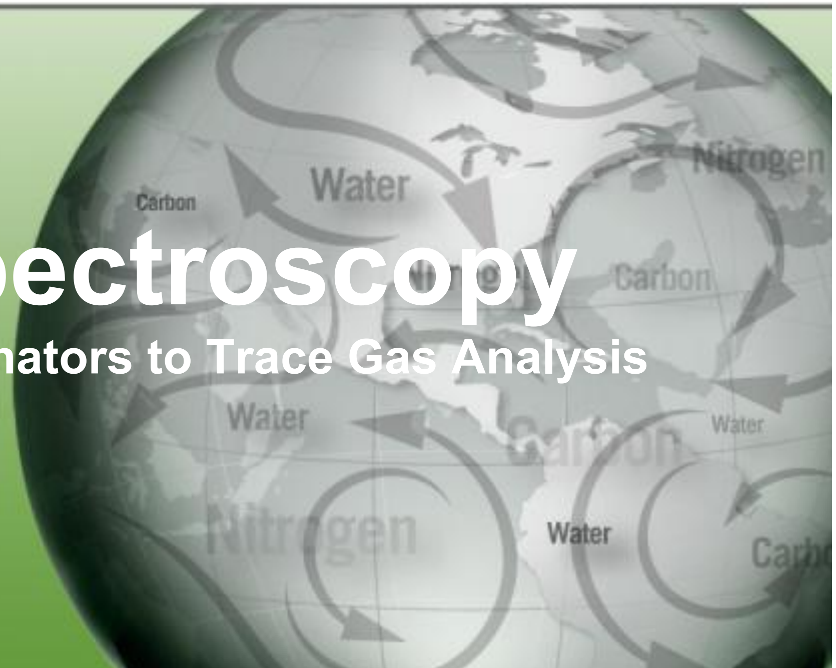
PICARRO

Cavity Ringdown Spectroscopy

an Application of High Finesse Optical Resonators to Trace Gas Analysis

Alex Farinas

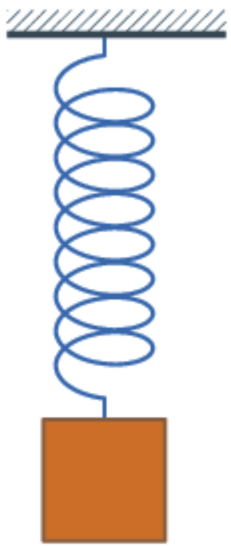


The World's Highest Performance and Easiest-to-Use Analyzers

Outline

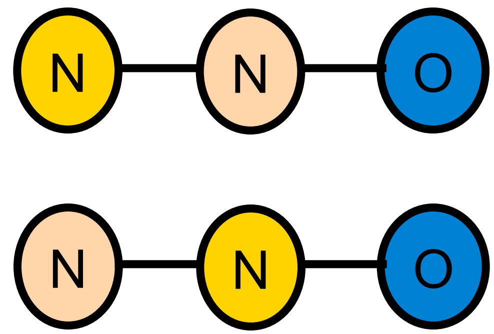
- Principles of Cavity Ringdown Spectroscopy
- Backscattered-Wave Correction
- About Picarro
- Selected Applications of CRDS

Resonant Optical Absorption



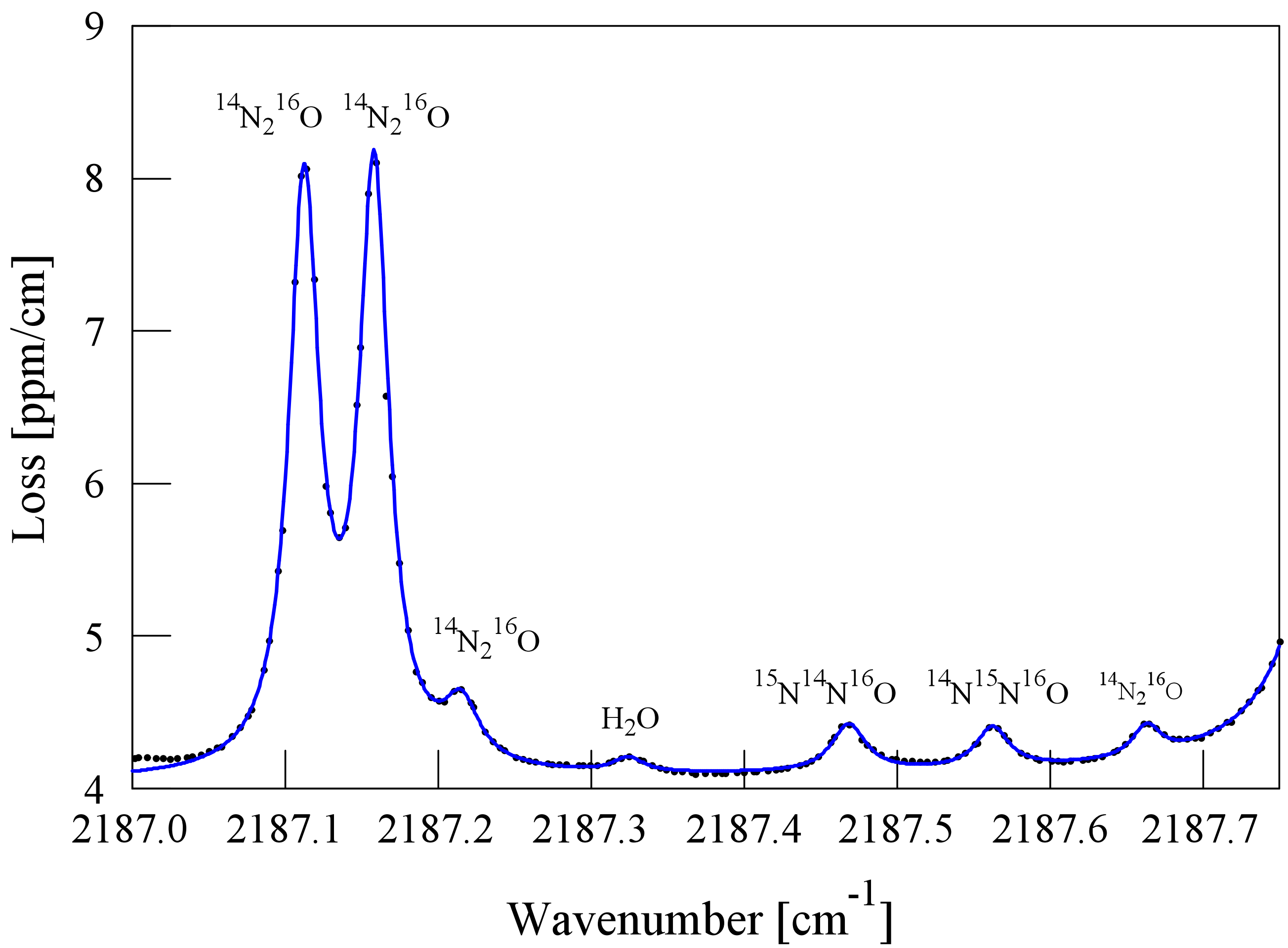
$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Reduced mass varies
with amount *and location*
of mass substitution



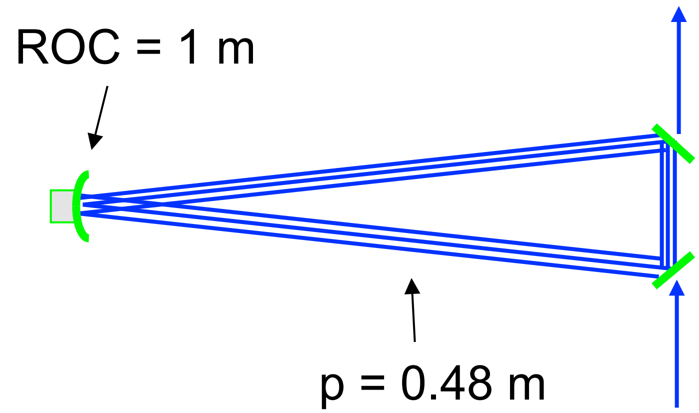
Even same-mass isotopomers have
different absorption spectra

