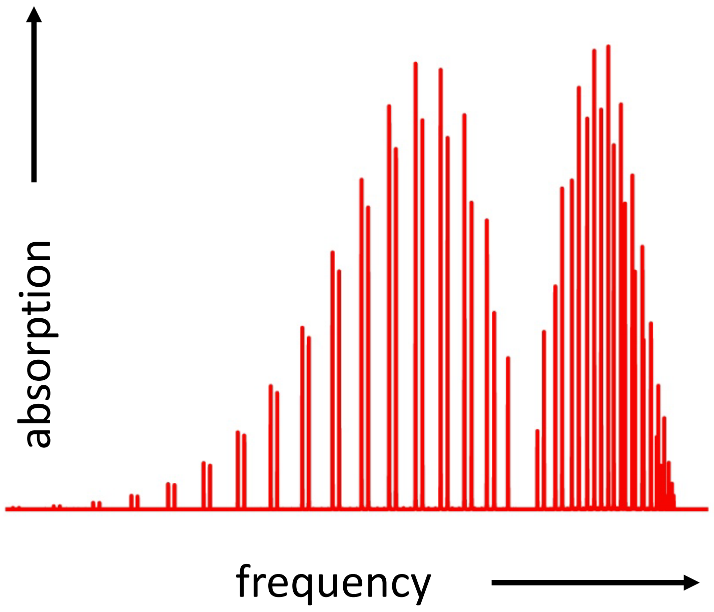
Spectra depend on molecular properties:

charge distribution, mass, molecular geometry, force constants, …



$$\nu_{21} = \frac{E_2 - E_1}{h}$$



“small” molecules (CO_2, CH_4, N_2O, CO, H_2O, O_2 …)

Each transition is characterized by:

q’’, q’	set of quantum numbers
ν	frequency
$\lvert\mu_{21}\rvert$	transition moment
S_{21}	intensity = const$\lvert\mu_{21}\rvert^2\{\exp(-E_1/k_bT)\}/Q(T)$

HITRANonline

hitran.org

HITRAN*online*

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The HITRAN Database

HITRAN is an acronym for *hi*gh-resolution *tran*smission molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere.

News

Articles describing HITRAN*Online*, HAPI and new line shape representations

Video tutorial for using HITRAN*online*. Recording from 10.26.2015 webinar

All inquiries can now be made to HITRAN's support team at *info@hitran.org!*

Database Updates

Correction of quantum identification of 50 HOCl lines in the 1200-1300 cm^{-1} region

Inclusion of HFC-23 and addition of new HFC-134a cross-sections

Addition of HT profile parameters in the v_3 band of N_2O

Update of SO_3 lines in the pure rotational band

Addition of HCN lines above 3500 cm^{-1}

Update of the CH_3Cl line list

Implementation of the Hartmann-Tran profile: H_2 case study

Update of broadening parameters for HO_2

4:08 PM 10/13/2016

What is the Role of Gas Standards?

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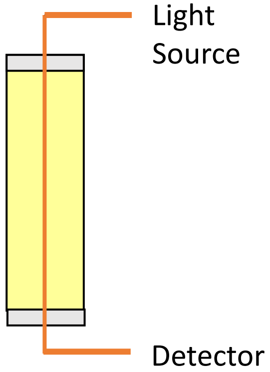
Measurements of intrinsic molecular property – line intensities (*S*)

- Well characterized sample (n,T,p, etc.)
- “State-of-the-art” spectroscopic measurement
- Models & uncertainty analysis



Line intensity
Peak area
number density

$$S = A / n$$

where $n = \chi\, n_T$

$$n_T = P / (k_B\, T)$$

Spectroscopy goals:

- Reduce the need for repeated production of primary standard
- Cross-check the stability of primary mixtures and low-concentration standards
- Expand the suite of supported species
- Enables standards for reactive & unstable mixtures

Absorption spectroscopy can yield low-uncertainty measurements of gas concentration in terms of intrinsic molecular properties that are linked to the SI

Gravimetric Standards and χ

Required to provide a traceable measure of the mole fraction.

For a gas mixture, the mole fraction (χ) is provided by a gravimetric gas standard

Line intensity
Peak area
number density

$S = A / n$

where $n = \chi\, n_T$

$n_T = P / (k_B\, T)$

Measuring the Line Intensity, *S*

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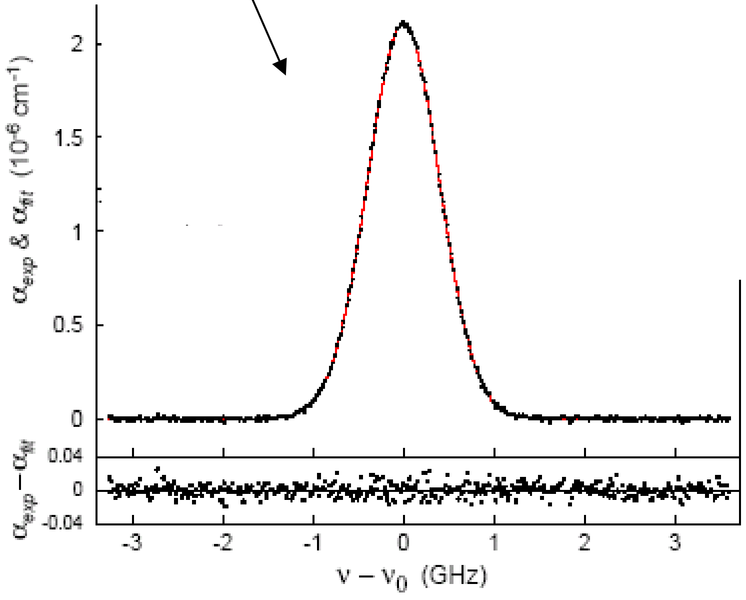
$$S = A/\{\, n \int g(\nu)\, d\nu \,\}$$

spectrum area *absorber concentration* *line profile*



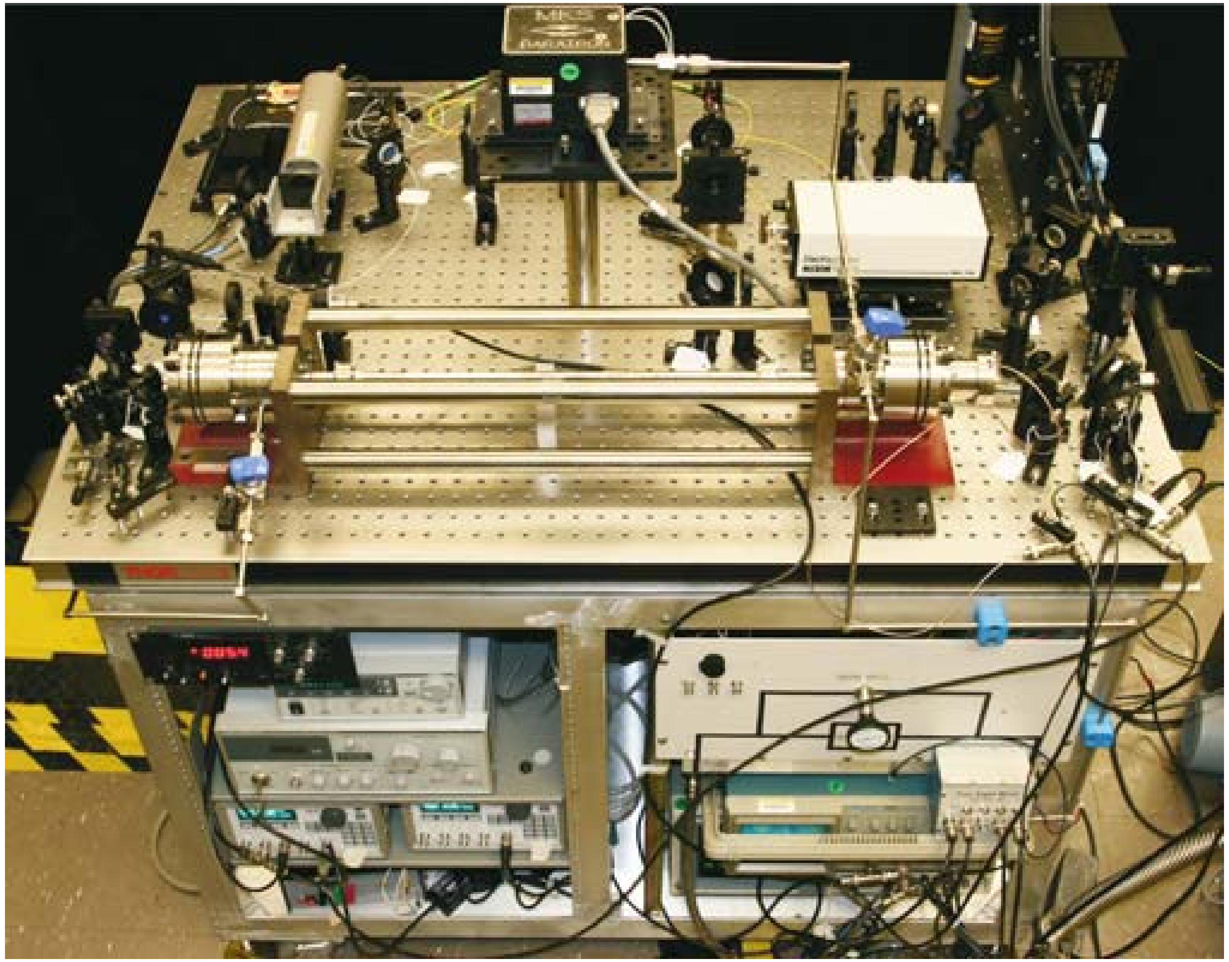
Measurement of *S* with low (< 1%) combined uncertainty requires the accurate determination of 3 difficult-to-characterize quantities:

