GHG Measurements

Roger van Zee

August 1, 2014

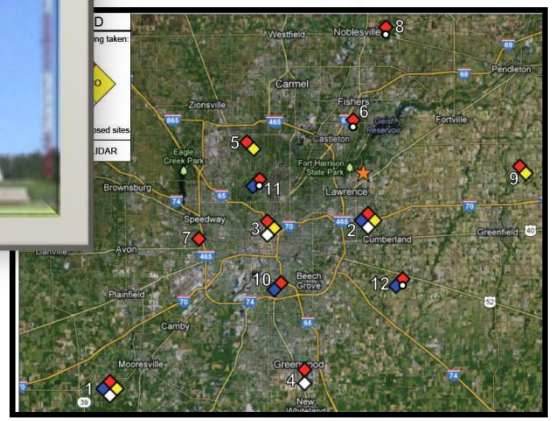
Enabling Inventories

- Reference Data Measurement
- Technology Development
- Standard Reference Materials

Inventories

- Measured at surface, by plane, by satellite

TCCON

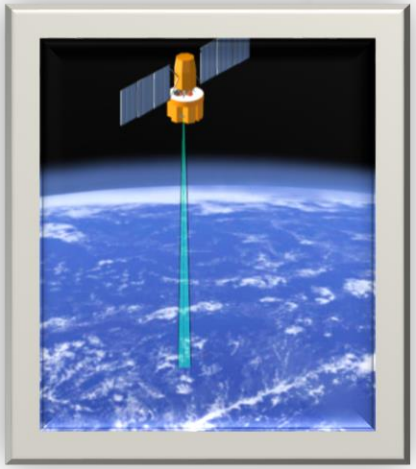


INFLUX

OCO

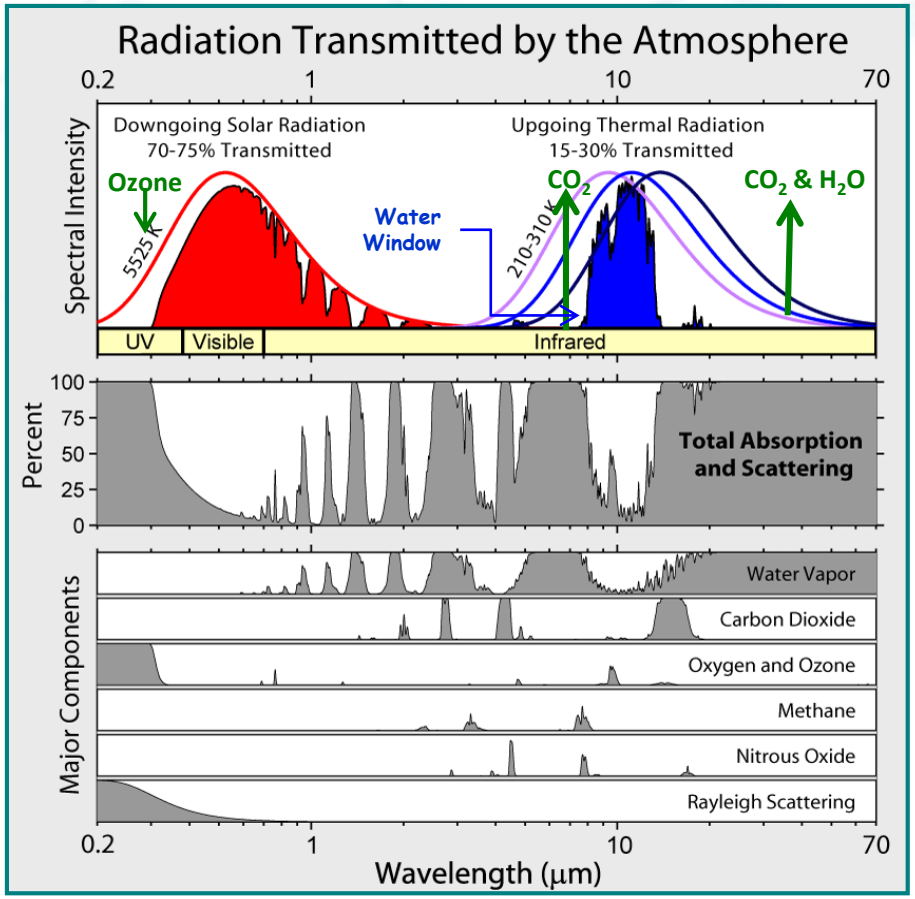
- Rely on spectroscopic measurement,

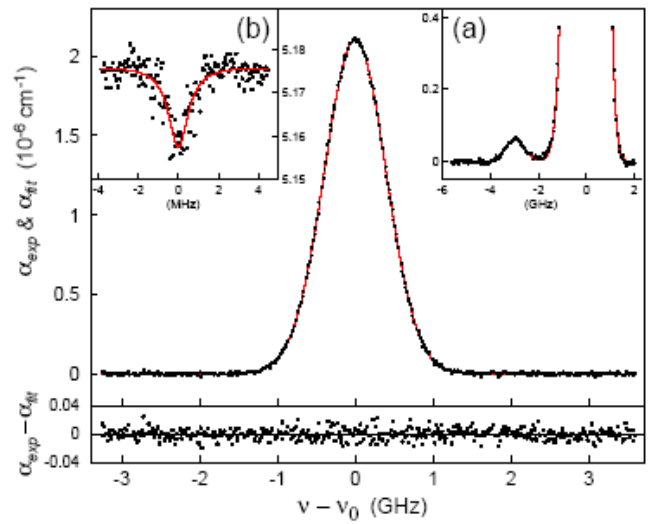
$$[GHG] \propto \frac{A}{\sigma\, l}$$



ASCENDS

Spectroscopic Measurements





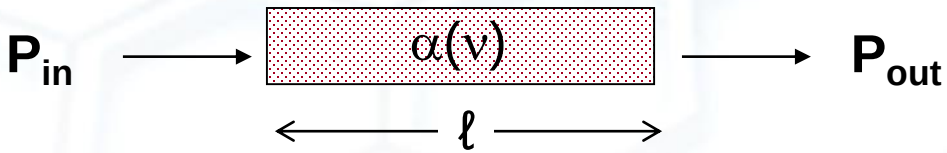