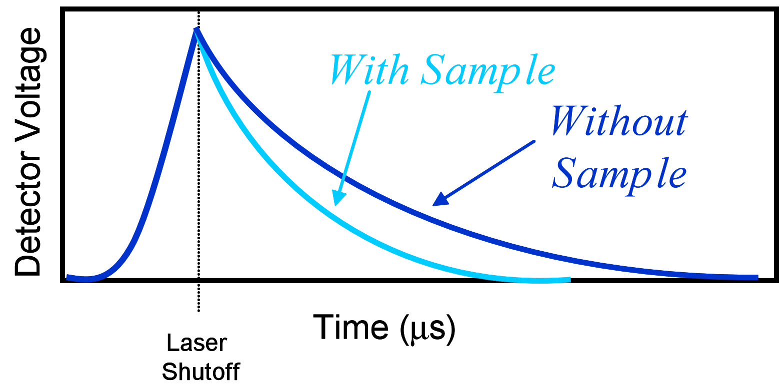
Spectral Fingerprints



Cavity Ringdown Spectroscopy

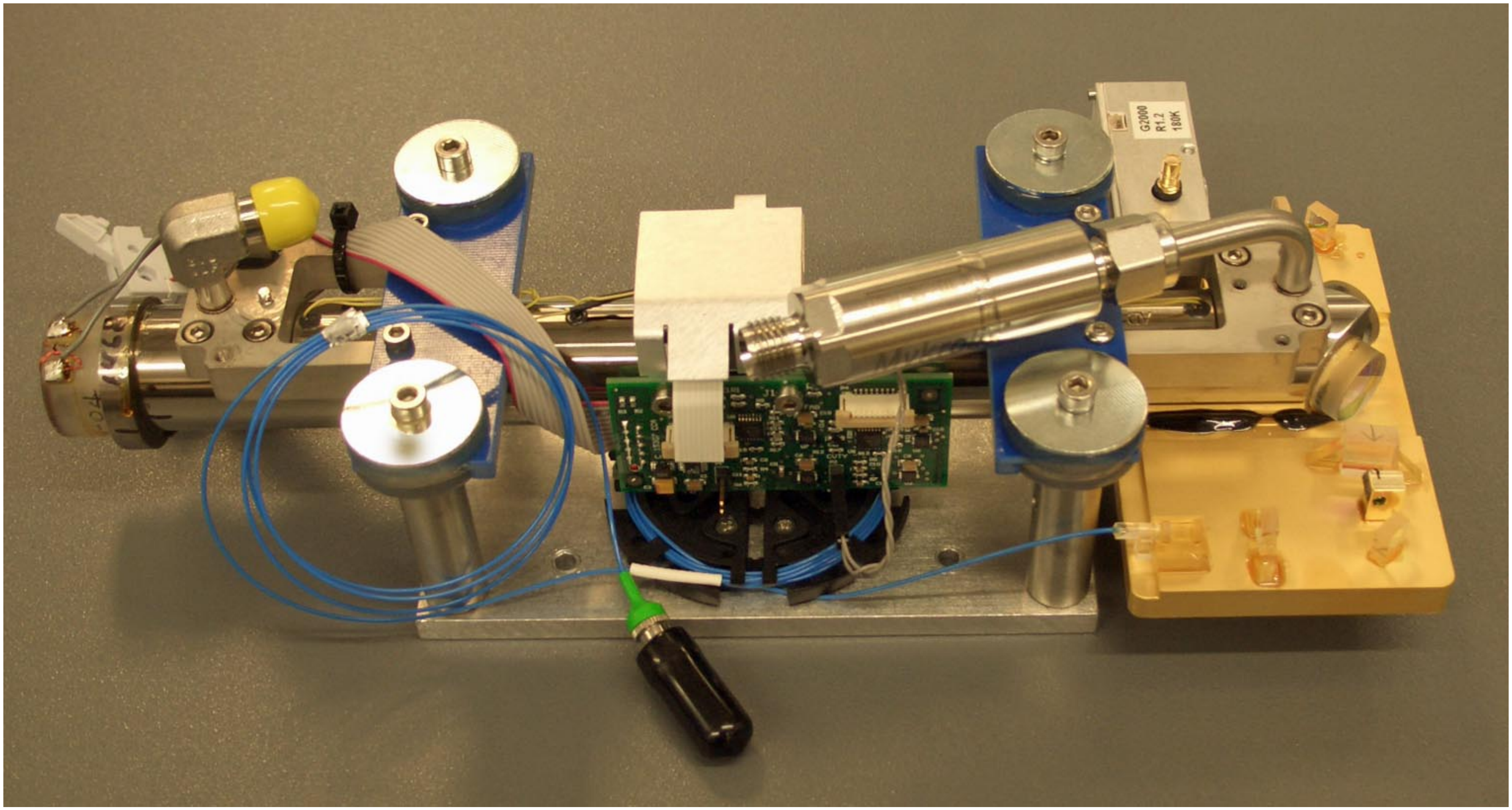
- Very long effective pathlength (> 10 km)
- Compact (35 cc) flow cell
- Time based measurement
- Laser is off during measurement