Instrumental distortion (*x* and *y* axes) of spectrum

Absorber number density, *n*, to “calibrate” *S*
For strong lines may have molar fractions < 10^{-5}

“True” line shape not well known (small deviations from standard models become important)

How do we do this at NIST?



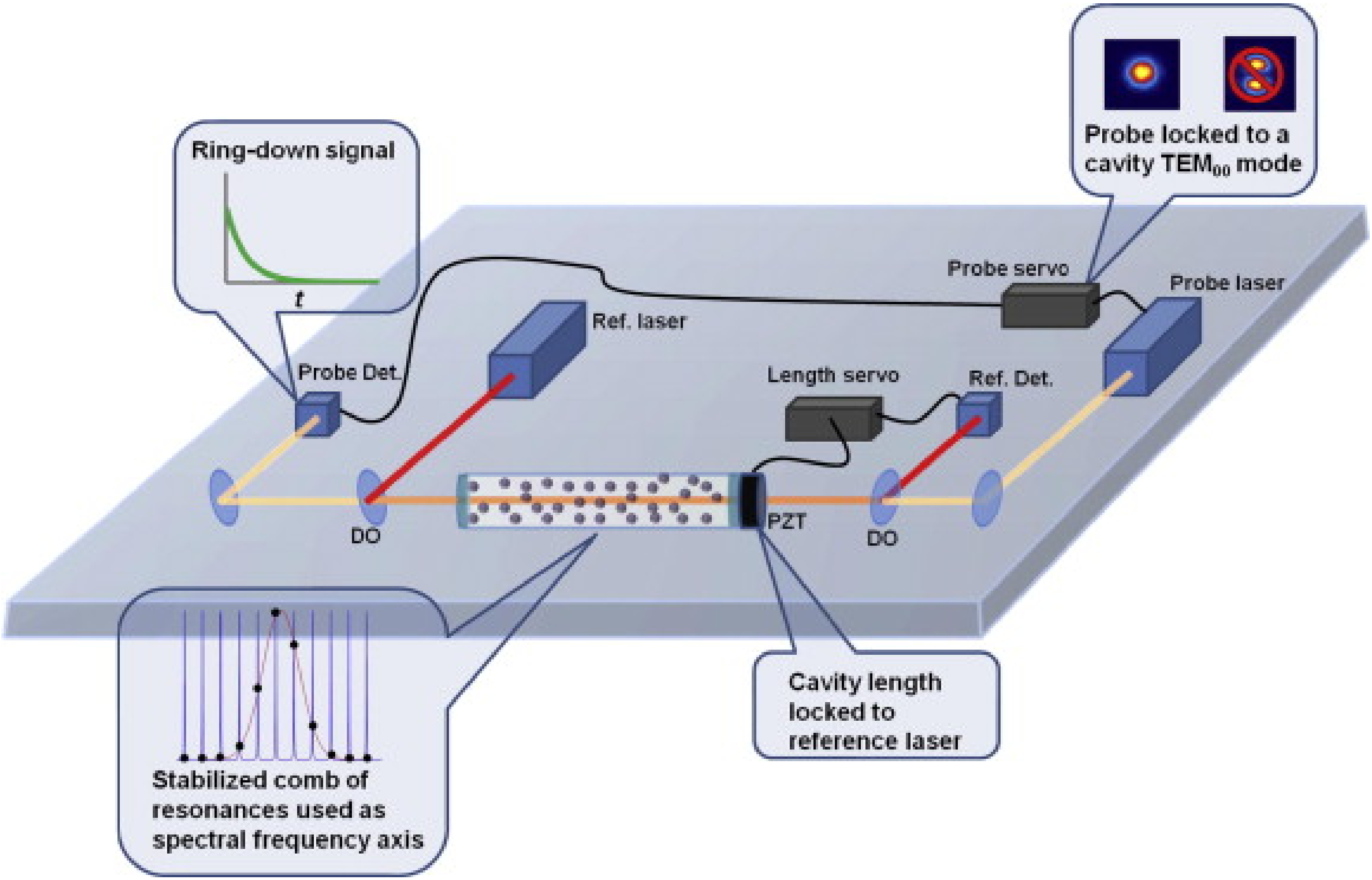
J.T. Hodges and D. Lisak, *Appl. Phys. B* **85,** 375 (2006)

Frequency-stabilized CRDS

Length servo – frequency ruler
1 part in 10^{10}

Probe servo – high acquisition rate
$10^4 – 10^6$ per second

External cavity diode laser
150 cm^{-1} bandwidth



J.T. Hodges et al., *Rev. Sci. Instrum.* **75,** 849 (2004)
D.A. Long et al., *Chem. Phys. Lett.* **536**, 1 (2012)

Optical Resonator Properties

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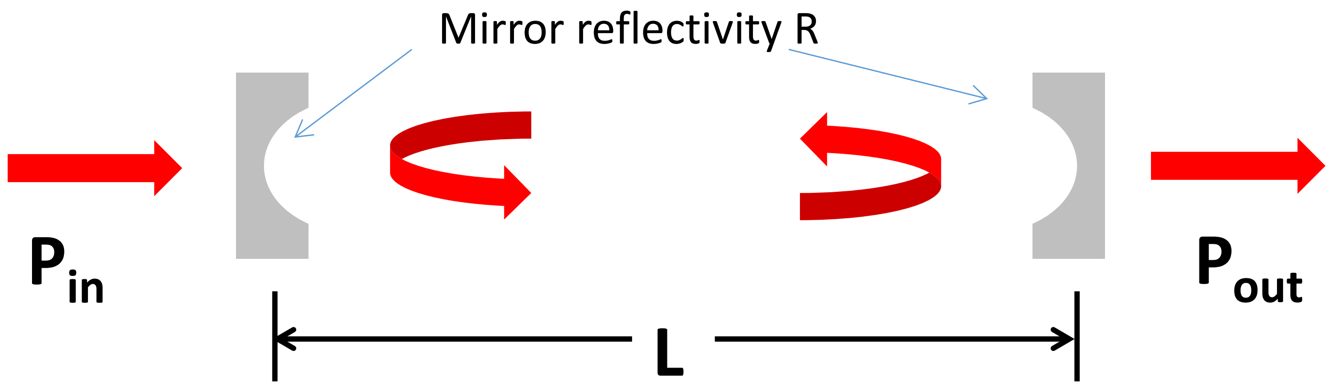
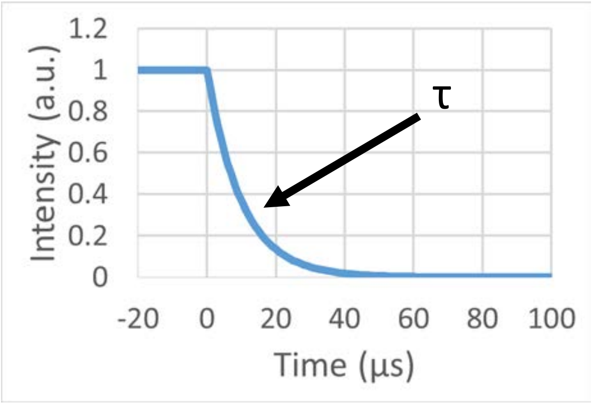