$$[GHG] = \frac{\int \alpha(\nu)\,d\nu}{n \int \alpha(\nu)\,d\nu}$$

BACKGROUND

J Hodges, H Layer, D Long, P Looney, G Scace, R van Zee

ABSORPTION SPECTROSCOPY BASICS

Beer-Lambert Law



$$P_{out} = P_{in} \exp[-\alpha(\nu)\,\ell]$$

P – power

ℓ – length

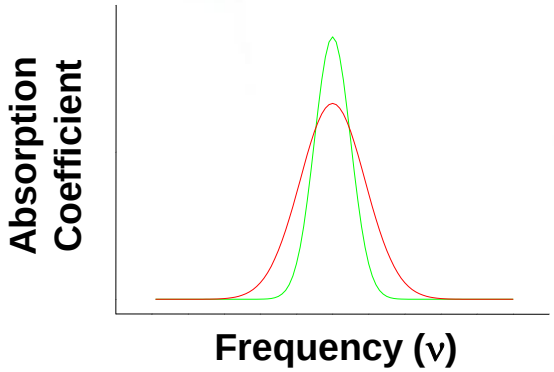
α(ν) – absorption coefficient (length^{-1})

Line-Shape Relations

$$\Rightarrow \quad \alpha(\nu) = \sigma(\nu)\rho$$

$$\sigma(\nu) = S\,g(\nu)$$

$$\int d\nu\,\sigma(\nu) = S$$



σ(ν) – cross-section (area)

ρ – amount-of-substance (amt sub/length^3)

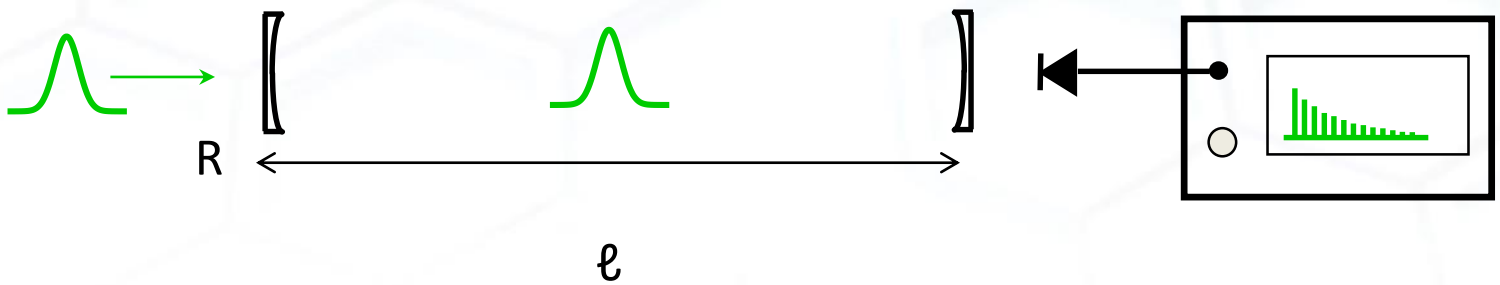
S – line-strength (area·frequency)