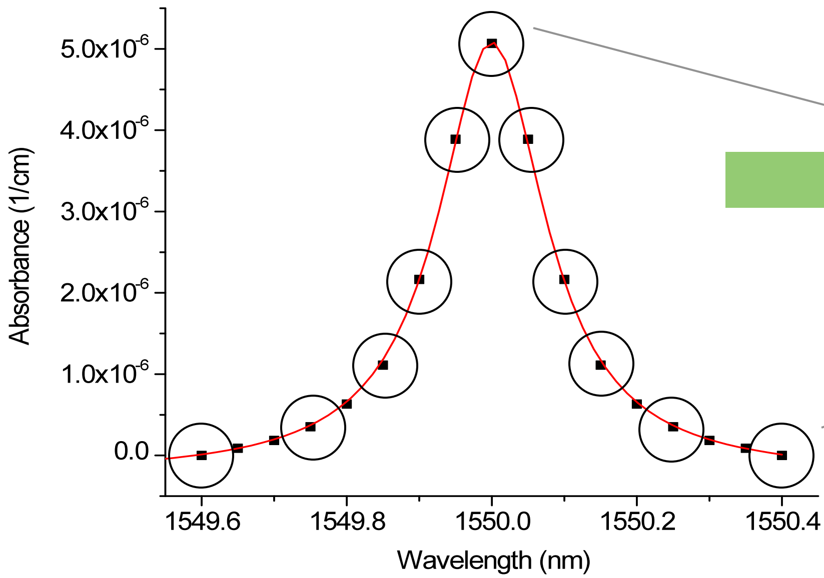
PICARRO

The Ringdown Cavity

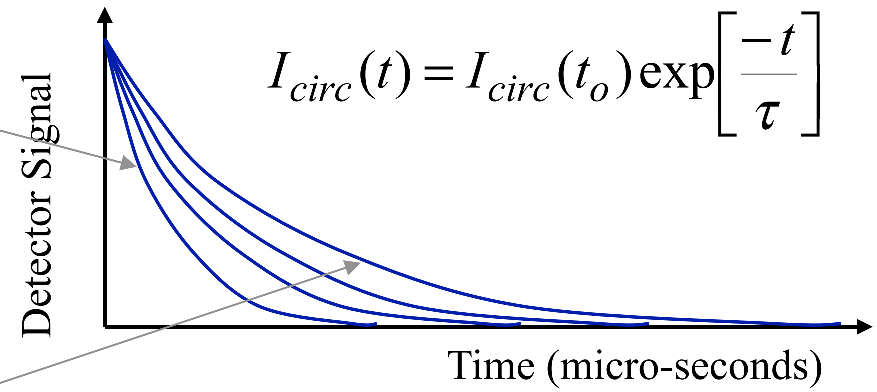


Turning Ringdowns into Concentrations

Select wavelength using λ-monitor



Measure decay time using CRDS



$$I_{circ}(t) = I_{circ}(t_o)\exp\left[\frac{-t}{\tau}\right]$$

Calculate loss

$$d = 1/ct_{ringdown}$$

Gas concentration is proportional to the area under the curve

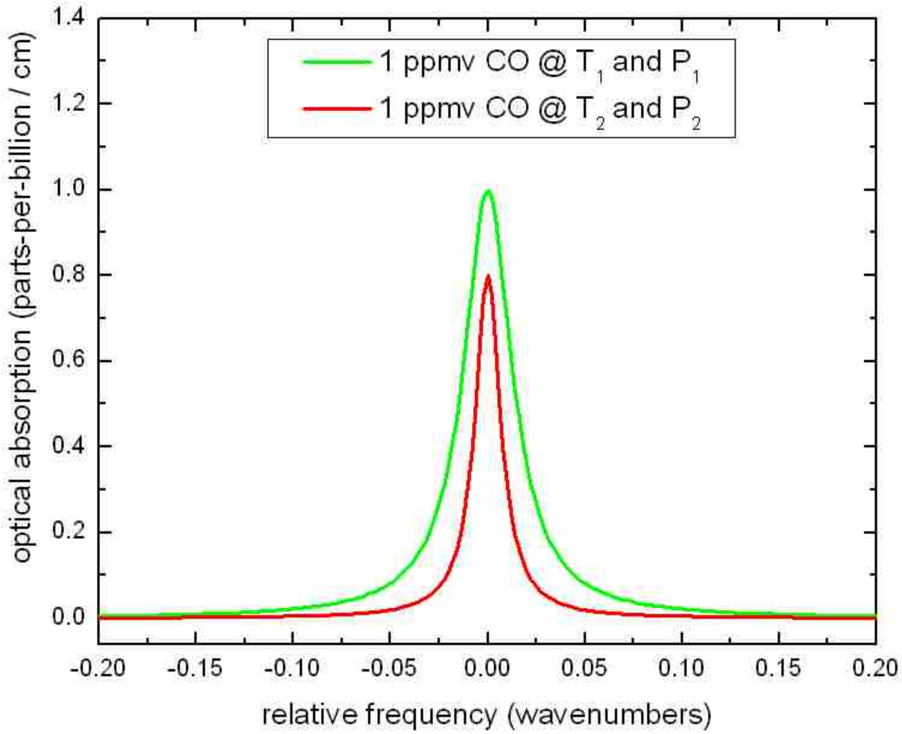
Where,
I: light intensity in the cavity
c: Speed of light
d : Loss per unit length

PICARRO

Temperature and Pressure Control

- In a given gas matrix, only two parameters affect the lineshape
  - Temperature
  - Pressure

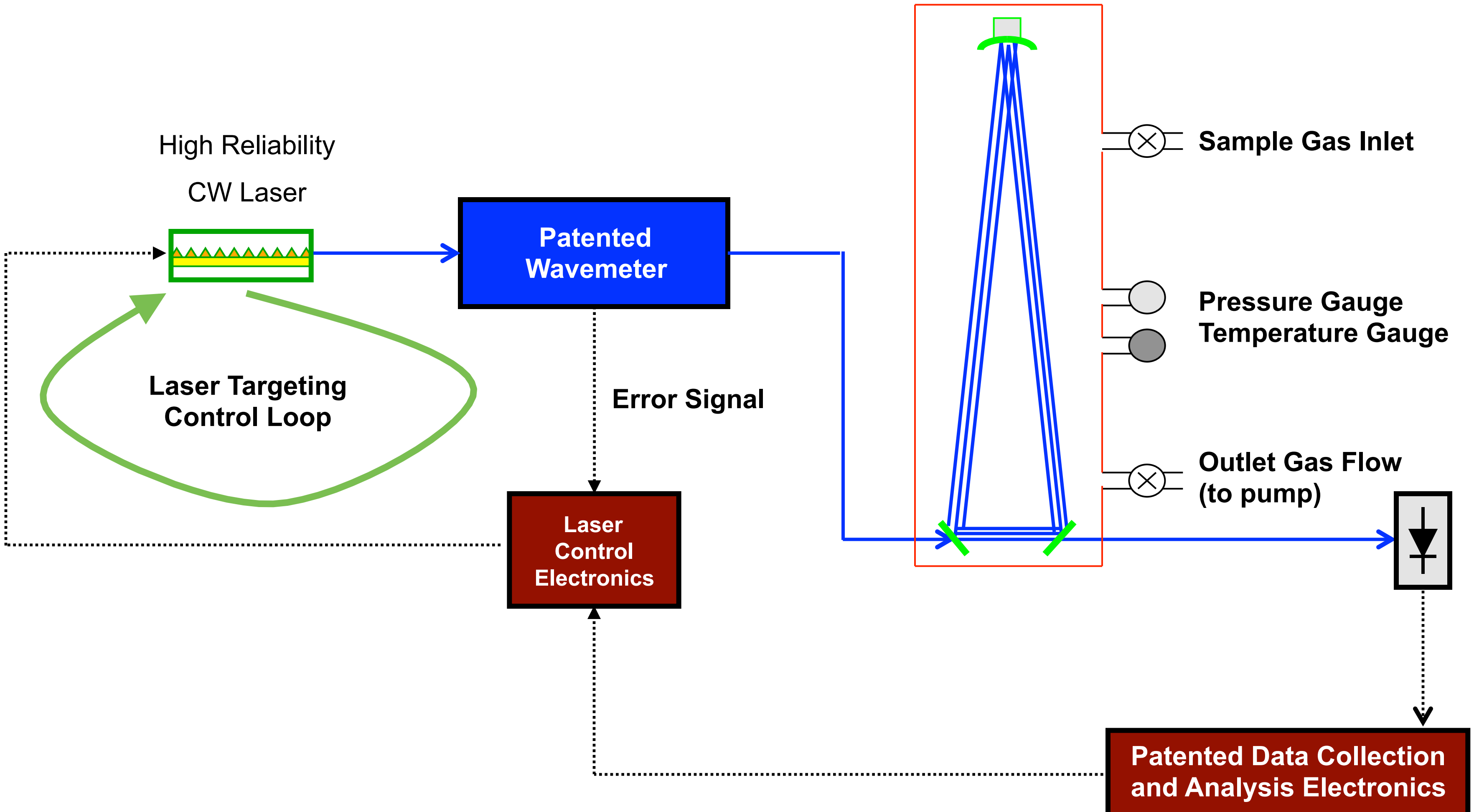
- Tiny temperature and pressure instabilities means BIG concentration and isotopic errors



Accurate gas measurements require ***stable*** spectroscopic features

PICARRO

Instrument Block Diagram



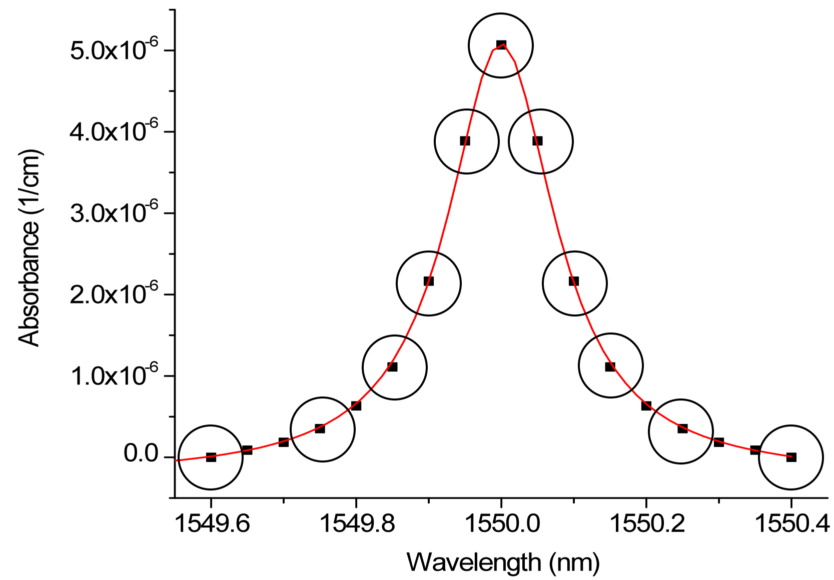
PICARRO

The Instrument

CRDS Summary

1. Need to Measure or Control

Absorption (measured)
Wavelength (controlled)
→ **Spectrum** →



Pressure (controlled)
Temperature (controlled)