Resonances occur at multiples of c/2L — **comb-like structure, may provide spectrum "ruler"**

$F = (c/2L)/(\Delta\nu_{mode}) = \pi/(1 - R)$ — **cavity finesse**

Resonance width is $\Delta\nu_{mode} = (c/2L)/F$ — **exceptionally good frequency filter, [typically ~1 to 50 kHz]**

Effective interaction path length is $L_{eff} = (F/\pi)*L$ — **yields high-sensitivity to light absorption by cavity medium**

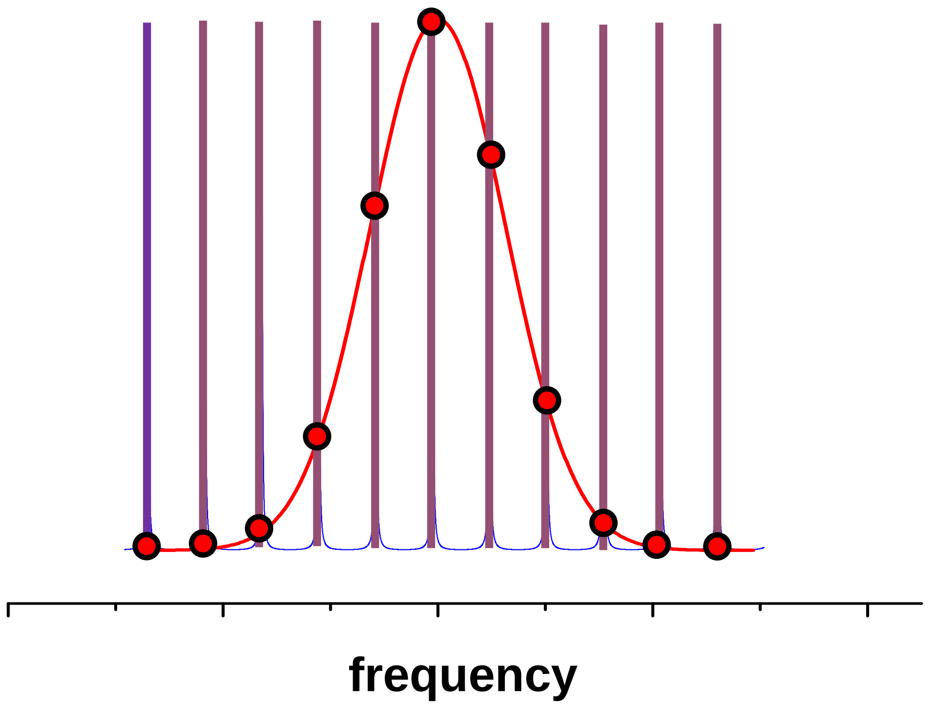
Can be interrogated via cw transmission or by observing passive decays (ring-down)

Scanning in FS-CRDS

March from one mode of the cavity to the next, with high fidelity

Tuning temperature, current, or external cavity

Maintain cavity transmission with low-bandwidth transmission lock or with stabilization to a high-resolution wavelength meter



Beer-Lambert Law

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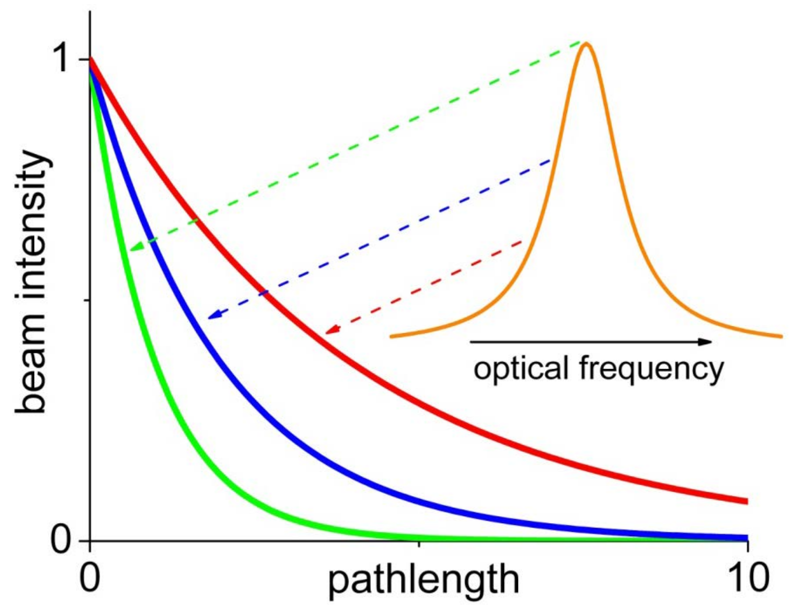

$$\alpha = 1 / (c\, \tau)$$

$$\alpha(\nu) = S\, n\, g(\nu - \nu_0)$$

$$T(\nu) = \exp(-\alpha(\nu)\, L_{eff})$$

Summary of FS-CRDS Advantages

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Extremely high sensitivity due to effective path length!

Precision measurement of the absorption path length is not required!

CRDS is immune to laser light amplitude fluctuations!

Gas absorption is measured in the time domain, *x*-axis is frequency!

High frequency agility is achieved using modern telecom components!

Traceability to the SI!

J.T. Hodges et al., *Rev. Sci. Instrum.* **75,** 849 (2004)
D.A. Long et al., *Chem. Phys. Lett.* **536**, 1 (2012)

Linking FS-CRDS to the SI

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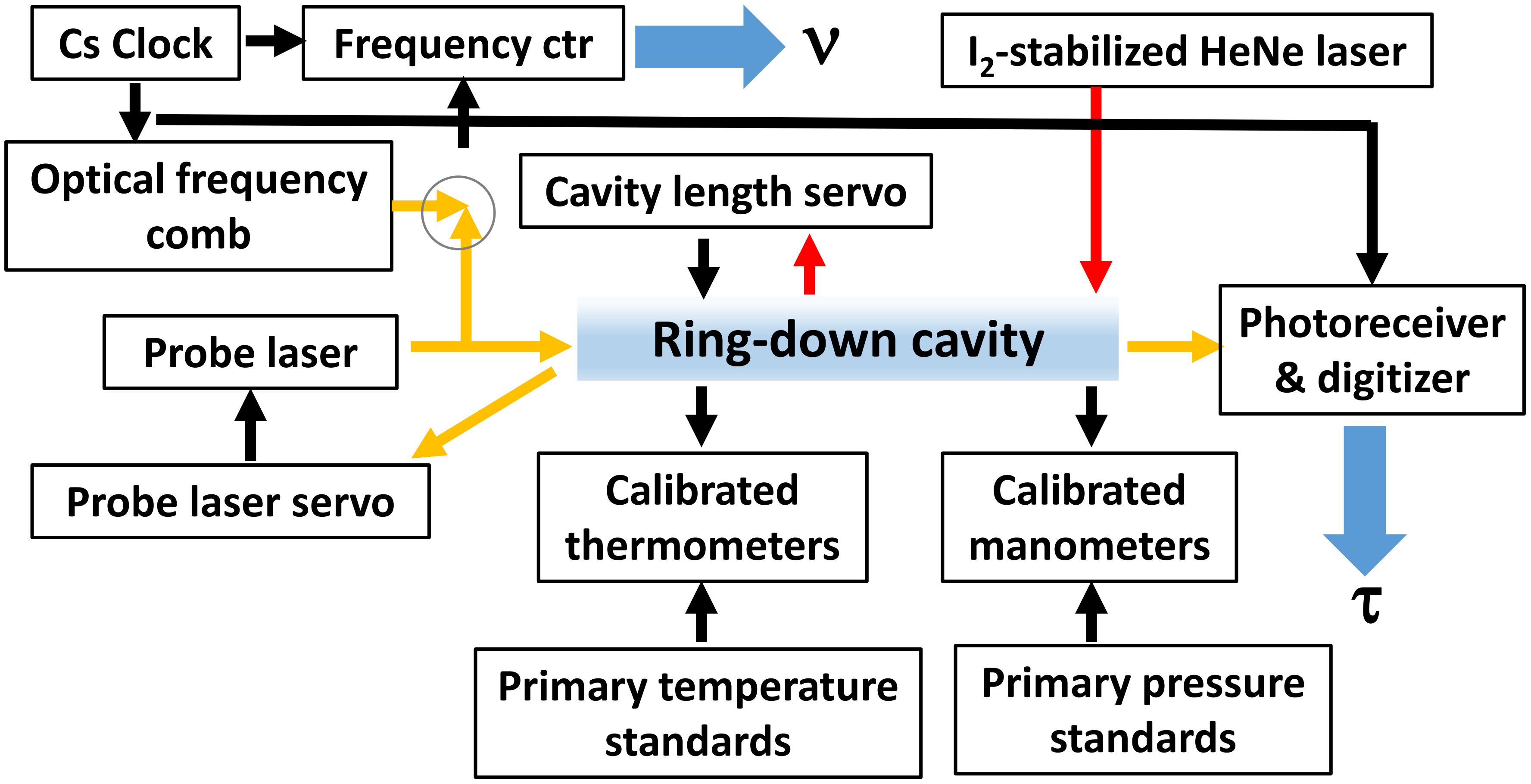