S is constant

g(ν) depends on environment

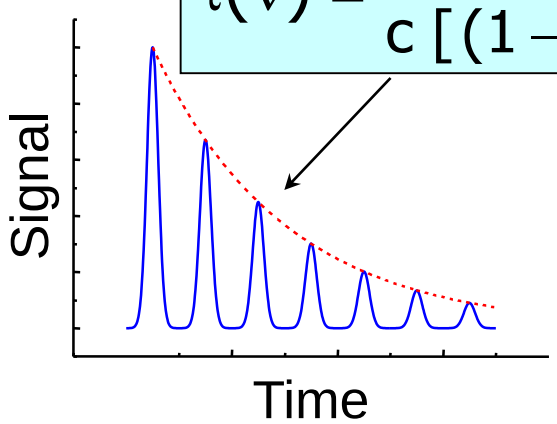
Background

- Partial pressure standards
- Humidity in process gases

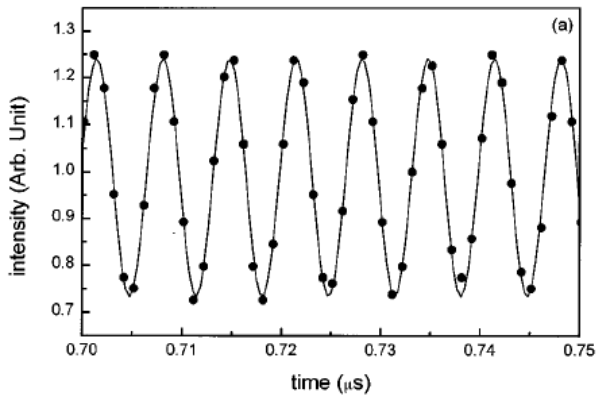


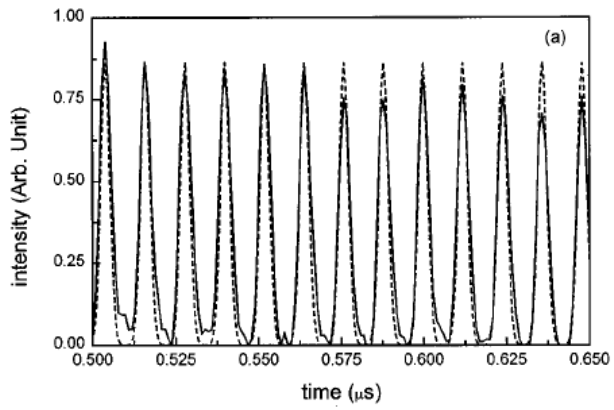
$$\tau(\nu) = \frac{\ell}{c\,[(1-R) + \alpha(\nu)\ell\,]}$$

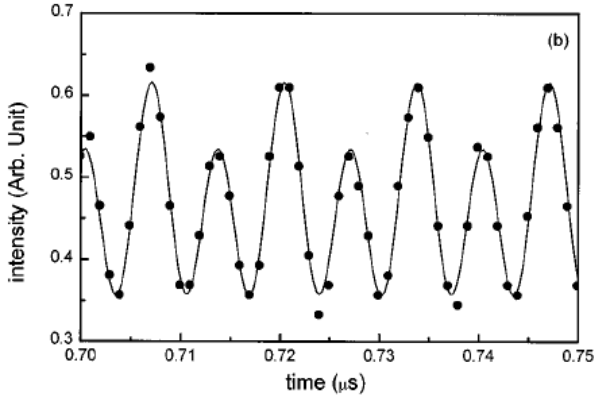
Signal(t) $\propto$ P_{in}(t) Exp[- t / τ]

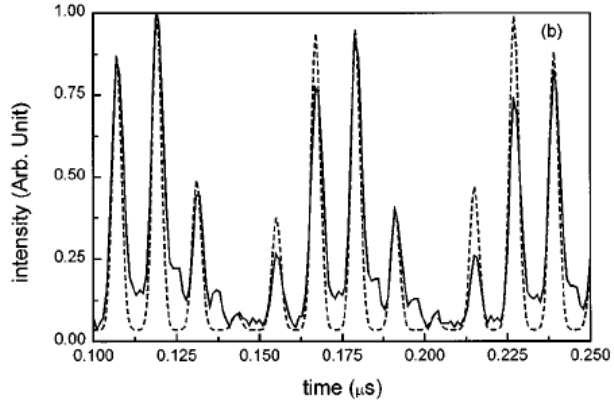


“Noisy” signals









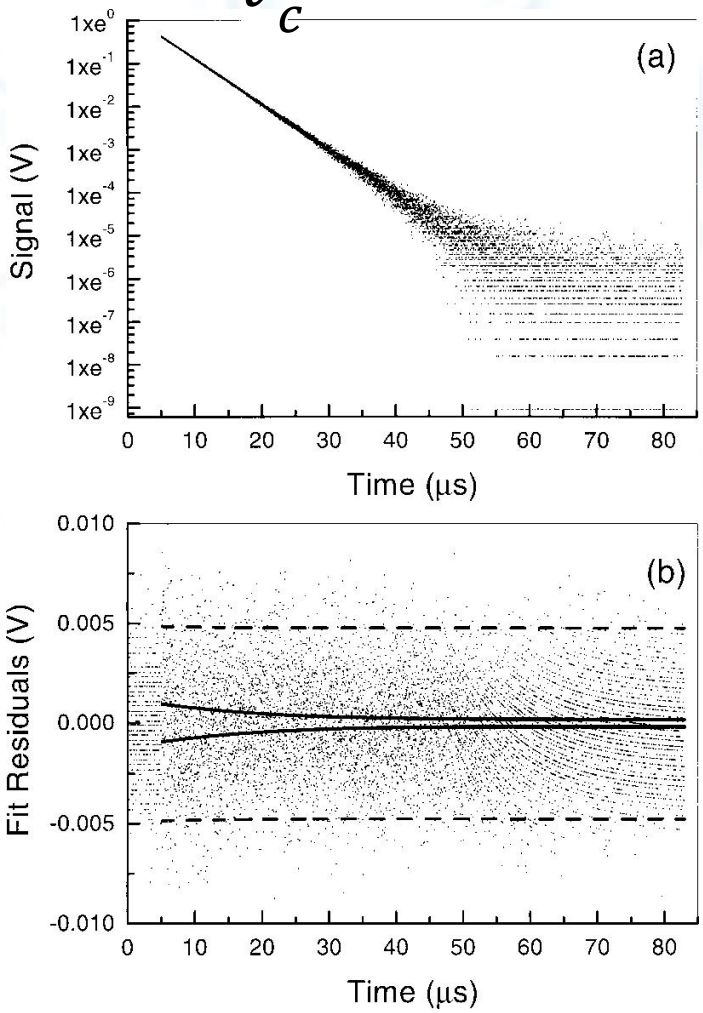
Response of a Ring-down Cavity to an Arbitrary Excitation

$$\mathcal{E}(t) \propto \sum_{mn} |C_{mn}|^2 \left\{ \Gamma^2{}_{mn} e^{\frac{-\Delta\omega^2}{2\sigma^2}} \quad e^{-2\Gamma_{mn} t} \right.$$