Measured Spectrum
+
Pressure and Temperature
||
Concentration or Isotopic Ratio

2. Analyzer Must Incorporate

High reliability components
No consumables
Control software that enable out of the box operation

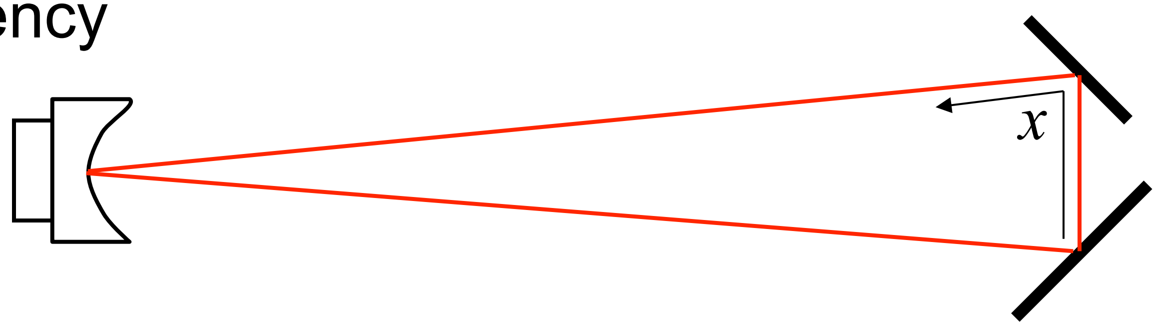
PICARRO

Performance Limits of CRDS

- CRDS relies on measuring spectra:
  - optical absorption (loss) as a function of frequency.
- At a single frequency, random fluctuations in the ring-down time (shot-to-shot noise) limits performance.
  - Shot to shot = standard deviation(t)/average(t)
- Over a spectrum, any frequency variation of the empty-cavity loss (baseline ripple) can make it difficult to fit spectral features of comparable extent.
  - If the baseline does not change, it can be measured and calibrated out.
- Scattering in a traveling wave cavity can affect both of these.

Travelling Waves in a Ring Cavity

- Ring cavity has two travelling wave modes at each frequency



$$E(x,t) = E_F \exp(ikx)\exp(-i\omega t) + E_B \exp(-ikx)\exp(-i\omega t)$$

- If mirrors are lossless and perfect, complex amplitudes remain constant and are independent.

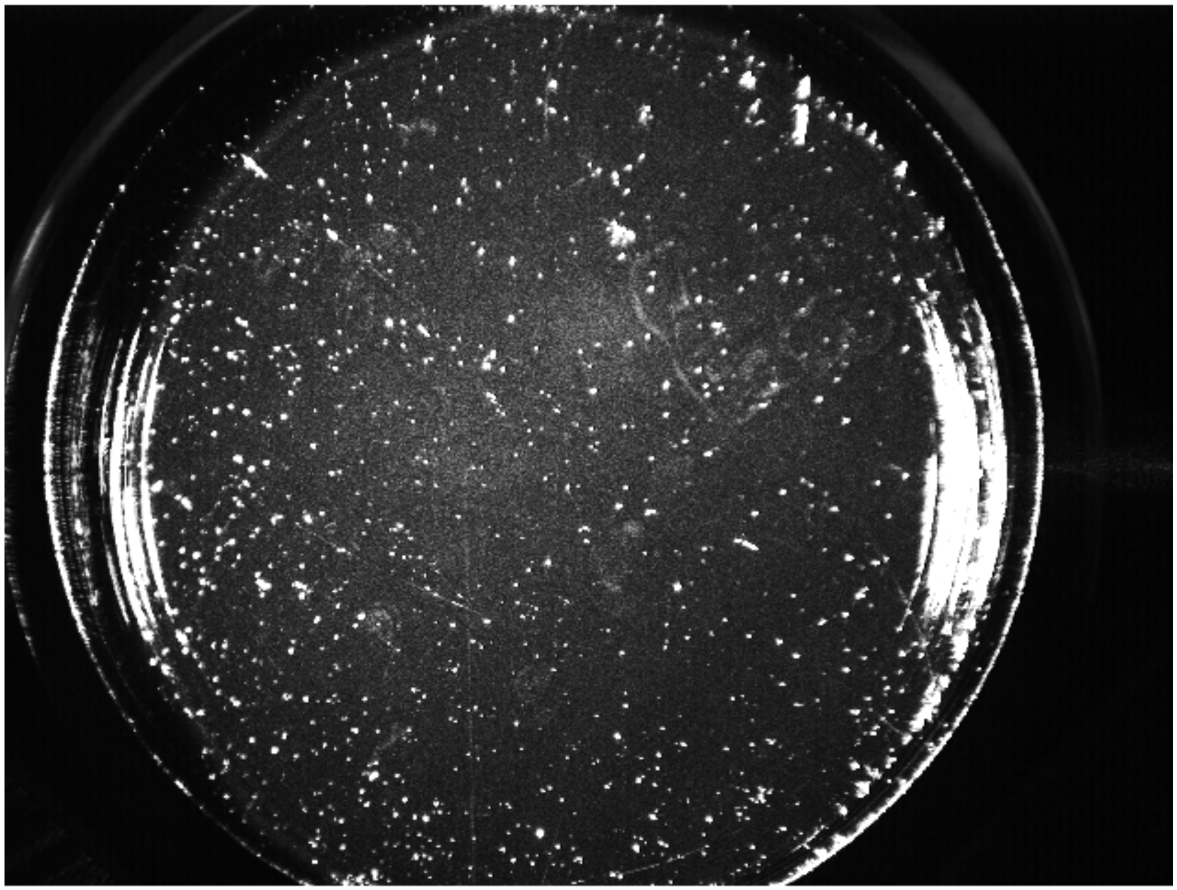
$$\frac{dE_F}{dt} = 0$$

$$\frac{dE_B}{dt} = 0$$

PICARRO

Scattering of Light from Mirrors

- All mirrors have scattering losses.



Coupled Undamped Modes

- Scattering provides a weak coupling between modes

$$\frac{dE_F}{dt} = i\eta E_B$$
$$\frac{dE_B}{dt} = i\eta E_F$$

Coupling chosen to be imaginary to conserve energy – neglect scattering into free-space modes

- Solution:

$$E_F = E_F(0)\cos\eta t + iE_B(0)\sin\eta t$$
$$E_B = E_B(0)\cos\eta t + iE_F(0)\sin\eta t$$

- Intensities if $E_B(0) = 0$:

$$I_F = |E_F|^2 = |E_F(0)|^2 \cos^2 \eta t$$
$$I_B = |E_B|^2 = |E_F(0)|^2 \sin^2 \eta t$$

Periodic energy transfer between modes

PICARRO

Coupled Damped Modes

- With loss out of the cavity modes, we have

$$\frac{dE_F}{dt} = -\gamma E_F + i\eta E_B$$

$$\frac{dE_B}{dt} = -\gamma E_B + i\eta E_F$$

- New solutions:

$$E_F = \left[E_F(0)\cos\eta t + iE_B(0)\sin\eta t \right]\exp(-\gamma t)$$

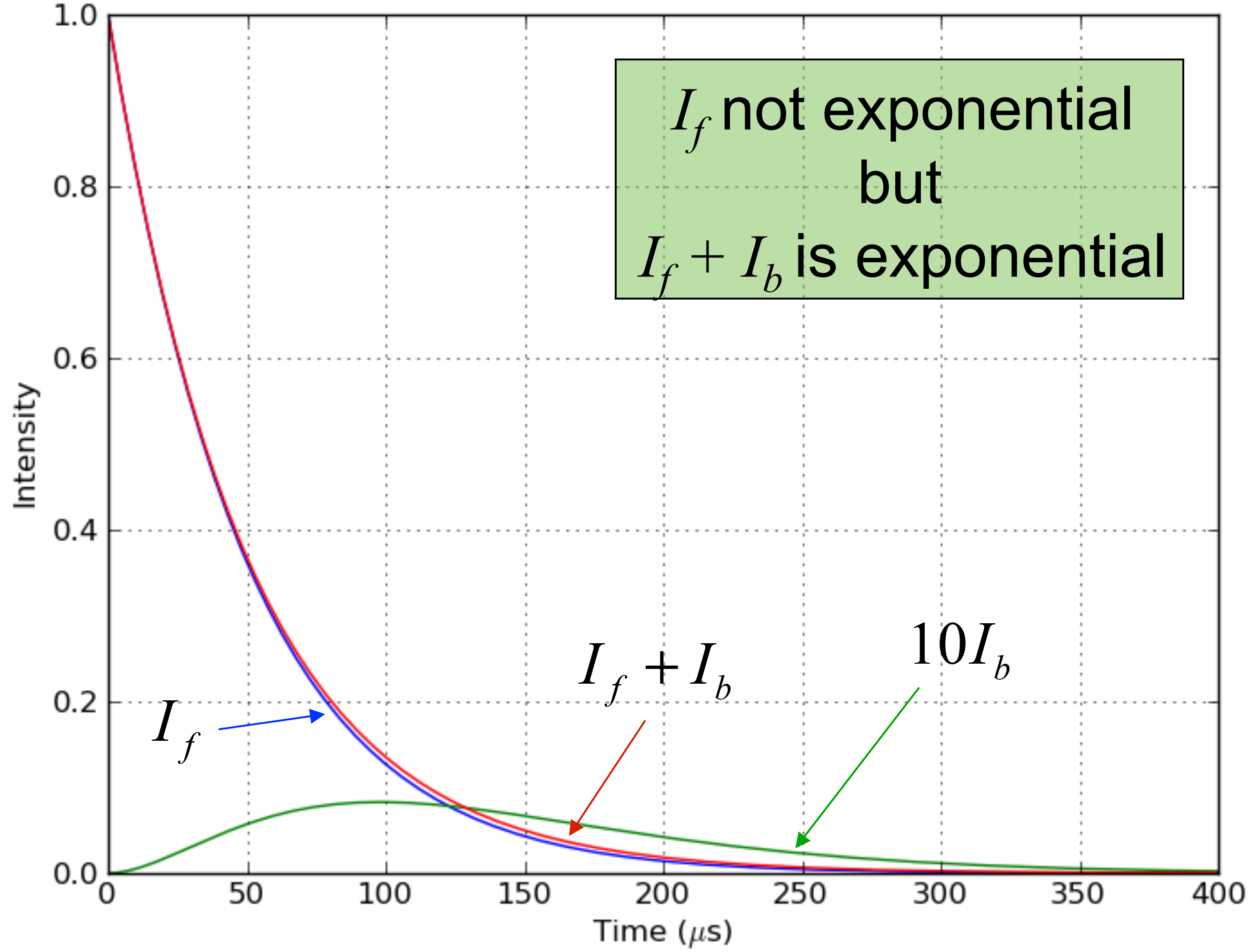
$$E_B = \left[E_B(0)\cos\eta t + iE_F(0)\sin\eta t \right]\exp(-\gamma t)$$

- Intensities if we only have forward wave at t=0:

$$I_F = |E_F|^2 = |E_F(0)|^2 \exp(-2\gamma_r t)\cos^2\eta t$$

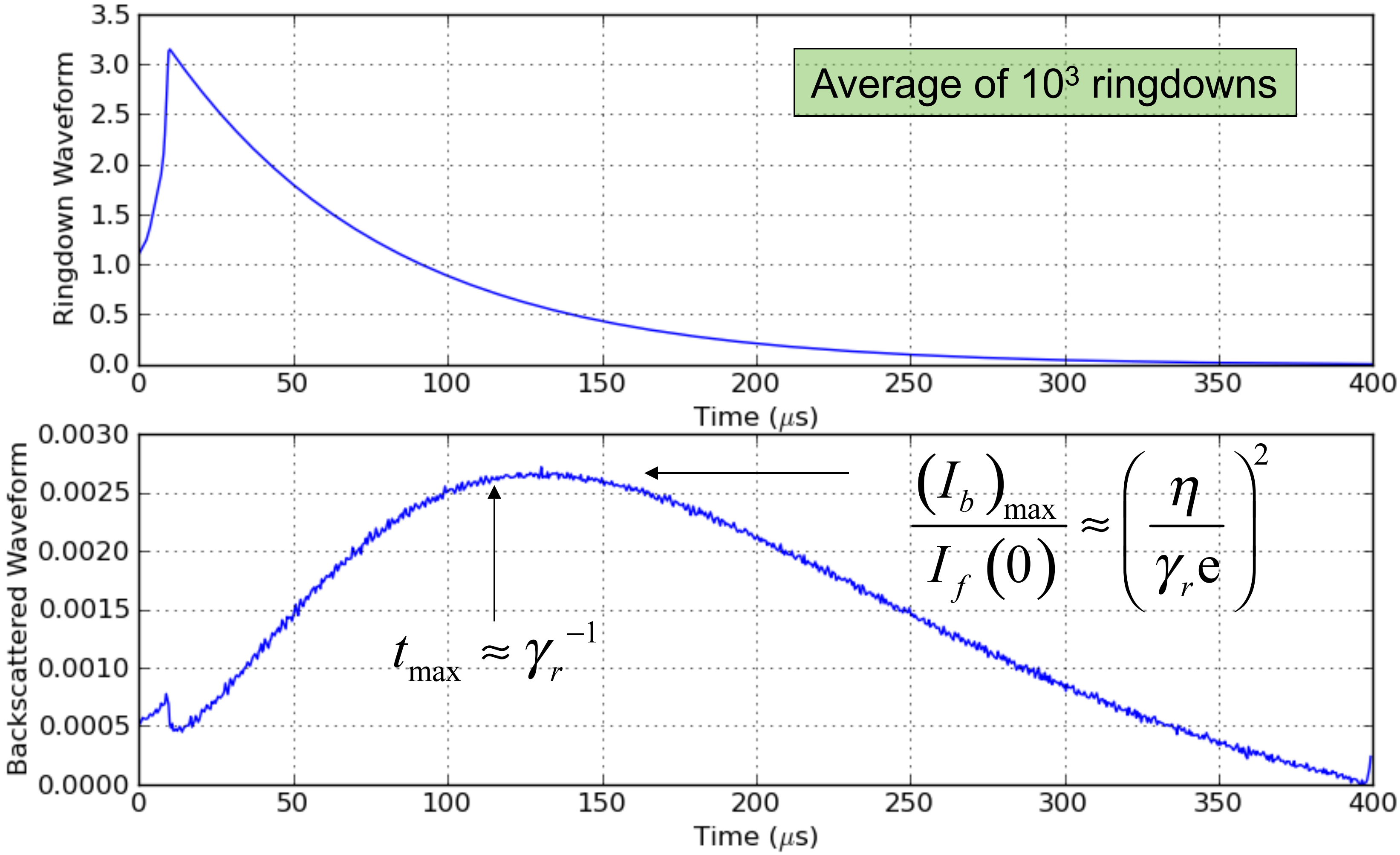
$$I_B = |E_B|^2 = |E_F(0)|^2 \exp(-2\gamma_r t)\sin^2\eta t$$

Example with $\eta = \frac{1}{4}\gamma_r$



Experimental Results

- Typically $h \ll g_r$, here $h \approx 0.075\, g_r$.