Instruments Currently at NIST

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Exp.	Molec.	Spec. region (nm)	Base losses (ppm)	Cavity length (cm)	Setup	NEA (cm^{-1} $Hz^{-1/2}$)	Studies
1	CO_2, CO, CH_4	1570 & 2000	20-150	73	DFB laser, fiber amplifier, mobile, FARS	10^{-11} – 10^{-10}	line shapes, absolute line intensities, isotopic ratios (dual-wavelength setup)
2	O_2, H_2O	1280	50	73	ECDL, link to OFC	10^{-11} – 10^{-10}	line shapes, absolute line intensities, absolute positions
3	CO_2, CO, CH_4 C_2H_6	1570-1670	20	139	ECDL, fiber amplifier, link to OFC	$4x10^{-12}$	line shapes, absolute line intensities, absolute positions
4	CO_2, CO	1570-1630	150	73	PDH-locked ECDL, FARS technique, link to OFC	$2x10^{-12}$	line shapes, absolute positions, shifts, extremely rapid scanning, wide spectral coverage
5	$^{14}CO_2$	4530	50-200	139	low temperature cavity, QCL	10^{-11}-10^{-10}	measurement of radio-carbon at natural abundance
6	CO_2, CH_4	1570-1670	20	80	DFB, with monolithic invar cavity	10^{-11}	Temperature dependence of line shapes (220 – 300 K) with mk-level stability
7	O_2	760-780	20 – 200	73	ECDL	10^{-10}	Line mixing and line shape effects in O_2 A-band

Highlights of Recent Work

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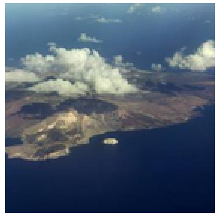
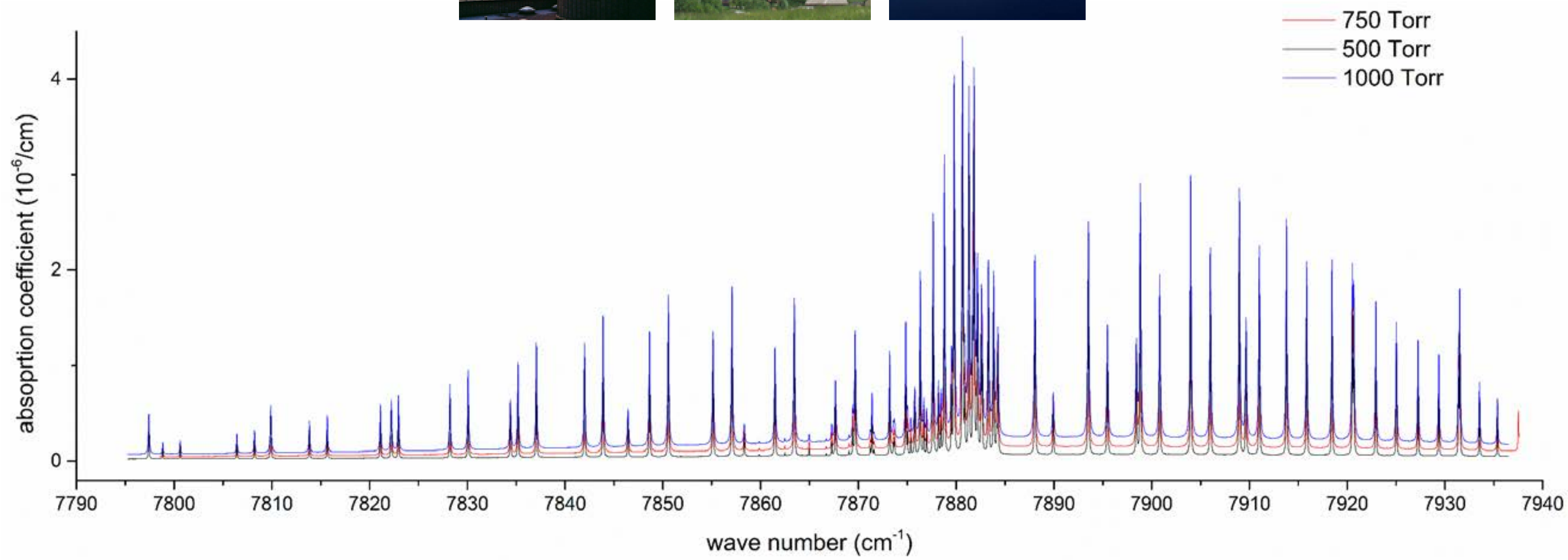
Improving TCCON Retrievals



TCCON

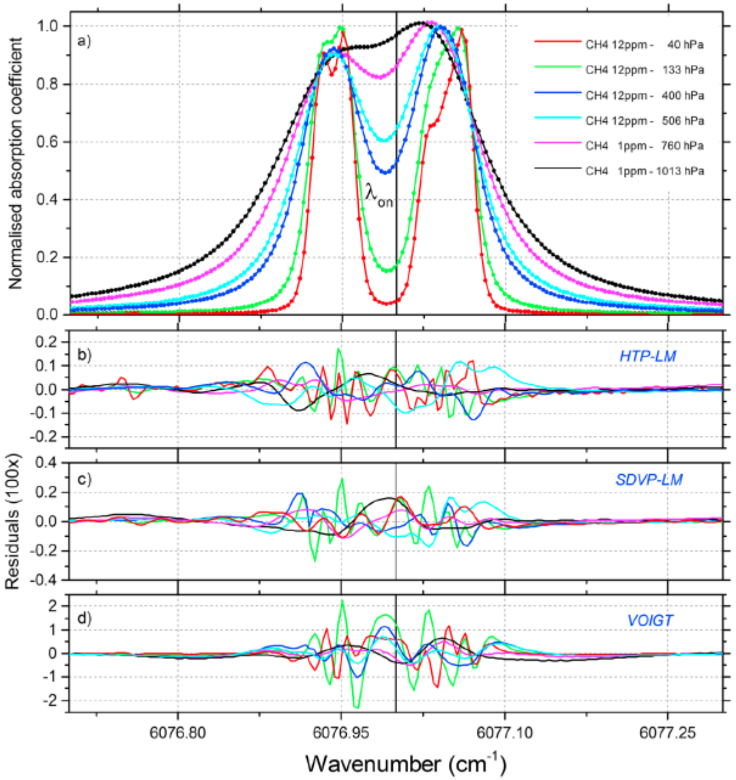


7-fold reduction in airmass dependence correction after incorporating new O_2 line list