But if $\frac{\ell}{\ell_c} \ll 1, then$

$$S(t) \propto e^{-\alpha\ell} e^{-2\Gamma_{qmn}}$$

Working in the $\frac{\ell}{\ell_c} \ll 1$ Limit



Frequency Stabilized CRDS

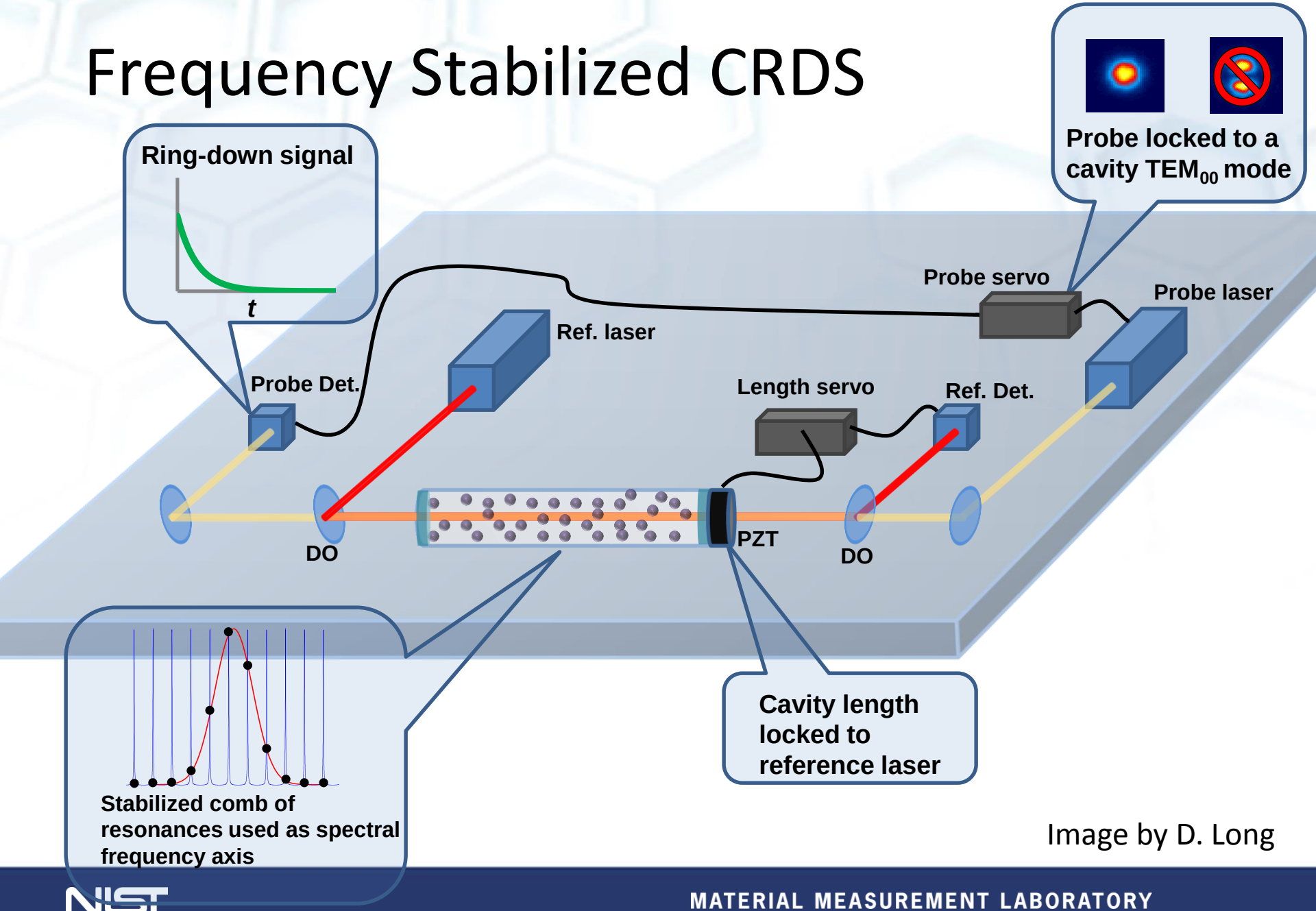
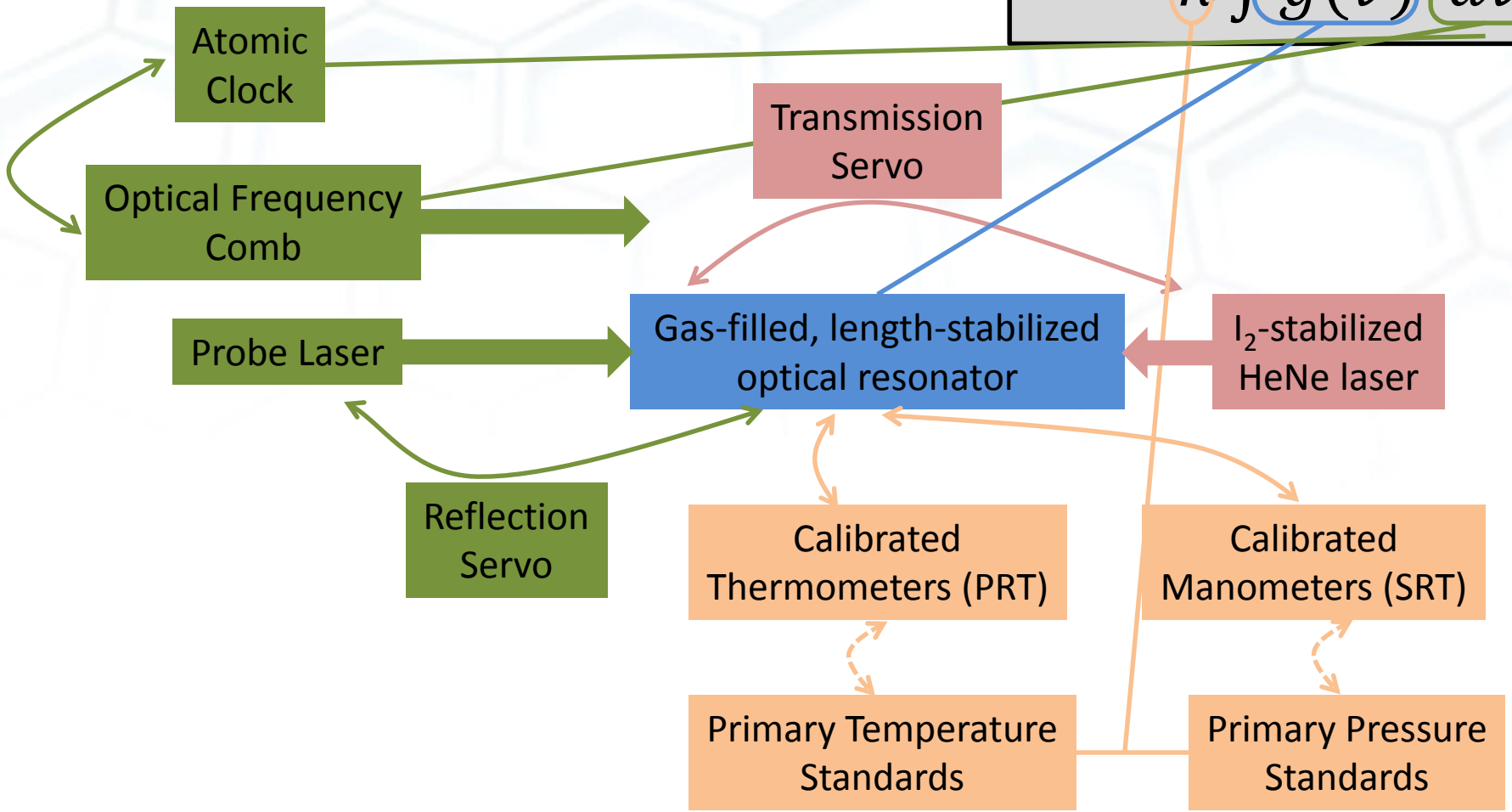