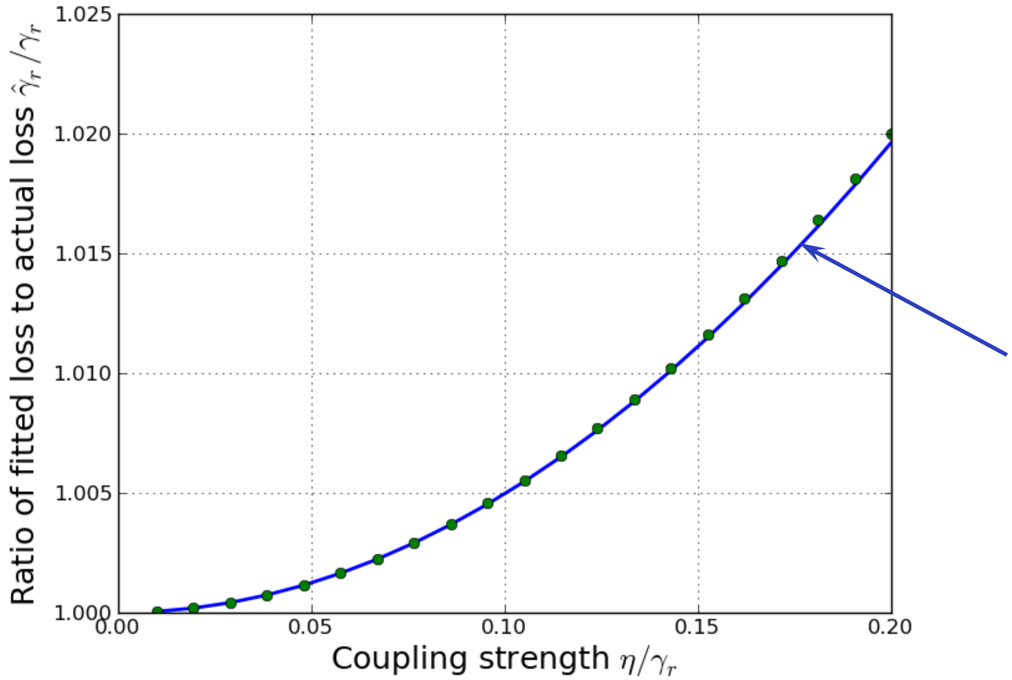


Effect of Fitting Only the Forward Wave

- If we only detect forward wave and fit to an exponential

$$I_F = \left|E_F\right|^2 = \left|E_F(0)\right|^2 \exp\left(-2\gamma_r t\right)\cos^2 \eta t$$

- A least squares fit to $I_F = I_0 \exp\left(-2\hat{\gamma}_r t\right)$ yields erroneous $\hat{\gamma}_r$
- Simulation:

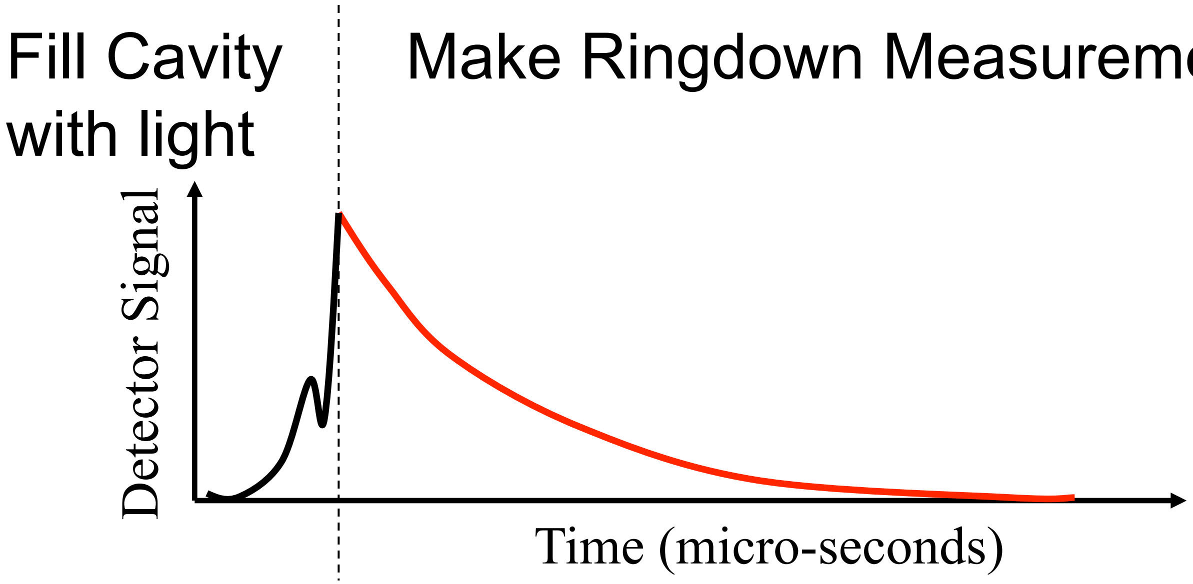


$$\frac{\hat{\gamma}_r}{\gamma_r} \approx 1 + \frac{1}{2}\left(\frac{\eta}{\gamma_r}\right)^2$$

PICARRO

Build-Up of Light in the Cavity

- So far we see that scattering can produce a bias in the loss measurement – but what about a variance?
- Need to look more closely at build-up of light in the cavity before a ring-down is initiated.



PICARRO

What is the effect on the shot-to-shot?

- Add a noisy driving term

$$\frac{dE_F}{dt} = -\gamma E_F + i\eta E_B + \varepsilon$$
$$\frac{dE_B}{dt} = -\gamma E_B + i\eta E_F$$

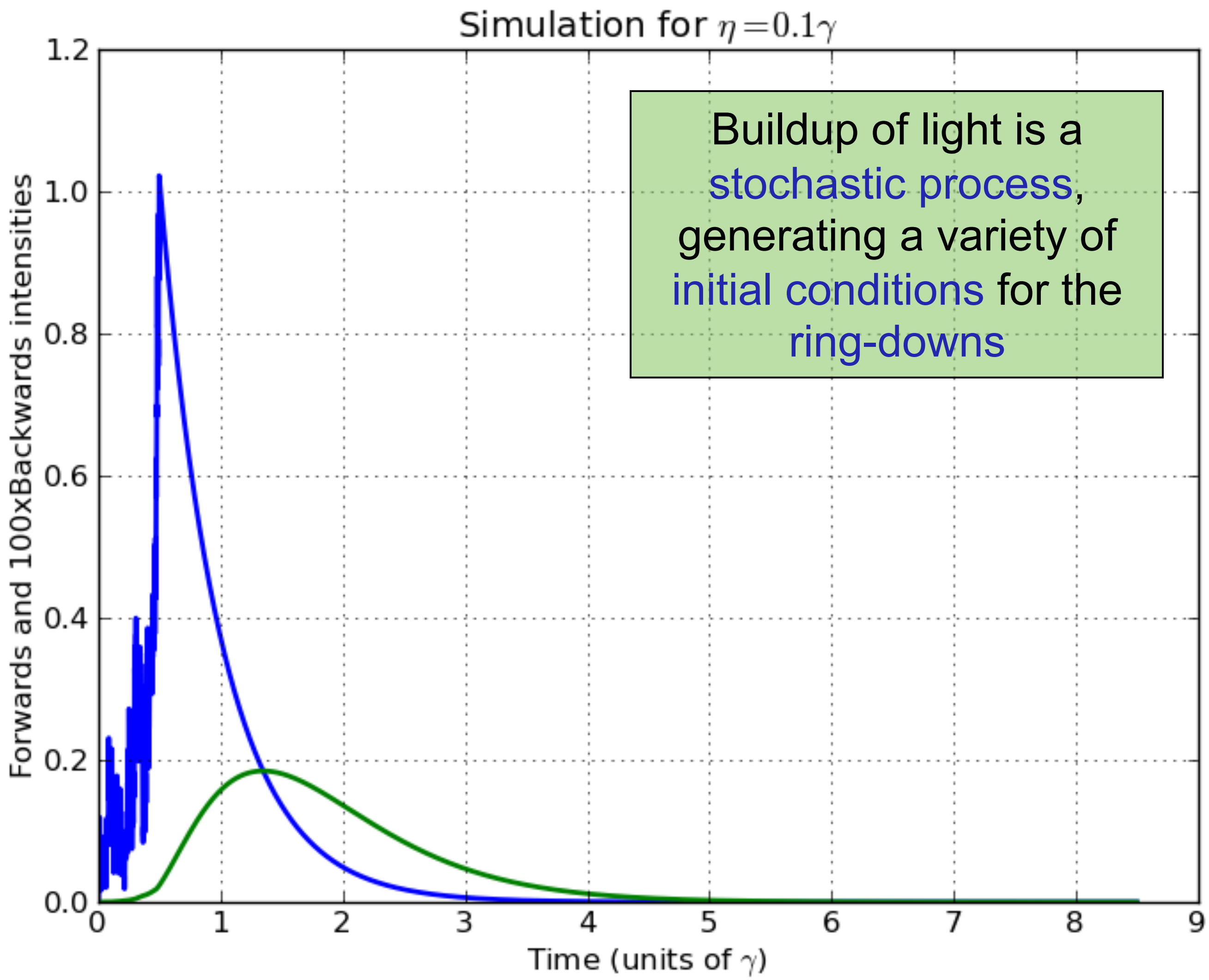
White noise (Wiener) process due to laser excitation of forward mode