J. Mendonca et al., *AGU Fall Meeting* (2015)

MERLIN

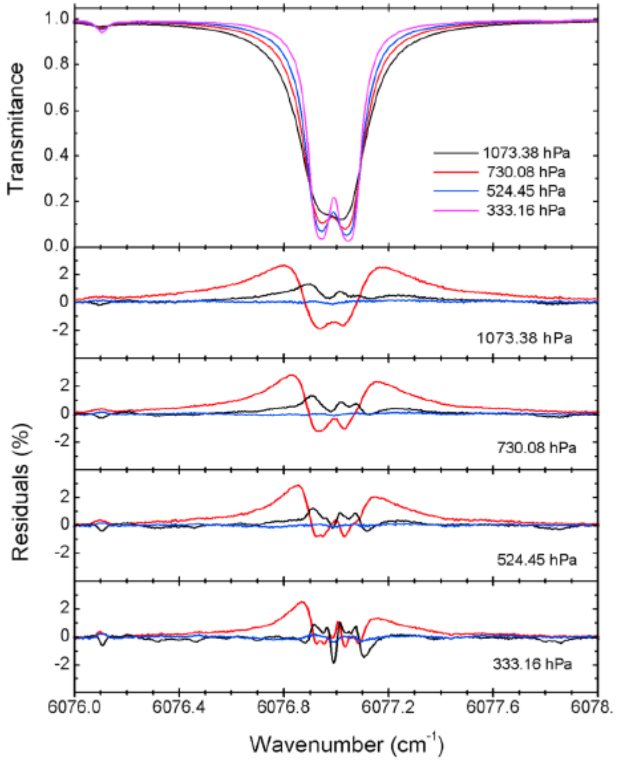
FS-CRDS spectra



Achieved residuals at 0.1 % level

T. Delahaye et al. *J Geophys Res.* **121,** 7360-7370 (2016)

FTS spectra



Line parameters from FS-CRDS

HITRAN 12 VP **HITRAN 08 VP**

Next step: Measure spectra from 220 K to 300 K

Measurement of Rare GHG Isotopes

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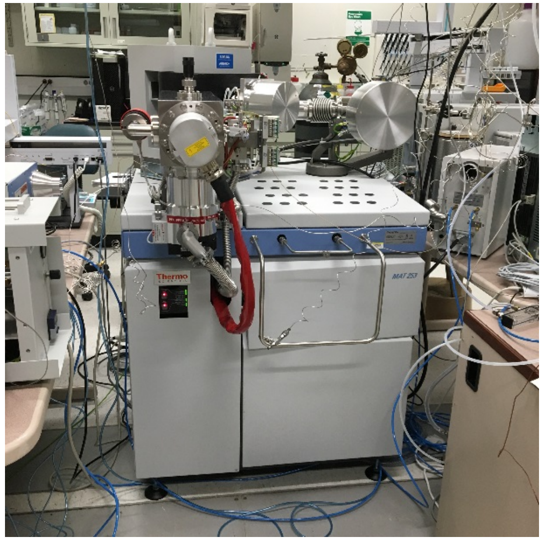
Goals & Applications

Characterizing isotopic composition of standard reference gas mixtures

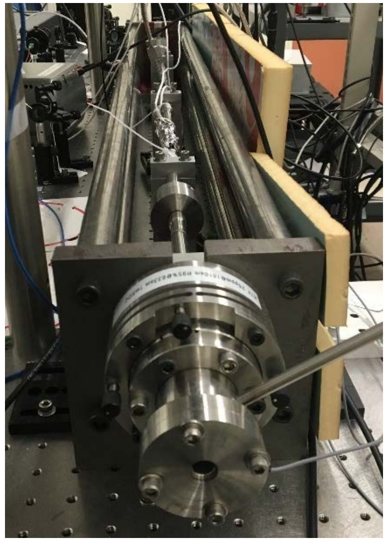
Establishing SI-traceable, spectroscopic measurements of carbon and oxygen isotope ratios of GHGs in terms of *ab initio* calculations and comparison with traditional scales based on isotope-ratio mass spectrometry of carbonate materials

MAT 253 (IRMS)



$\delta^{13}C$ & $\delta^{18}O$

Cavity ring-down spectroscopy



Multiplexed Spectroscopy

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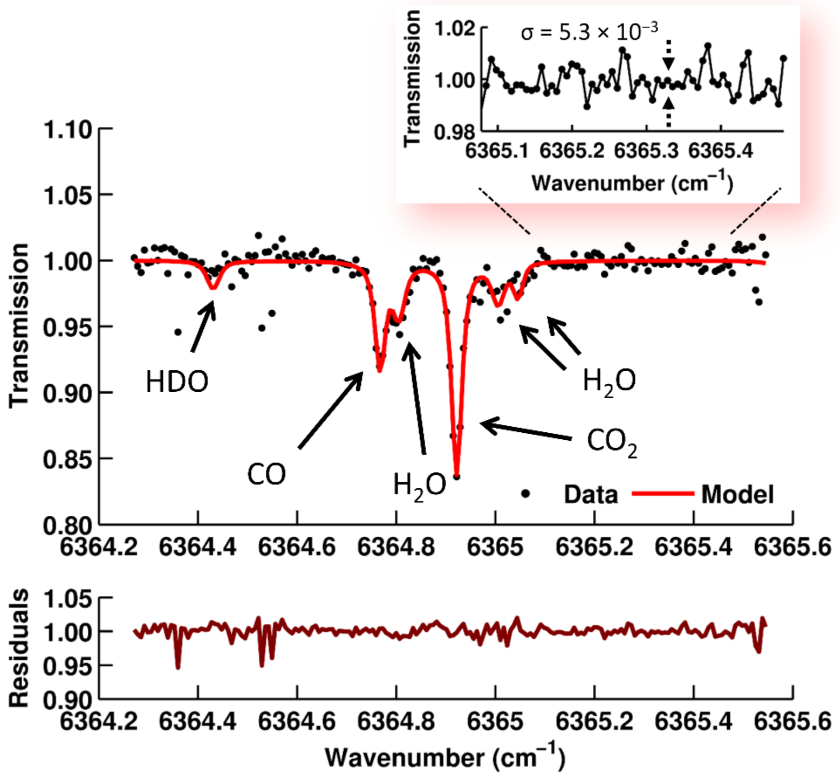


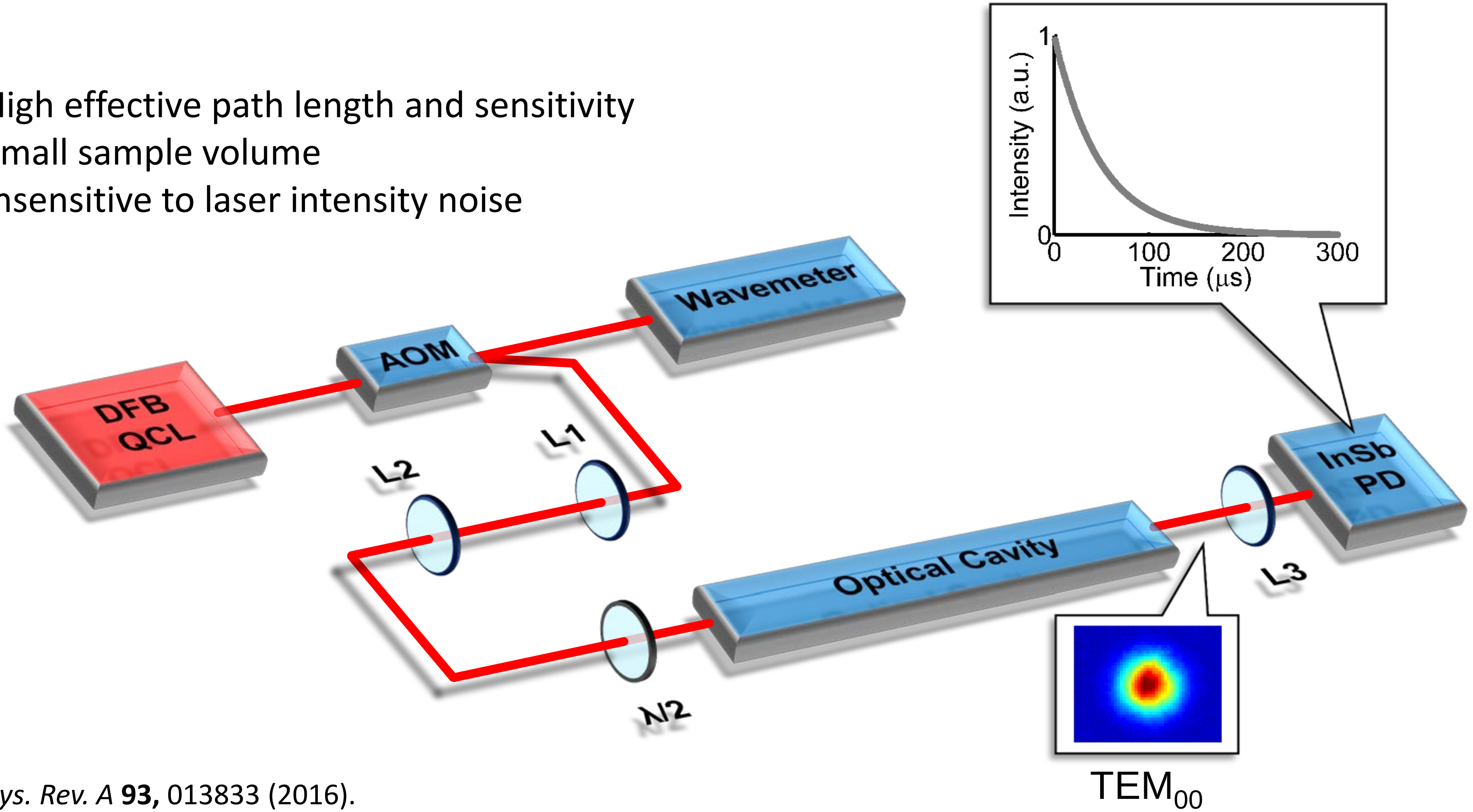
Optical frequency comb generators using standard fiber-coupled telecom components

