Quantitative Laser Spectroscopy for SI-Traceable Measurements of Greenhouse Gases

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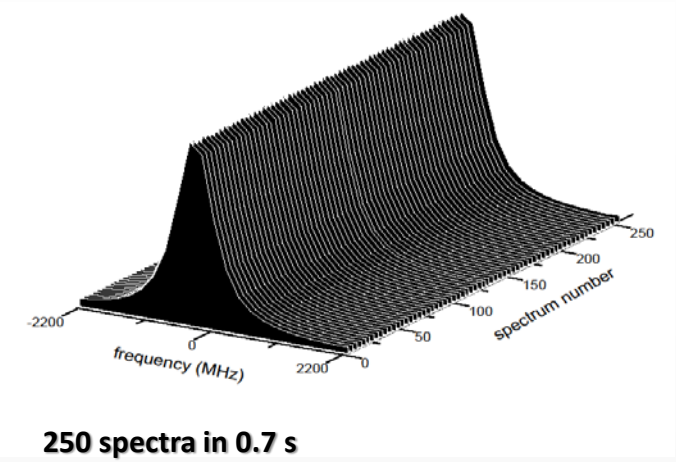
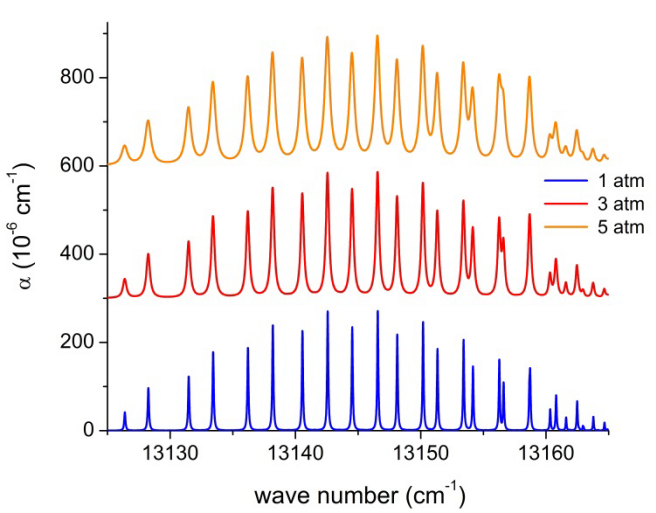
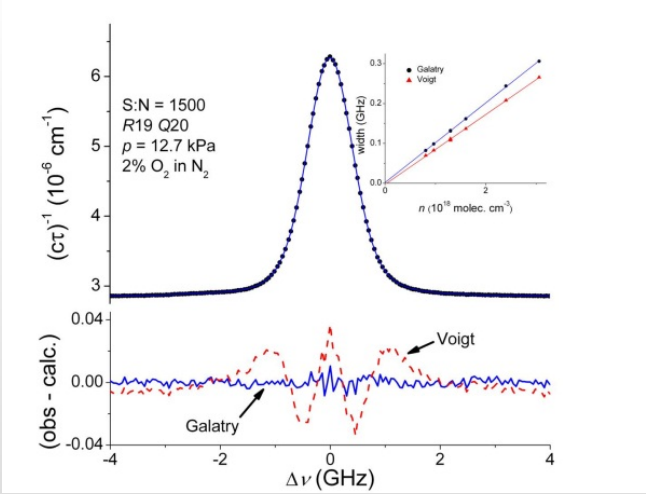


250 spectra in 0.7 s





NOAA Global Monitoring Conference, Boulder, CO; May 19-20, 2015

Outline

Line intensities as intrinsic standards for measurement of concentration

Frequency-stabilized cavity ring-down spectroscopy (FS-CRDS)

Comparison of measured and *ab initio* intensities for CO_2

Line shape effects

Development of mid-IR laser spectrometer for measuring $^{16}O^{14}C^{16}O$ at natural abundance

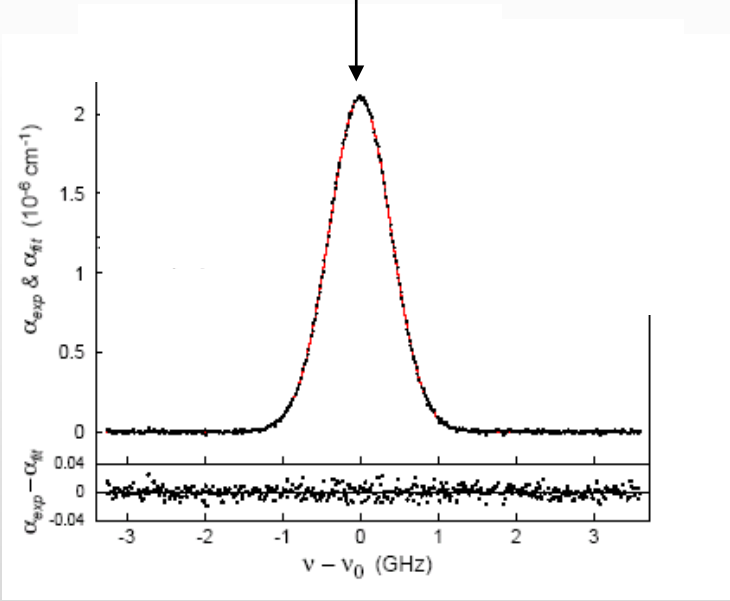
Measurement of Line Intensity (S) and Absorber Concentration (n)

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

measured absorption coefficient

line profile (unity area)

fitted spectrum area



Once the intrinsic property ***S*** is known, then

$$n = A/S$$

Quantum (ab initio) calculation of line intensity, S_{12}

$$\mu_{12} = \int \Psi_1 \underline{\mu} \Psi_2 d\tau$$

Transition dipole

$$S_{12} = \text{fn}(T) * |\mu_{12}|^2$$

nuclear coordinates
final wavefunction
dipole moment surface (DMS)
initial wavefunction