- We keep the laser turned on until $I_F = |E_F|^2$ reaches a threshold, then laser is turned off.
  - At that time, both E_F and E_B may be non-zero
  - Related to first crossing time problem for a random walk

PICARRO

Forward and Backward Intensities

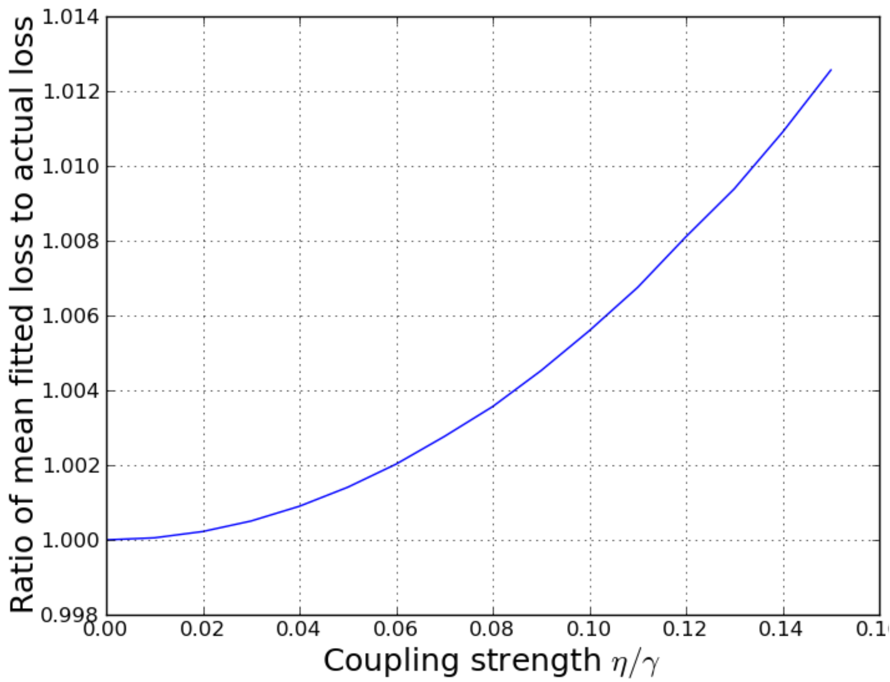
Threshold = 1 to initiate ring-down

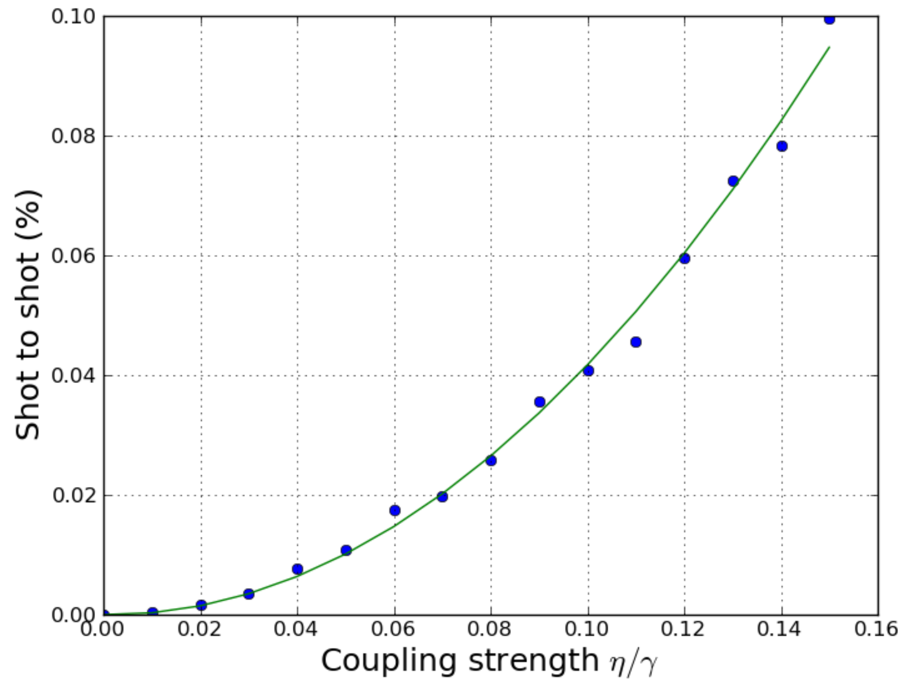


PICARRO

Mean Loss and Shot-to-Shot

- Simulate fitting forward intensity for 100 ring-downs with various coupling strengths



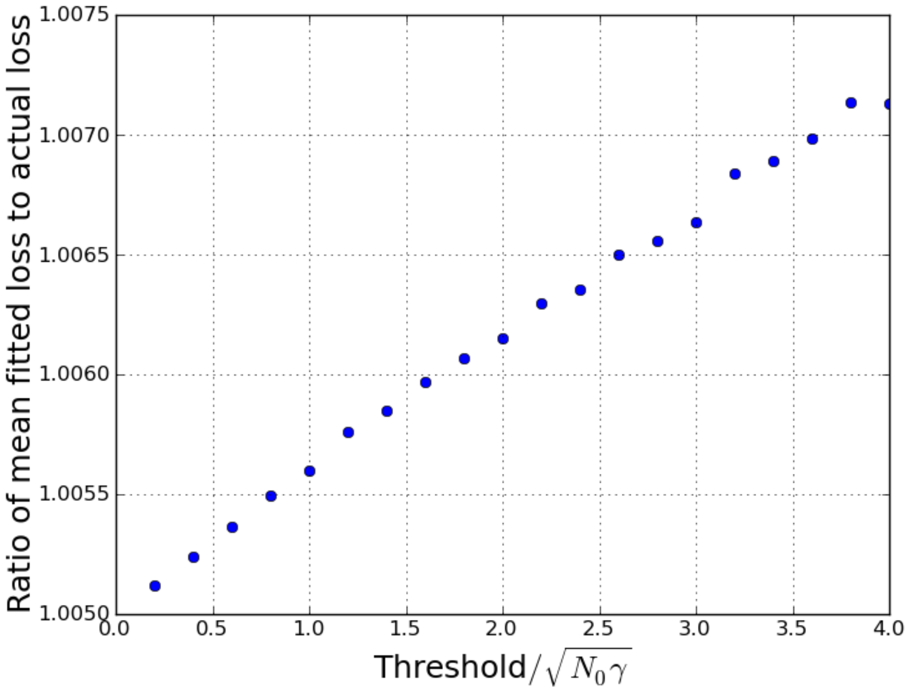


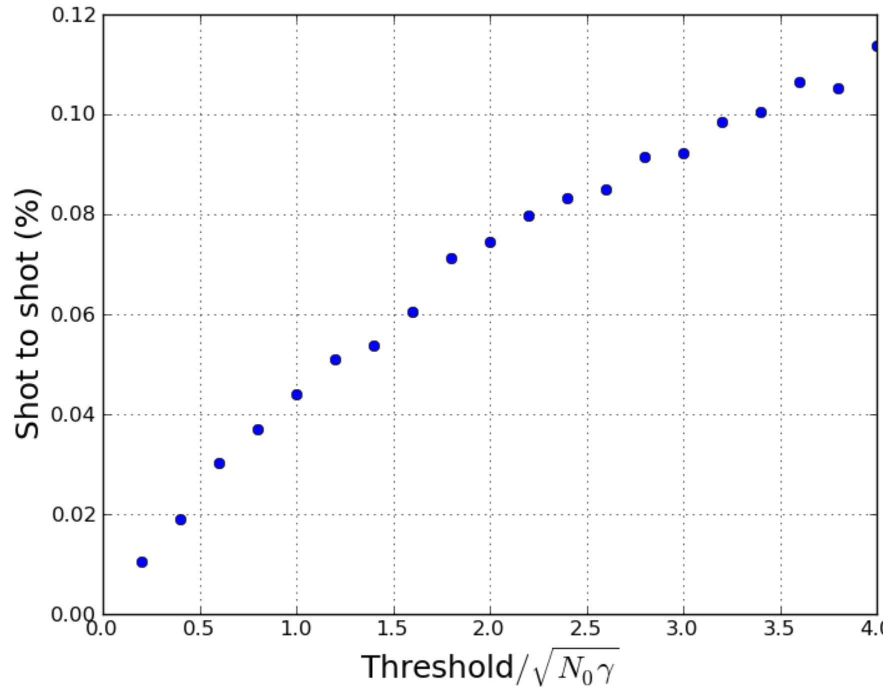
$$\frac{\text{threshold}}{\sqrt{N_0\gamma}} = 1$$