Multiplexed spectral acquisition in microseconds (10^{-6} s)

D.A. Long et al., *Opt. Lett.* **39,** 2688-2690 (2014).
A.J. Fleisher et al., *Opt. Express* **24,** 10424-10435 (2016).
D.A. Long et al., arXiv: 1609.06211 .

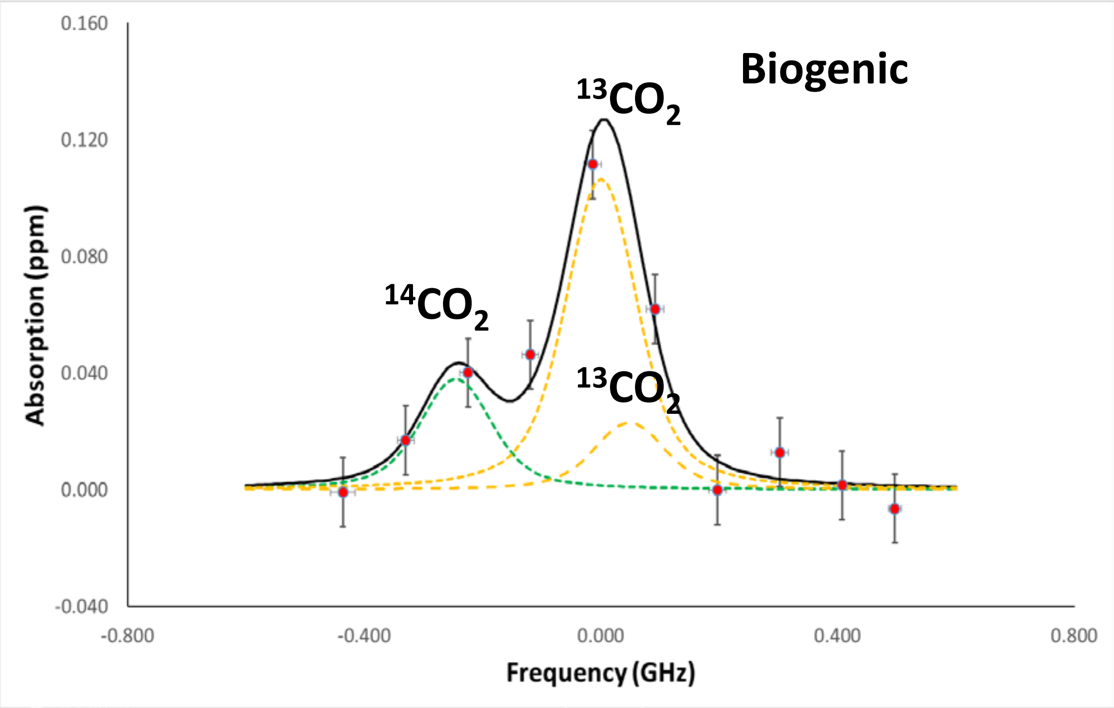
CRDS in the Mid-Infrared

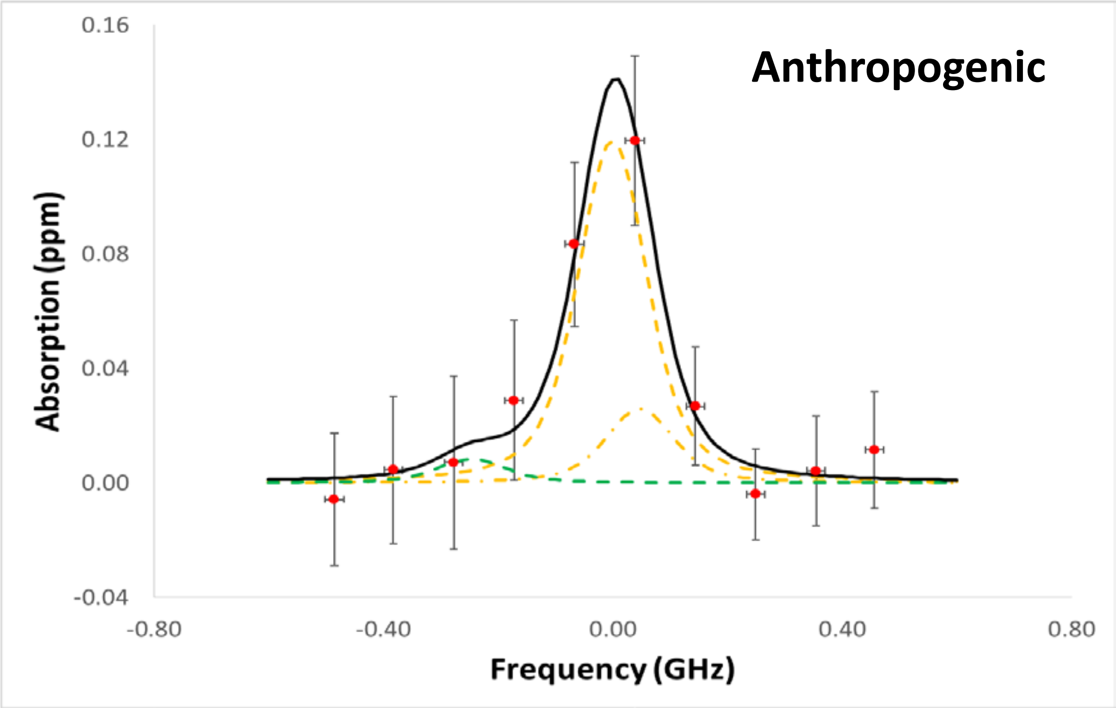
- High effective path length and sensitivity
- Small sample volume
- Insensitive to laser intensity noise



A. J. Fleisher et al., *Phys. Rev. A* **93,** 013833 (2016).
D. A. Long et al., *Opt. Lett*. **41,** 1612-1615 (2016).

Optical Detection of $^{14}CO_2$





D.A. Long et al., *AGU Fall Meeting* (2015)
D.A. Long et al., *CLEO Conference* (2016)