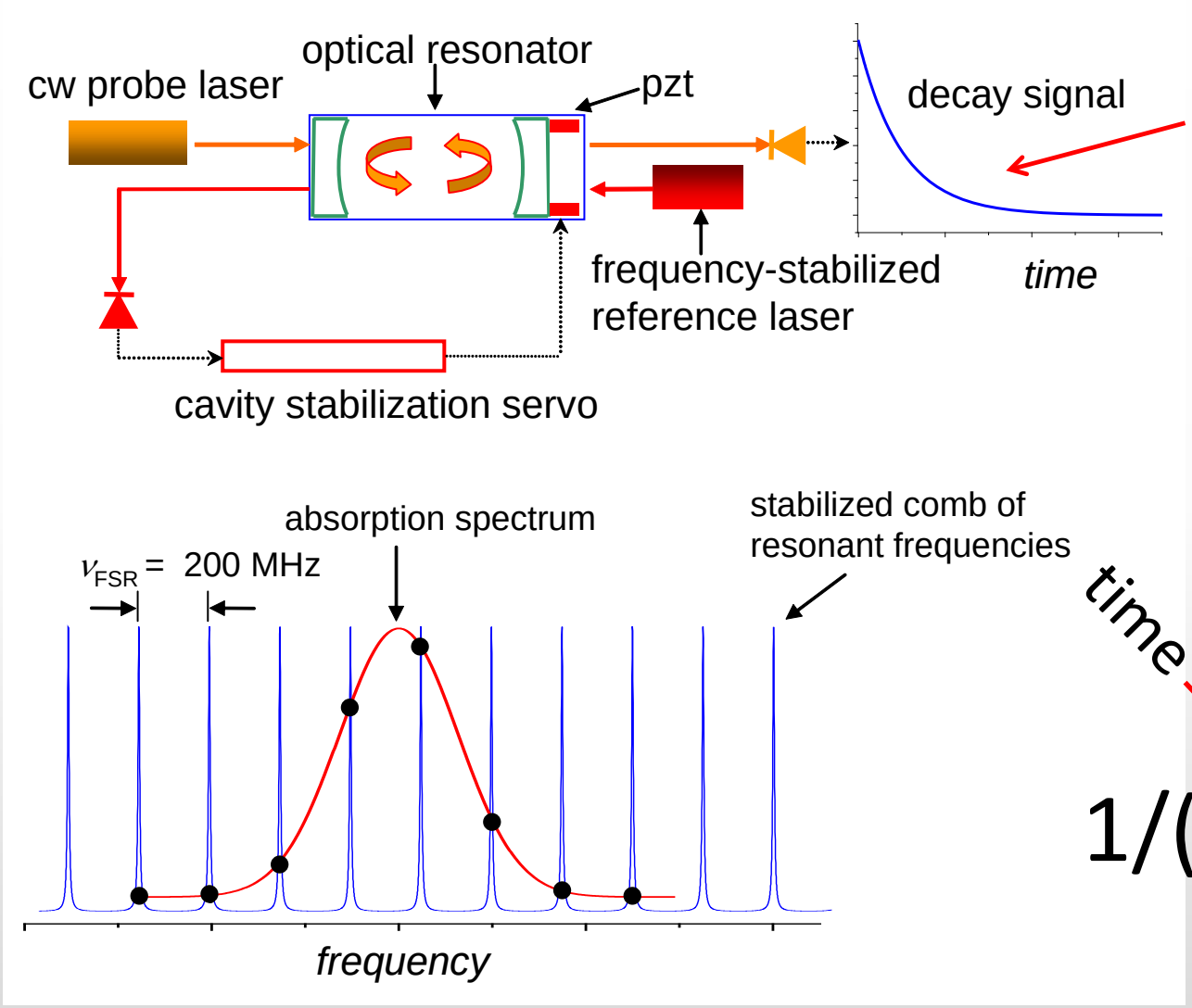
Boltzmann factor

H_2O: 10-electron system
CO_2 22-electron system

Calculation of S_{12} requires wave functions that are computed from potential energy surface (PES) and dipole moment surface (DMS)

O. Polyansky & J. Tennyson, University College of London

Frequency-stabilized cavity ring-down spectroscopy (FS-CRDS)



Enables high-fidelity and high-sensitivity measurements of transition areas, widths & shapes, positions and pressure shifts