Image by D. Long

Measuring Line Strengths

$$S = \frac{\int \alpha(\nu)\, d\nu}{n \int g(\nu)\, d\nu}$$



REFERENCE DATA

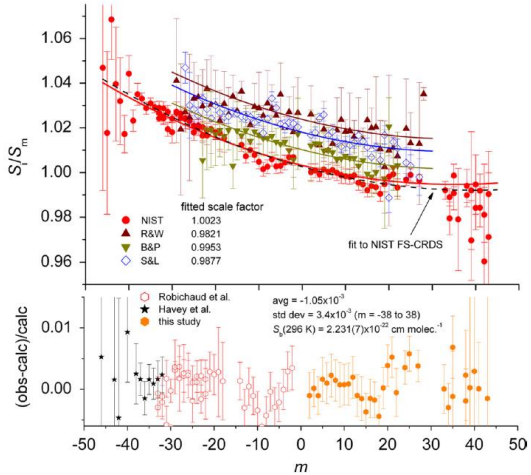
$$[GHG] \propto \frac{A}{\sigma\, l}$$

J K Bielska, R Ciurylo, A Cygan, A. Fleisher, K Gillis, D Havey, J Hodges,P Maslowski,
H Lin, D Lisak, D Long D Robichaud, Z. Reed, V Sironneau G Trong