Ab Initio Line Intensities

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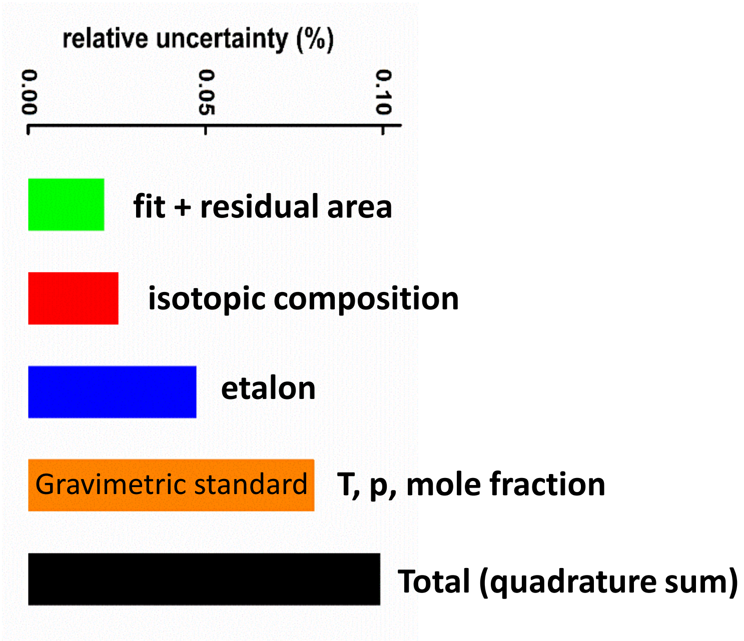
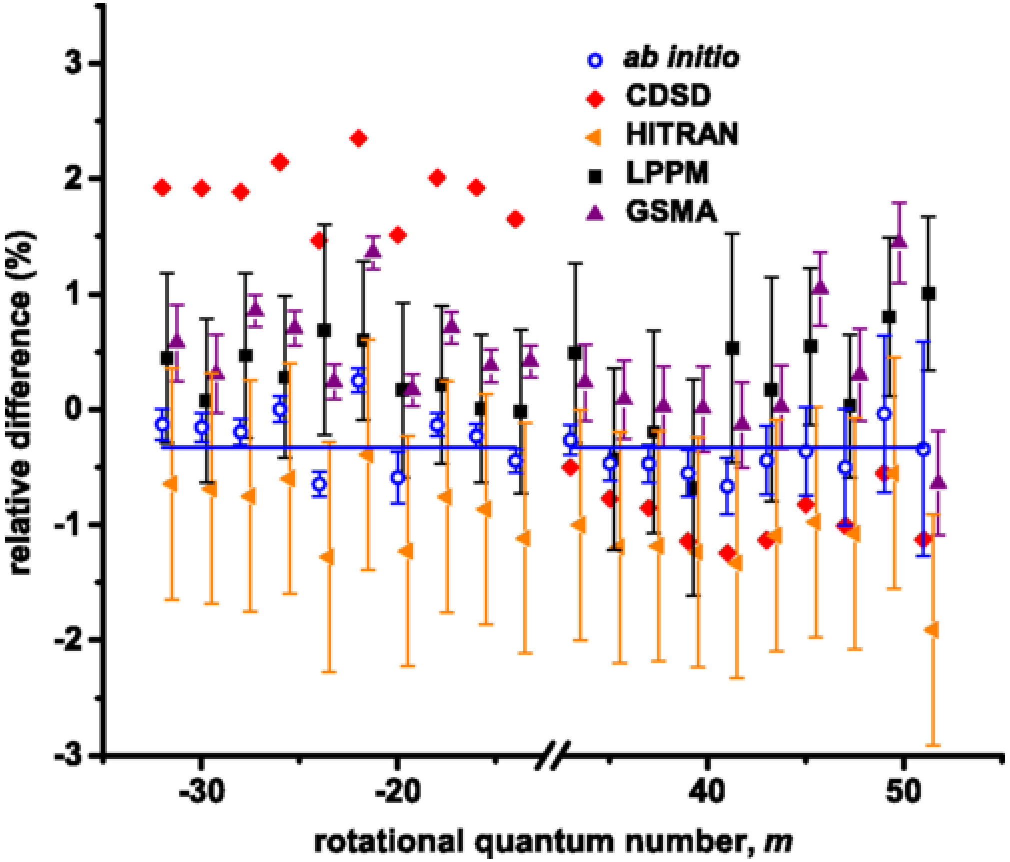
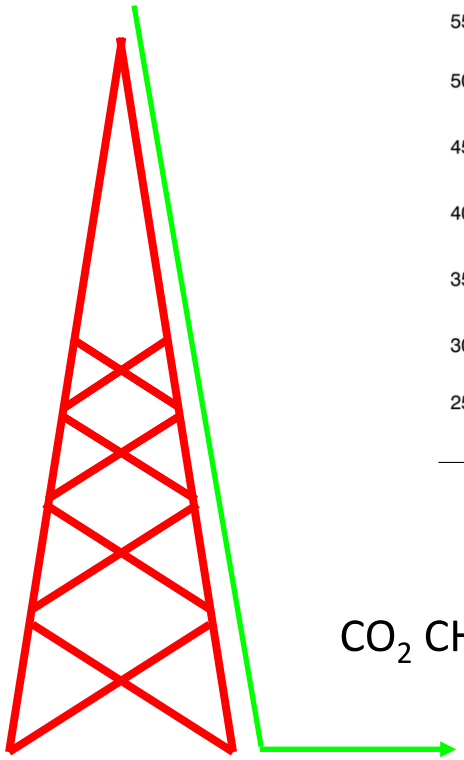
Measurement uncertainties





O. L. Polyansky et al., *Phys. Rev. Lett.* **114**, 243001 (2015)

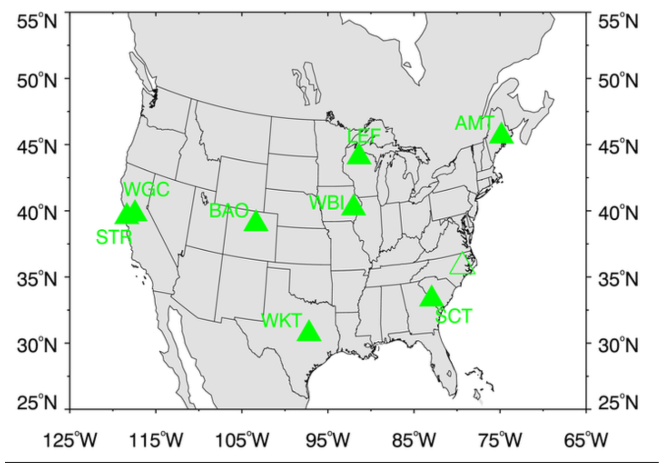
GHG and Carbon Flux Monitoring



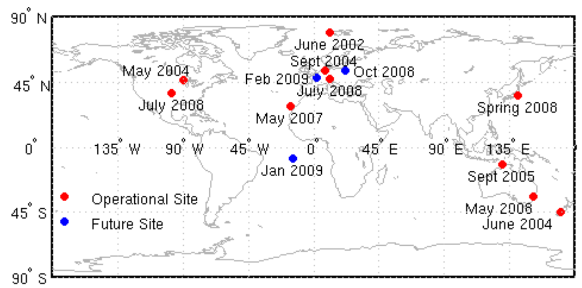
CO_2 CH_4 … analyzer

calibration gas
($$$$)

NOAA ESRL Tall Tower Network



Total Carbon Column Observing Network TCCON



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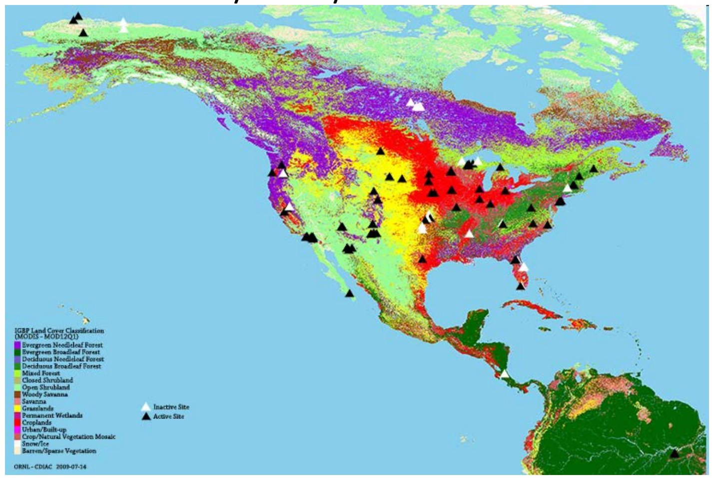
DOE/NASA/NSF