CO_2-in-air sample preparation

Primary Mixture 400 ppm CO_2

rel. unc. = 0.02 %

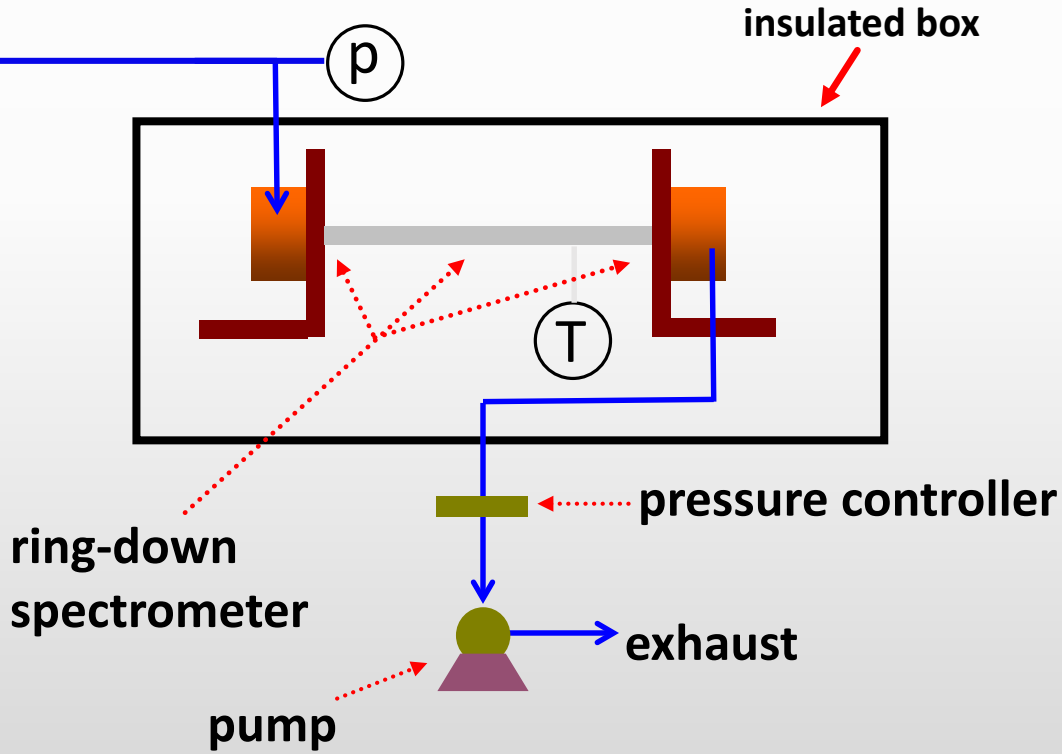
Primary standards

Secondary Mixture

rel. unc. = 0.07 %

High-precision comparator

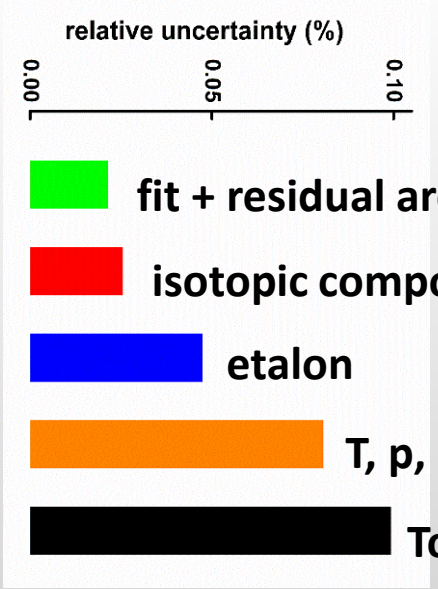
Need steady flow of sample gas to mitigate wall effects

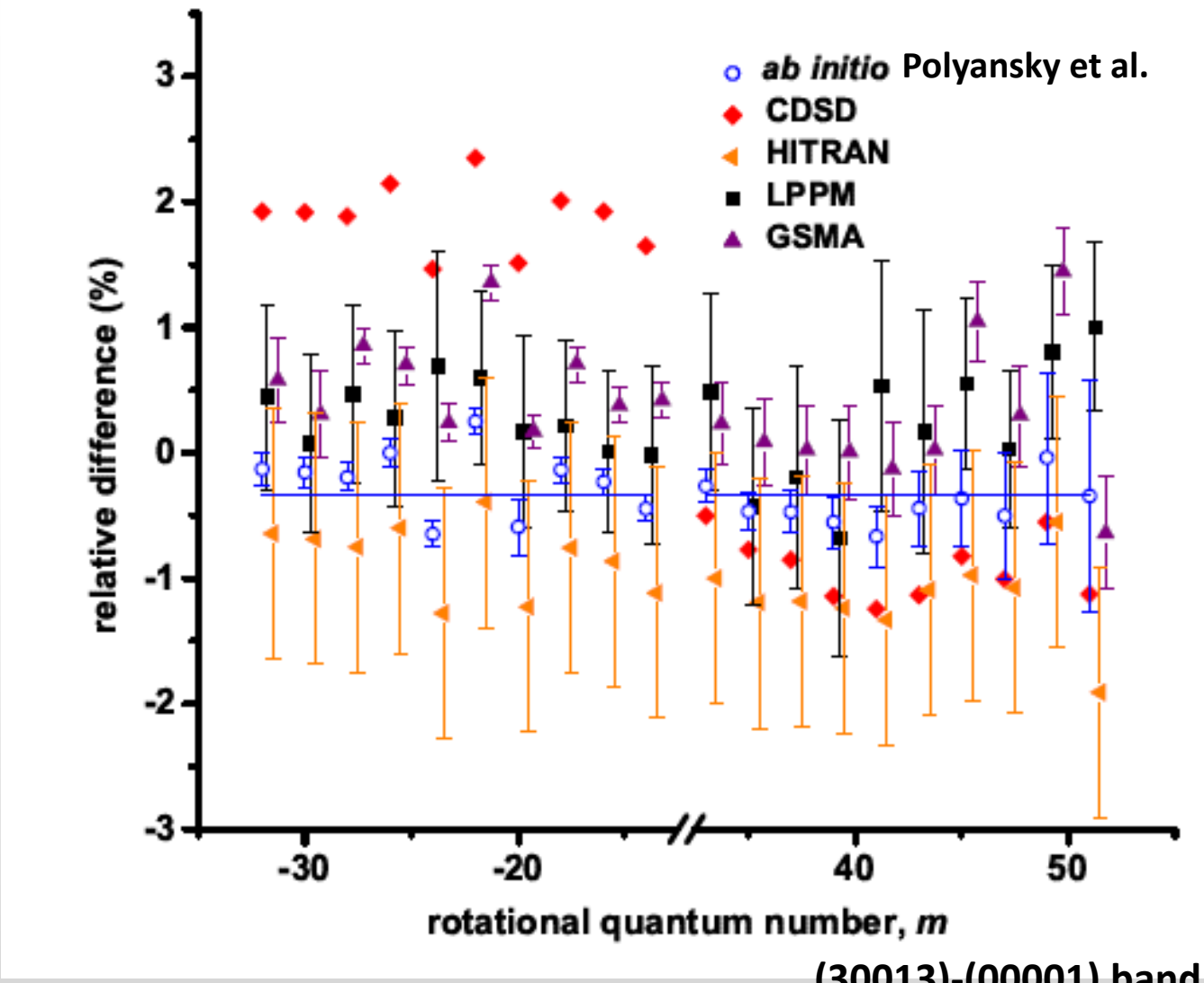


Accuracy of CO_2 intensity measurements: 1.6 um region

Polyansky et al., *High accuracy CO_2 line intensities from theory and experiment*, (under review)

uncertainties





(30013)-(00001) band

Partially correlated quadratic-speed-dependent Nelkin-Ghatak Profile (aka "Hartmann-Tran" profile)

$$\tilde{I}_{\mathrm{pCqSDNG}} = \frac{\tilde{I}_{\mathrm{qSDV}}(u; B_w\Gamma_0/\omega_D + \tilde{z})}{1 - \pi\tilde{z}\tilde{I}_{\mathrm{qSDV}}(u; B_w\Gamma_0/\omega_D + \tilde{z})}$$