Oxygen

- Critical to satellite retrievals
  - Used to get path length
- Comprehensive study of *A*-band completed
  - Line-positions, -intensities, & -shapes,
  - Pressure shift & broadening, mixing effects
  - Comprehensive study of isotopes
- Comprehensive study $^1\Delta$-band under way
  - Line-positions, -intensities, & -shapes,
  - Pressure shift & broadening
  - Comprehensive study of isotopes
- Reduced uncertainty in line parameters by an order of magnitude

$$[GHG] \propto \frac{A}{\sigma\, l}$$

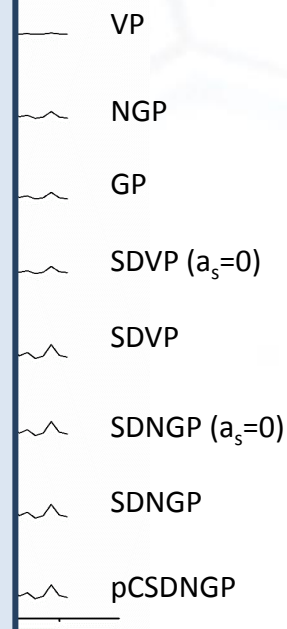


Water

7892.3021 cm $^{-1}$
S = 1.856x10^{-25} cm molec.$^{-1}$
(002) (000)
(10 5 6) – (9 2 7): Q' – Q''

- Water is the most important GHG
-
-

Component	%
Hygrometer frost-point temperature	0.45
Line shape uncertainty	0.25
Vapor pressure of ice	0.18
Hygrometer pressure	0.10
Cell pressure	0.10
Departure from ideal gas law	0.10
Uncertainty in FSR	0.10
Enhancement factor	0.05
Gas temperature	0.04
Background H_2O in cell	0.01
Isotopic composition of sample	0.007
H_2O dimer concentration	0.002
Spectrum measurement reproducibility and fit uncertainty	0.25
Relative combined standard uncertainty	0.64



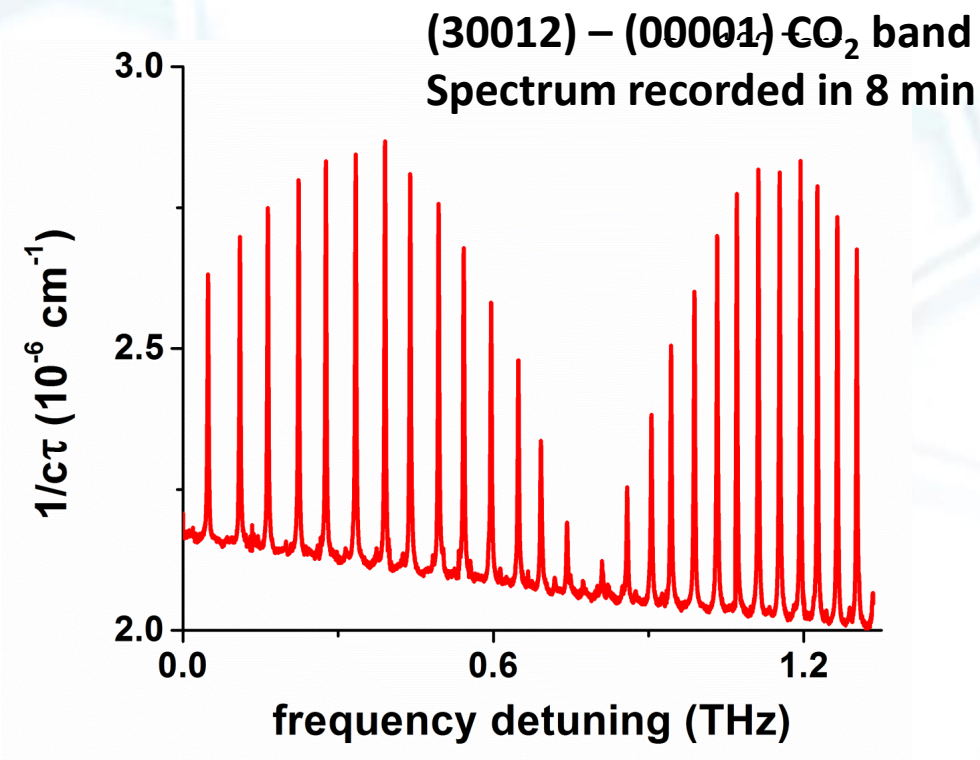
Carbon Dioxide

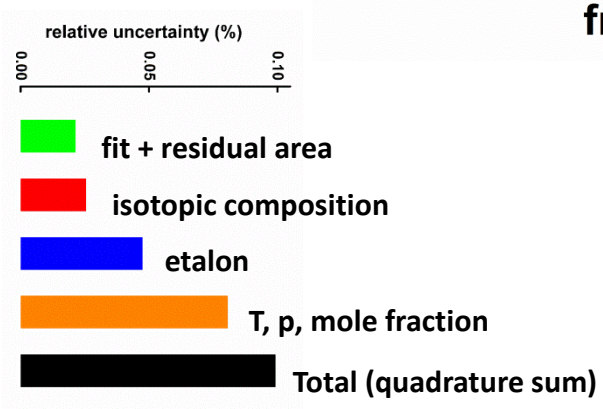
NIR (1.6 μm)

- Line-positions, -intensities, & -shapes,
- Pressure shift & broadening
- Comprehensive study of isotope