GHG and Carbon Flux Monitoring

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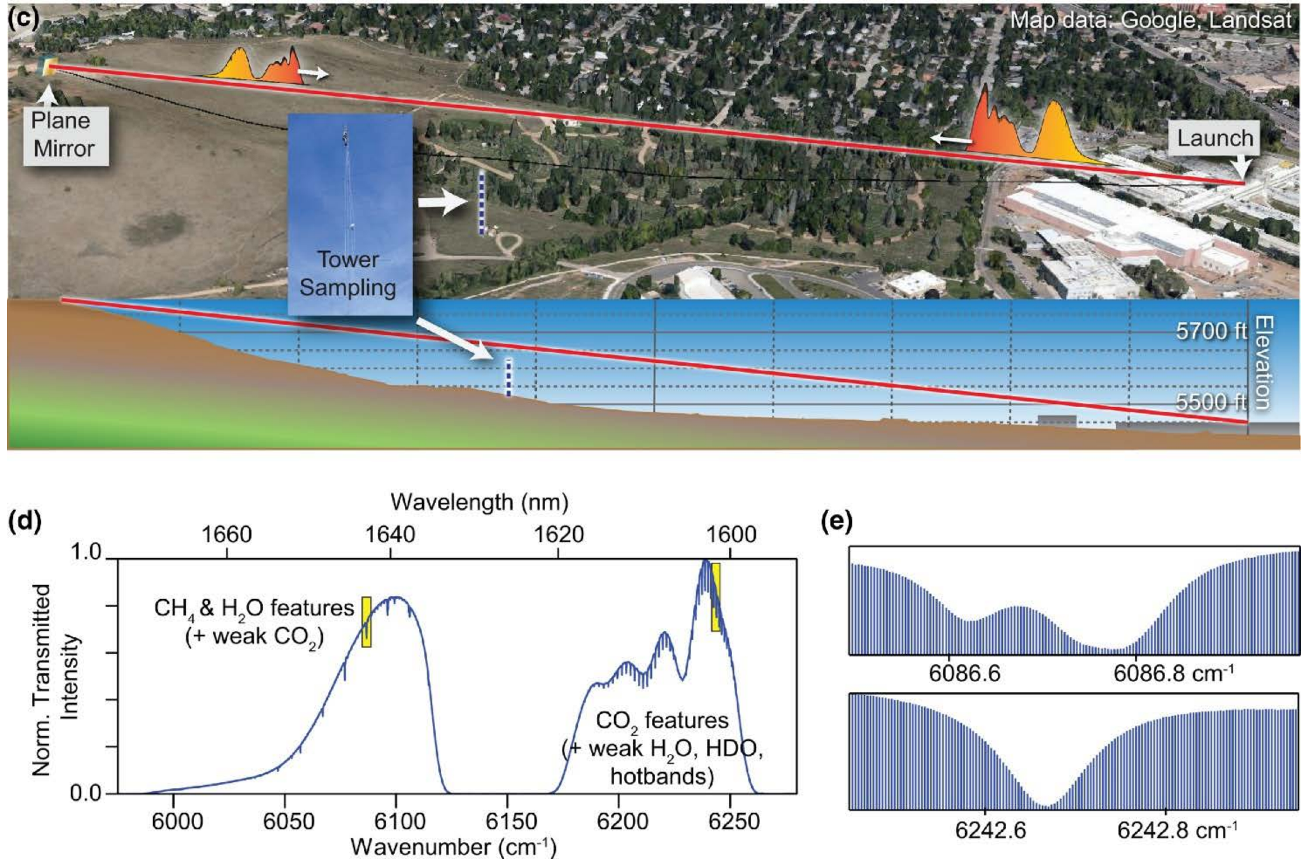
Dual-comb spectroscopy over an open path



Broadband spectroscopy of several thousand molecular absorption features recorded simultaneously

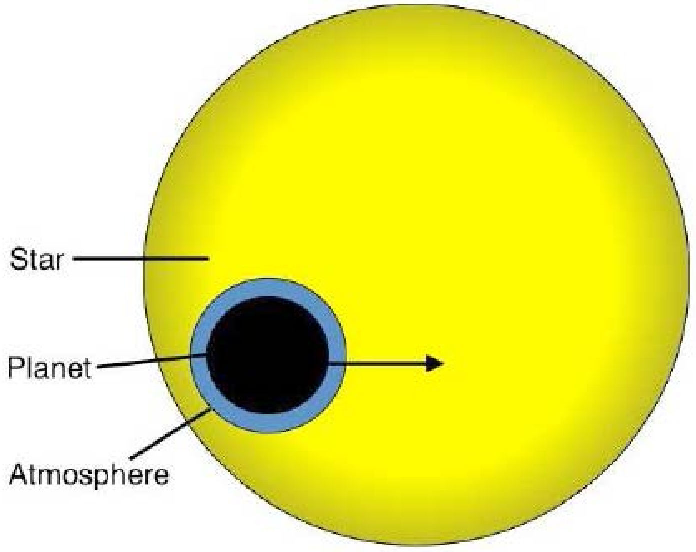
Included multiple species and multiple isotopologues

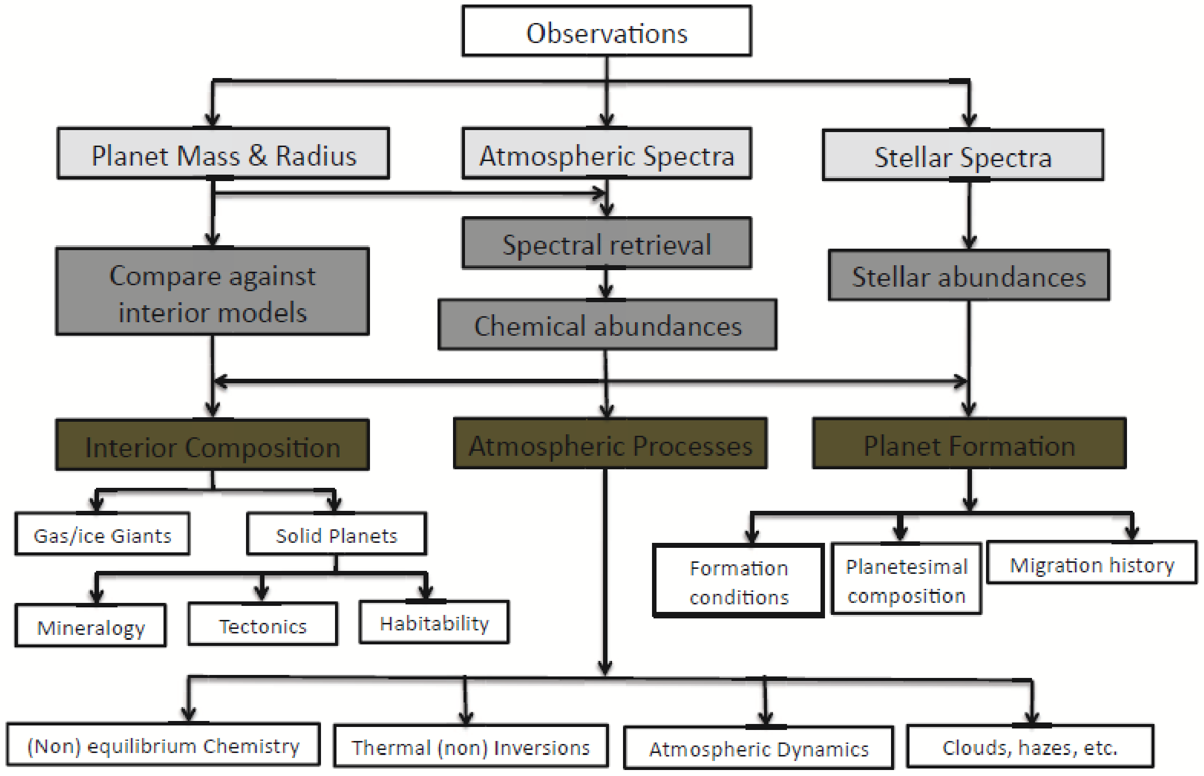
Line parameters are required over a very broad frequency range, and potentially at more exotic temperature and pressure regimes (combustion, exoplanetary searches, etc.)

G.B. Rieker et al., *Optica.* **1**, 290-298 (2014)

Exoplanetary Atmospheres

Planetary Transit





N. Madhusudhan et al., arXiv: 1402.1169v1.

Acknowledgements

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NIST Greenhouse Gas Measurements and Climate Research Program
NIST Innovation in Measurement Science (IMS) award
NASA OCO-2 Science Team
NRC Postdoc Program

Postdocs wanted: adam.fleisher@nist.gov

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How do we do this at NIST?

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U.S. Department of Commerce