Complex profile

$$\tilde{z} = \tilde{\nu}_{opt}/\omega_D = [\nu_{eff} - \eta(\Gamma_0 + i\Delta_0)]/\omega_D$$

Complex, normalized narrowing frequency

$$B_w(x) = 1 + a_w(x^2 - 3/2)$$
$$B_s(x) = 1 + a_s(x^2 - 3/2)$$

Quadratic approximation to speed dependence

Correspondence between pCqSDHCP and pCqSDNGP parameters

$$a_w = \Gamma_2/\Gamma_0$$

$$a_s = \Delta_2/\Delta_0$$

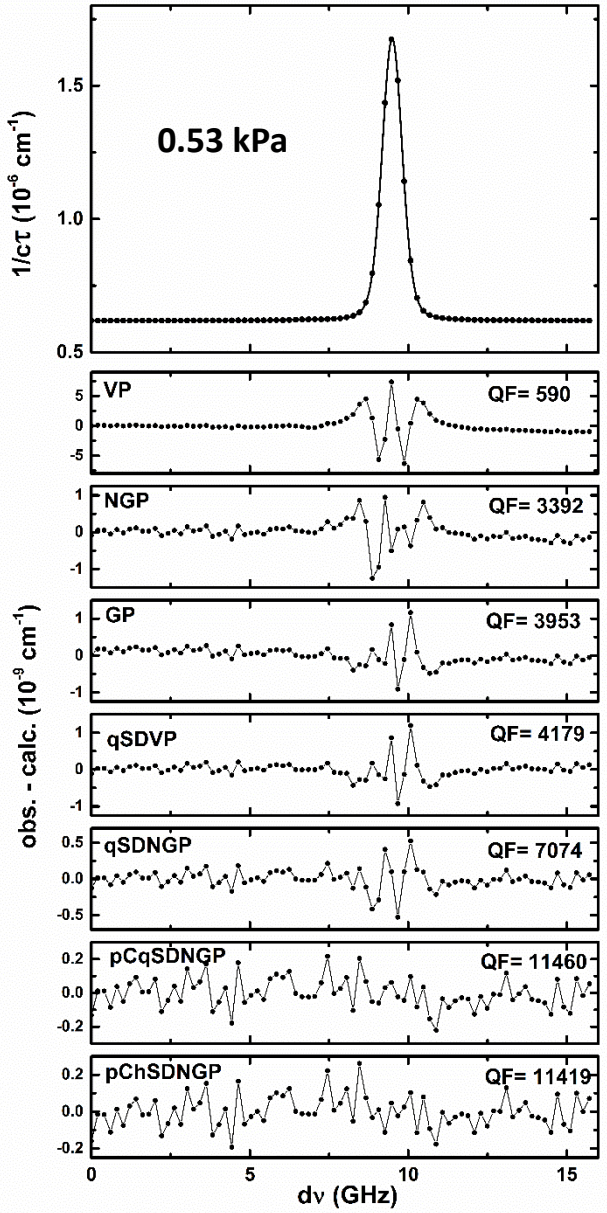
$$Re[\tilde{\nu}_{opt}] = \nu_{vc} - \eta\Gamma_0$$

$$Im[\tilde{\nu}_{opt}] = -\eta\Delta_0$$

Mechanisms: 1) collisional narrowing (hard-collision model), 2) speed-dependent broadening and shifting, 3) partial correlations between velocity-changing and dephasing collisions

H_2O line shape study

single-spectrum fit



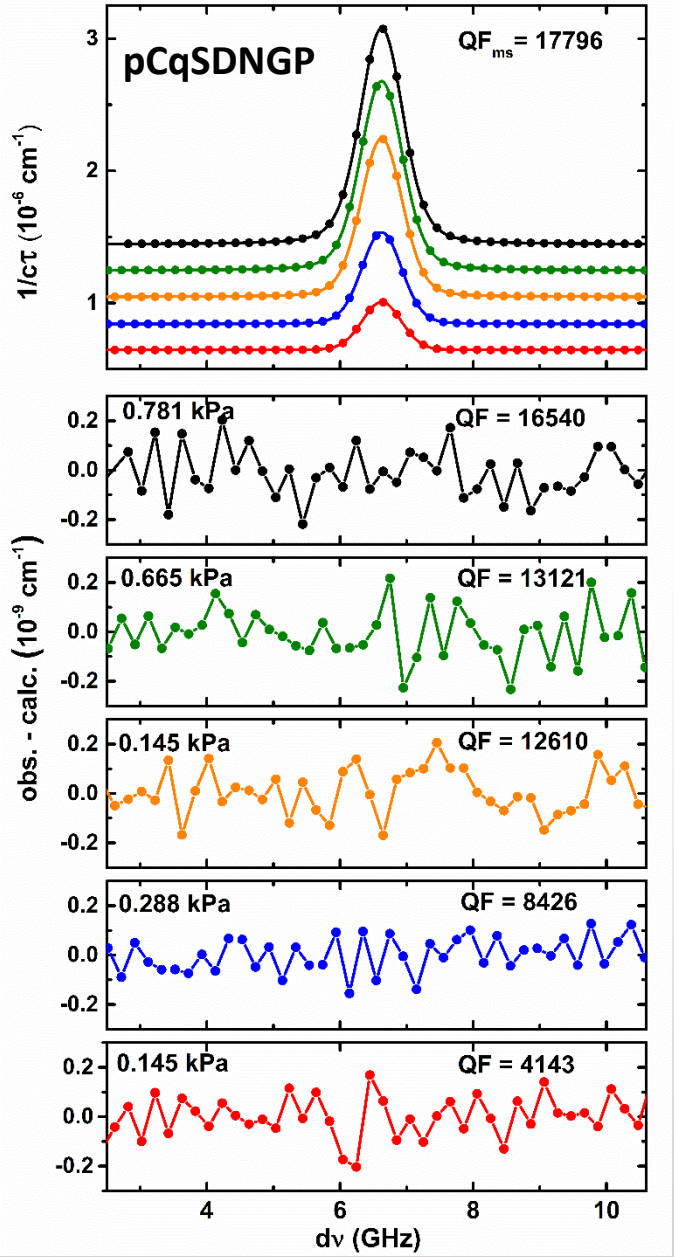
Need to include:

1. collisional narrowing
2. speed dependent effects
3. partial correlation between velocity-changing and dephasing collisions

7892.3021 cm $^{-1}$
S = 1.89x10^{-25} cm molec.$^{-1}$
(002)- (000)
(15 5 6) – (9 2 7): Q' – Q''

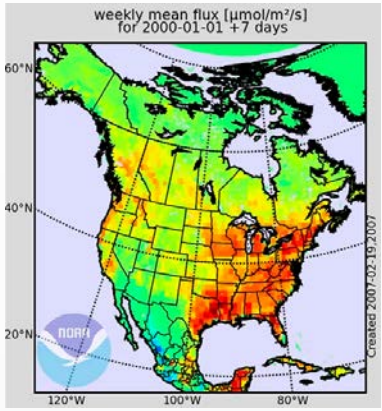
7799.9970 cm $^{-1}$
S = 2.58x10^{-25} cm molec.$^{-1}$
(002) - (000)
(10 4 6) – (9 3 7): Q' – Q''

multi-spectrum fit



^{14}C: A tool for identifying the origins of feedstocks and emissions

Biobased product verification



Partitioning GHG sources

^{14}C

Biofuel feedstock identification

Pollutant source identification

Current method: Accelerator mass spectrometry (AMS)

- Measurements of ^{14}C are extremely difficult due to low natural abundance (~1 ppt)
- AMS uses an accelerator to mass separate the analyte
- Then analyzed using mass spectrometry

- Disadvantages:

  -Expensive ($6M/facility)

  -Requires a large facility and highly trained staff

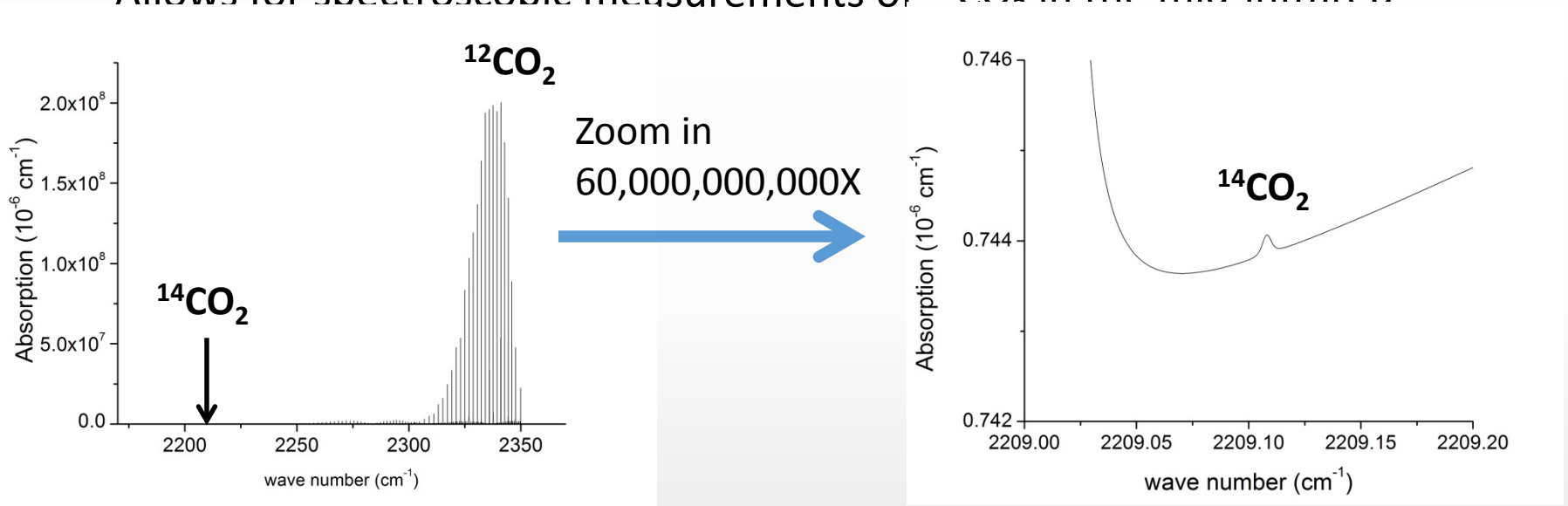
  -Only 10 facilities in the U.S.

  15-30 day lead time

Figure from LLNL

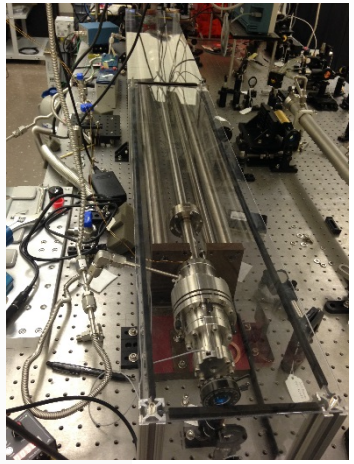
Optical measurements of $^{14}CO_2$

- $^{14}CO_2$ transitions are shifted relative to $^{12}CO_2$
  - Allows for spectroscopic measurements of $^{14}CO_2$ in the mid-infrared