- Additional work near 2 μm

p = 20 kPa
368 ppm CO_2 in air





TECHNOLOGY DEVELOPMENT

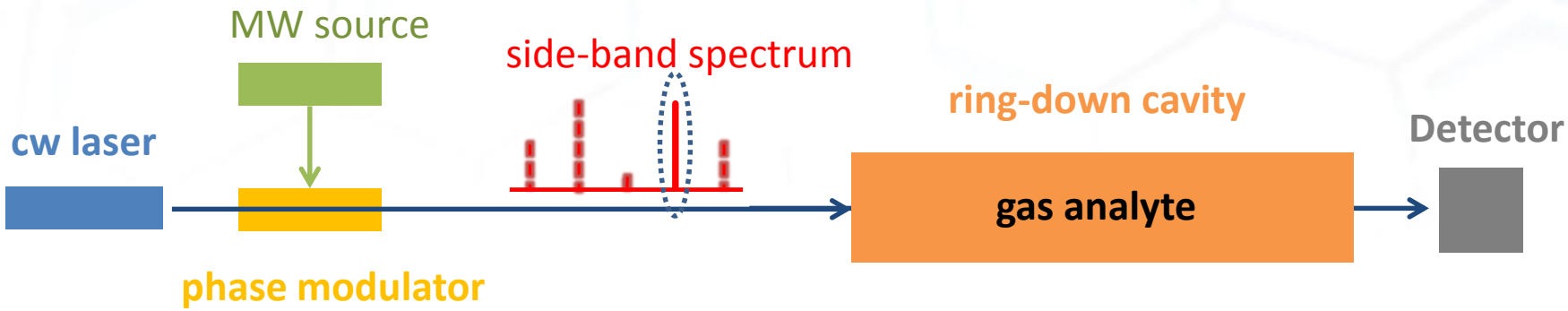
$$[GHG] \propto \frac{A}{\sigma\, l}$$

J Hodges, A. Fleisher, K Gillis, D Havey, D Long, Q Liu, Z. Reed, G Trong

Scanning

Method:

- Use waveguide electro-optic phase-modulator (PM) to generate tunable sidebands
- Drive PM with a rapidly-switchable microwave (MW) source
- Fix carrier and use ring-down cavity to filter out all but one selected side band



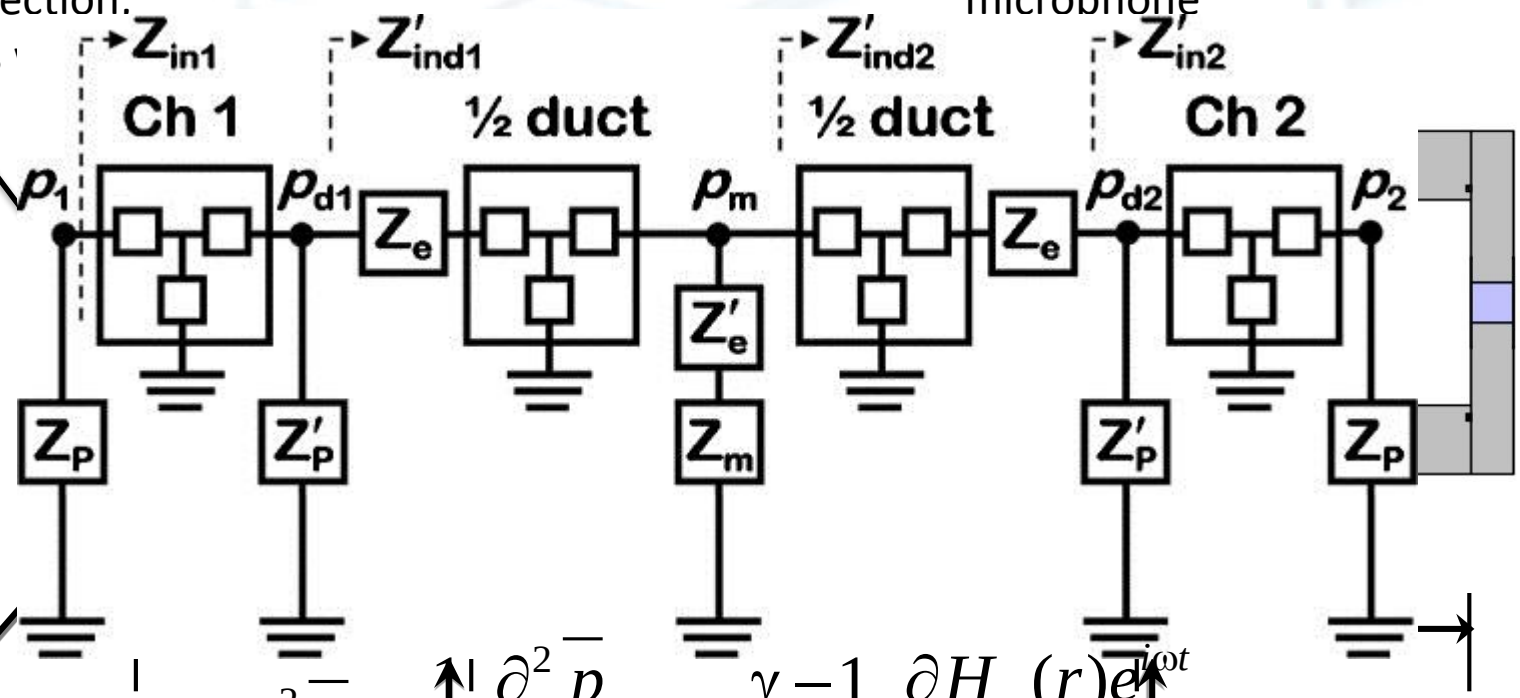
Advantages:

- Overcomes slow mechanical and thermal scanning
- Links optical detuning axis link to RF and microwave standards
- Wide frequency tuning range (> 90 GHz = 3 cm^{-1})

Photoacoustic Resonator

anti-reflection,
low-loss

microphone



$$\nabla^2 \overline{p} - \frac{1}{c_s^2}\frac{\partial^2 \overline{p}}{\partial t^2} = -\frac{\gamma - 1}{\beta_p T c_s^2}\frac{\partial H_\omega(r) e^{-i\omega t}}{\partial t}$$

chambers reduce signal
from window absorption

inlet/outlet located
at acoustic nodes

K Gillis

resonance frequency in air $f_0 \approx 1640$ Hz, $Q \approx 30$

Calculable Cell Constant

optical absorption coefficient

absorber density

absorber cross sectio

$$\alpha_i = n_i \, \sigma_{\mathrm{abs},i} = \frac{}{C}$$

cell constant

quality fact

(acoustic)

thermophysical properties of gas

function

geom. factor

$$C_{S1} = \frac{\gamma - 1}{\beta_P T} \frac{Q_{S1}}{2\pi f_{S1}} \frac{G_{S1} L}{V}$$

= 4569.5 Pa cm W^{-1}

K Gillis & Z Reed

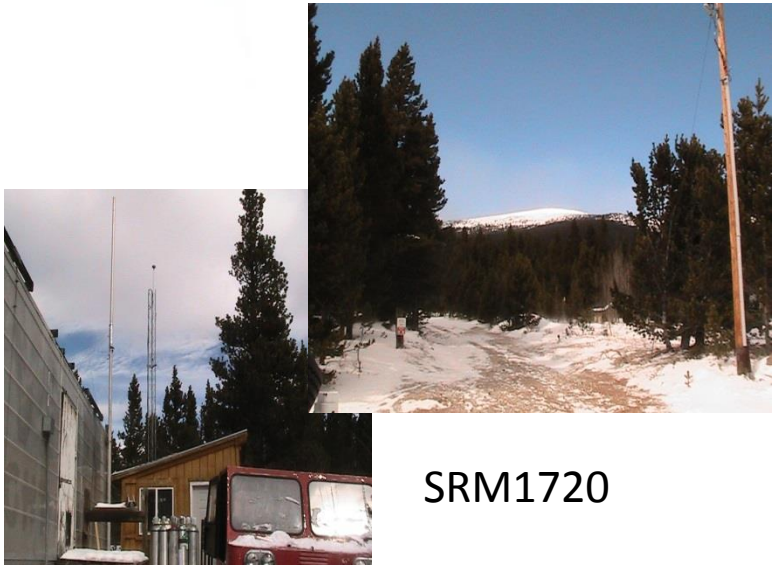
REFERENCE MATERIALS

Jennifer Carney, Frank Guenther, Mike Kelley, Bob Miller, Gerald Mitchell, Jerry Rhoderick

Standard Reference Materials

- Develop new gravimetric primary standard mixture (PSM) suites with very low uncertainties to meet WMO Data Quality Objectives (DQO)
  - 0.01 % to 0.05 %
  - CO_2, CH_4, N_2O, CO
- Collaborate with atmospheric research laboratories to develop dry, whole air SRMs
- Use new PSM suites to certify real air samples as SRMs

SRM1721



SRM1720

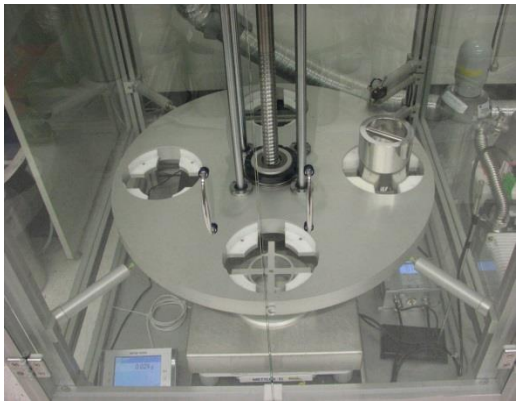
	WMO DQO*
CO_2	± 0.1 µmol/mol
CH_4	± 2 .0 nmol/mol
N_2O	± 0.1 nmol/mol

*k=1 uncertainty

PSM

- Prepared PSMs for each analyte using scrubbed air and pure analyte
  - Successive dilution with balance gas to achieve target level of analyte
  - Prepare several samples around the targeted concentration.

- Challenges
  - CO_2 loss to cylinder walls and transfer lines
  - N_2O trace level detection and possible isotope bias
  - CH_4 trace level measurement



Analysis Methods

- CO_2: Spectroscopic; Type-A uncertainty (p) of 0.01 % (0.04 µmol/mol)
- CH_4:
- N_2O:
- CO: Spectroscopic; p = 0.01 % (0.02 nmol/mol)

	Previous PSMs (nmol/mol)	New PSMs (nmol/mol)
CH_4	1804. ± 7.	1836.16 ± 0.75
N_2O	317.6 ± 1.6	317.95 ± 0.07

Projected Certifications

	Projected Assigned Values
CO_2	393. 32 ± 0.14 µmol/mol
CH_4	1873.8 ± 1.0 nmol/mol
N_2O	323.04 ± 0.20 nmol/mol
CO	160 ± 4 nmol/mol

FUTURE DIRECTIONS

QUESTIONS