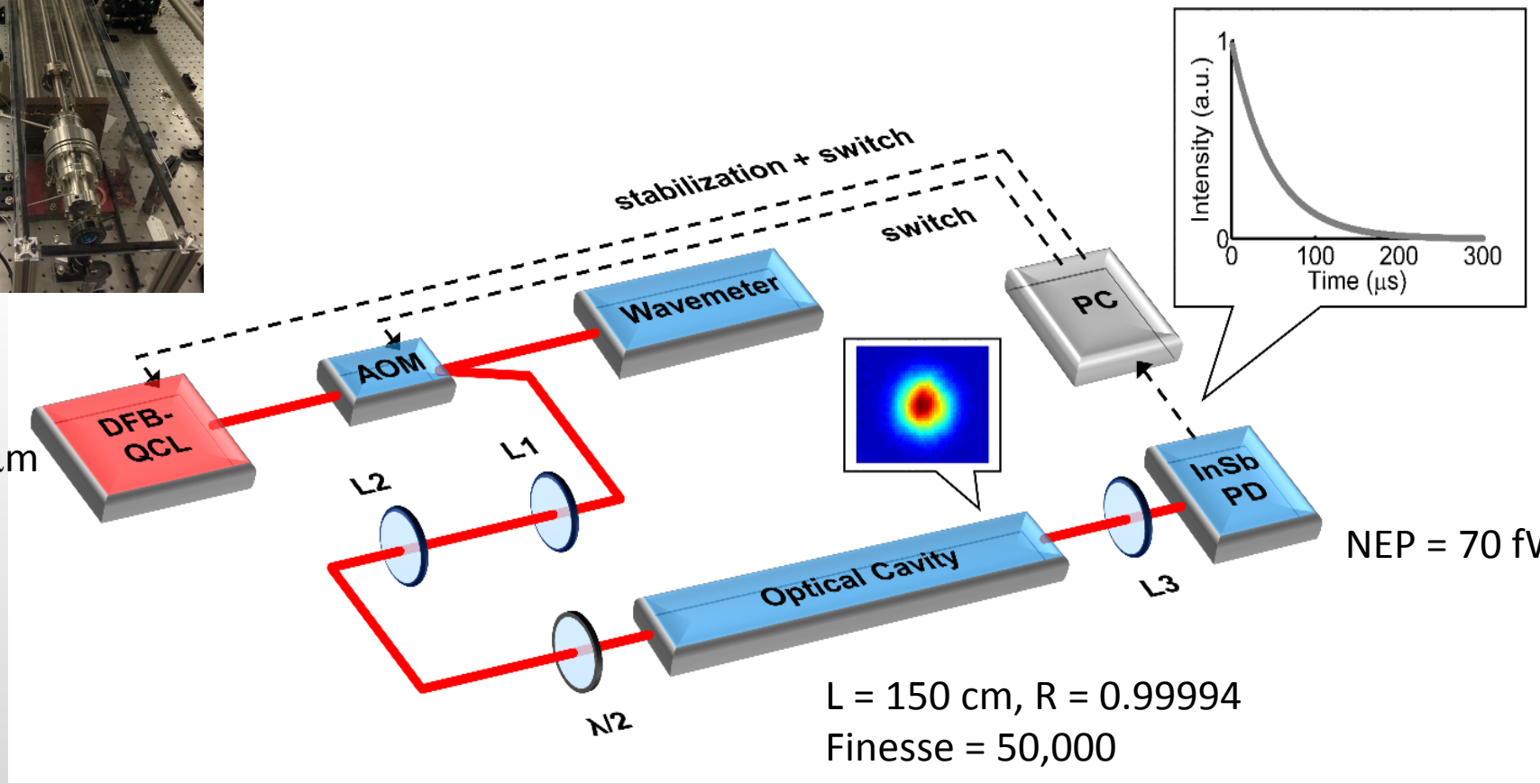


Because of the <u>ultralow</u> abundance of $^{14}CO_2$ (1.2 ppt) optical detection has only recently been demonstrated in the laboratory [Galli et al. PRL v107, 270802 (2011)] using a spectrometer at 195 K.

Mid-IR spectrometer for measuring ^{14}C at natural abundance



λ =4.5267 μm



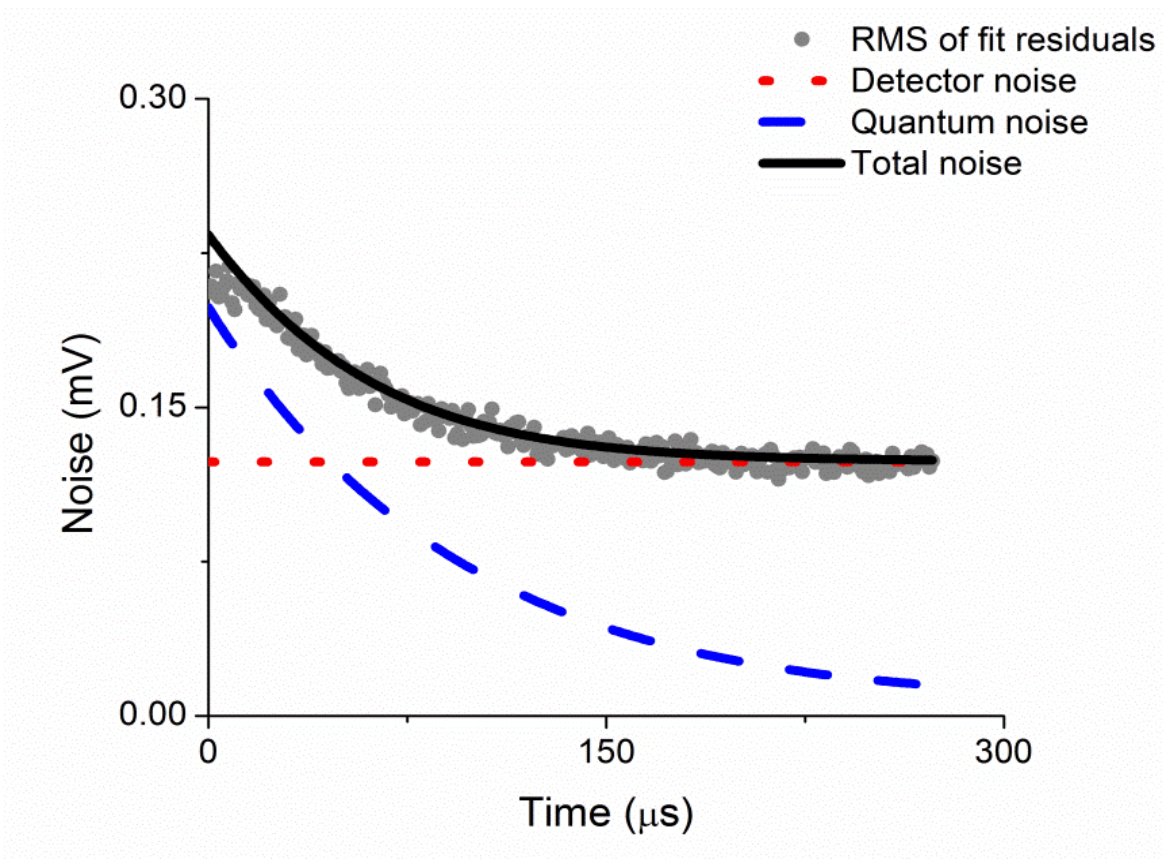
NEP = 70 fW $Hz^{-1/2}$

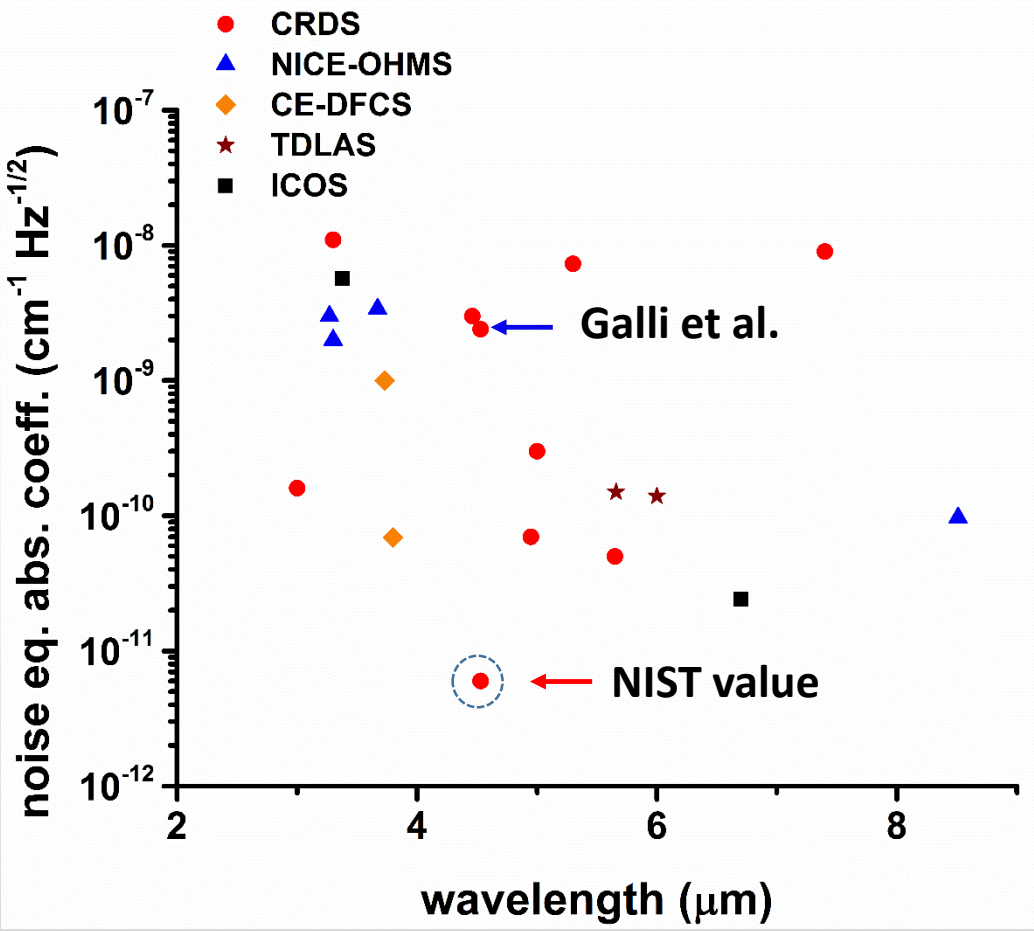
L = 150 cm, R = 0.99994

Finesse = 50,000

Ultra-high sensitivity in mid-IR region

Quantum-noise-limited residuals in fitted decay signals

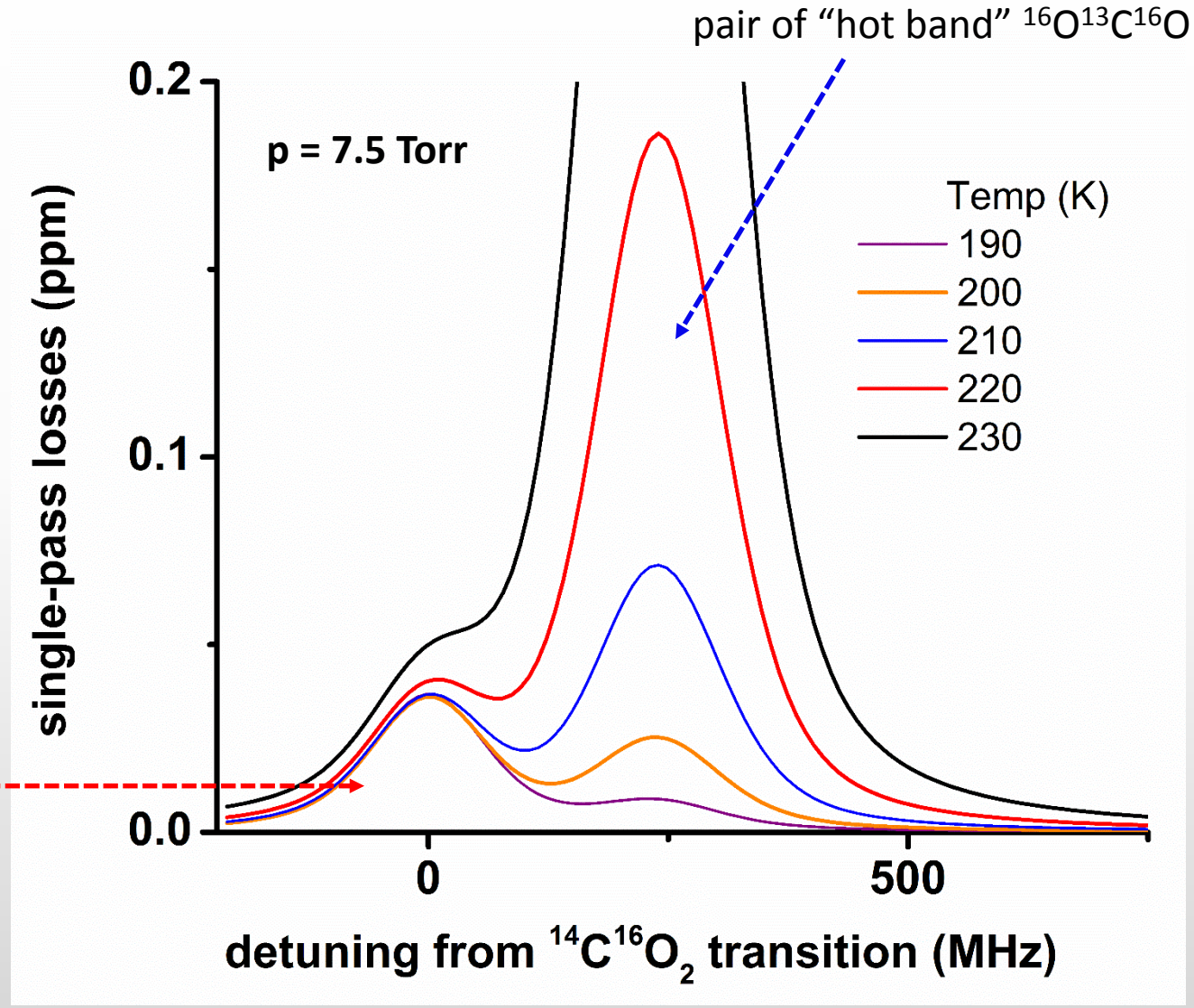




Calculated Absorption Spectra of Radiocarbon

Short-term precision of 0.0012 ppm
will give peak SNR of ~30:1

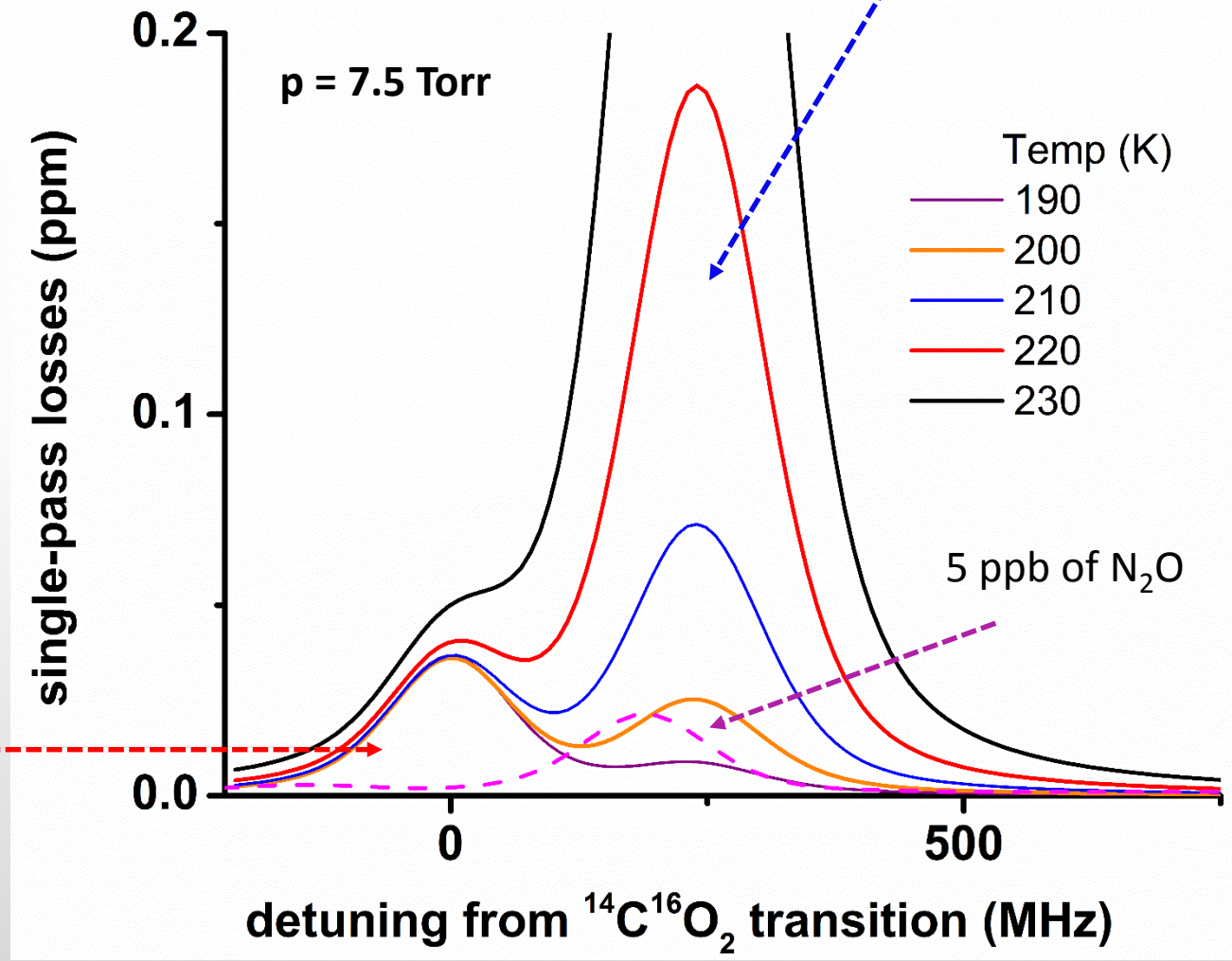
$^{16}O^{14}C^{16}O$ transition
at λ = 4526.7137 nm
1.2 parts-per-trillion



Calculated Absorption Spectra of Radiocarbon

N_2O desorption from walls is another interferent

pair of "hot band" $^{16}O^{13}C^{16}O$ transitions



$^{16}O^{14}C^{16}O$ transition
at λ = 4526.7137 nm
1.2 parts-per-trillion

Conclusions

SI-traceable measurements of concentration at (~0.2 % uncertainty level) over a range of *p*, *T* and mixture composition can be realized provided that

both the x and y axes of absorption spectra are acquired with high fidelity, and the absorber intensity is known from experiment or calculation.

This intrinsic standard approach is attractive for trace and reactive species as well as for rare isotopologues and for measurements of isotopic ratios.

Mid-IR QC laser, cavity-enhanced spectroscopy for the measurement of $^{14}CO_2$ provides a promising alternative to AMS-based methods.

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