Loss is always overestimated and shot-to-shot is degraded with increased backscattering

PICARRO

Dependence on Ringdown Threshold, Laser Power and Linewidth





For low laser power or large laser linewidth, N_0 is small.
This gives a longer random walk, which degrades performance.
N.B. Shot-to-shot due to electronic noise is inversely proportional to threshold

PICARRO

Mitigation Strategy

- During ring-down,

$$\frac{dE_F}{dt} = -\gamma E_F + i\eta E_B$$

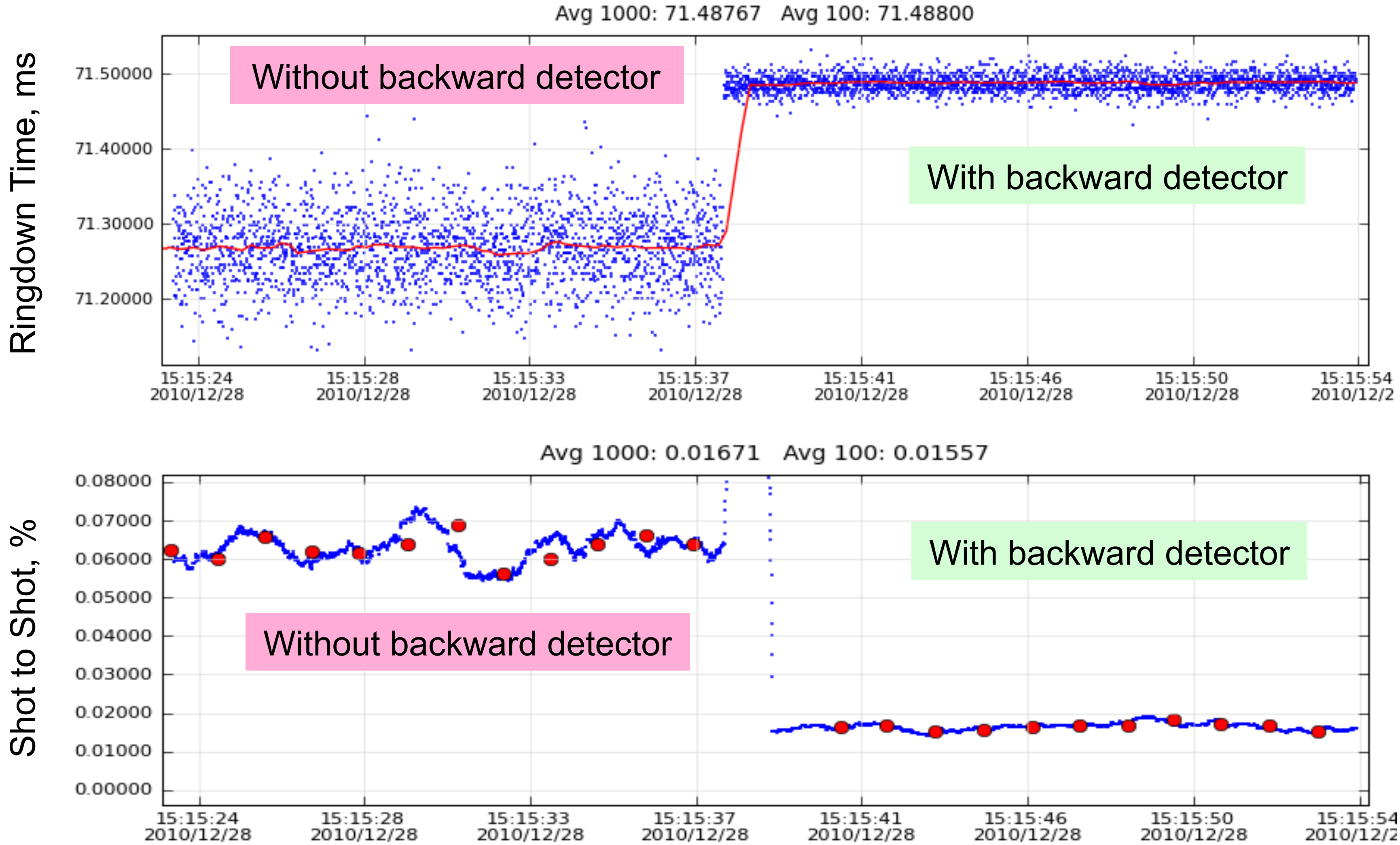
$$\frac{dE_B}{dt} = -\gamma E_B + i\eta E_F$$

- Consider sum of forward and backward intensities:

$$\frac{d\left(E_F E_F^{\ *} + E_B E_B^{\ *}\right)}{dt} = -2\gamma_r \left(E_F E_F^{\ *} + E_B E_B^{\ *}\right)$$

- Sum decays exponentially

Experimental Results



PICARRO

Backscattered Wave Summary

- Scattering couples the forward and backward travelling waves in the cavity
- With this coupling the forward wave no longer decays exponentially
- Variations in the build-up of light in the cavity lead to noise in the fitted ringdown time
- Fitting the sum of the forward and backward intensities removes this noise

Picarro, Inc.

- We invent and build products in Silicon Valley
- 85 employees, 30% are Ph.D.s

PICARRO

What is Picarro all About?

- Developing and Selling Truly Field Deployable Analyzers that,
  - are extremely high accuracy and precision (ppb-ppt),
    - Greenhouse gases, HF, iH_2O, iCO_2, and many more
  - provide reliable results under the conditions found at the field site,
    - minimal drift over ambient temperature
    - minimal effect from mechanicals vibration such as pumps and people
  - require little or no human intervention while operating in the field,
    - reliable software
  - can survive the long trip to the field site without breakage.
    - shock and cold storage

Picarro's Current Customers

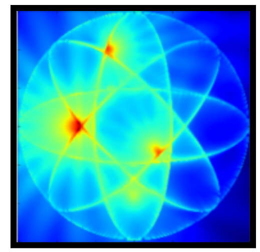
- Focused on Environmental Applications
  - Greenhouse gas and isotopic analyzers in over 52 countries and 7 continents.
  - Products are used by scientist conducting real-time measurements
    - On the Greenland ice sheet
    - In the African desert
    - On aircraft
    - In climate controlled state-of-the-art research laboratories



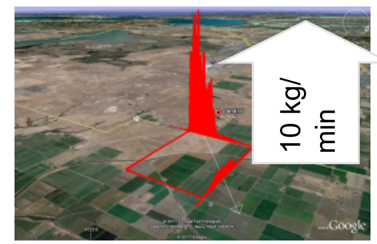

What do Picarro's Instruments Enable?

Mobile Measurements

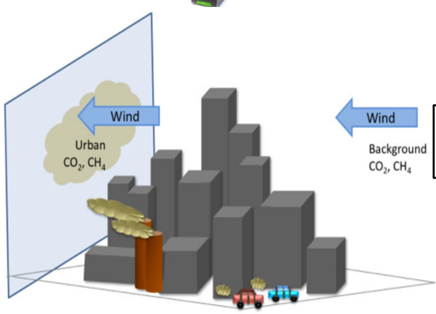
Networks



Atmospheric Models



Emissions Maps



Aircraft Measurements

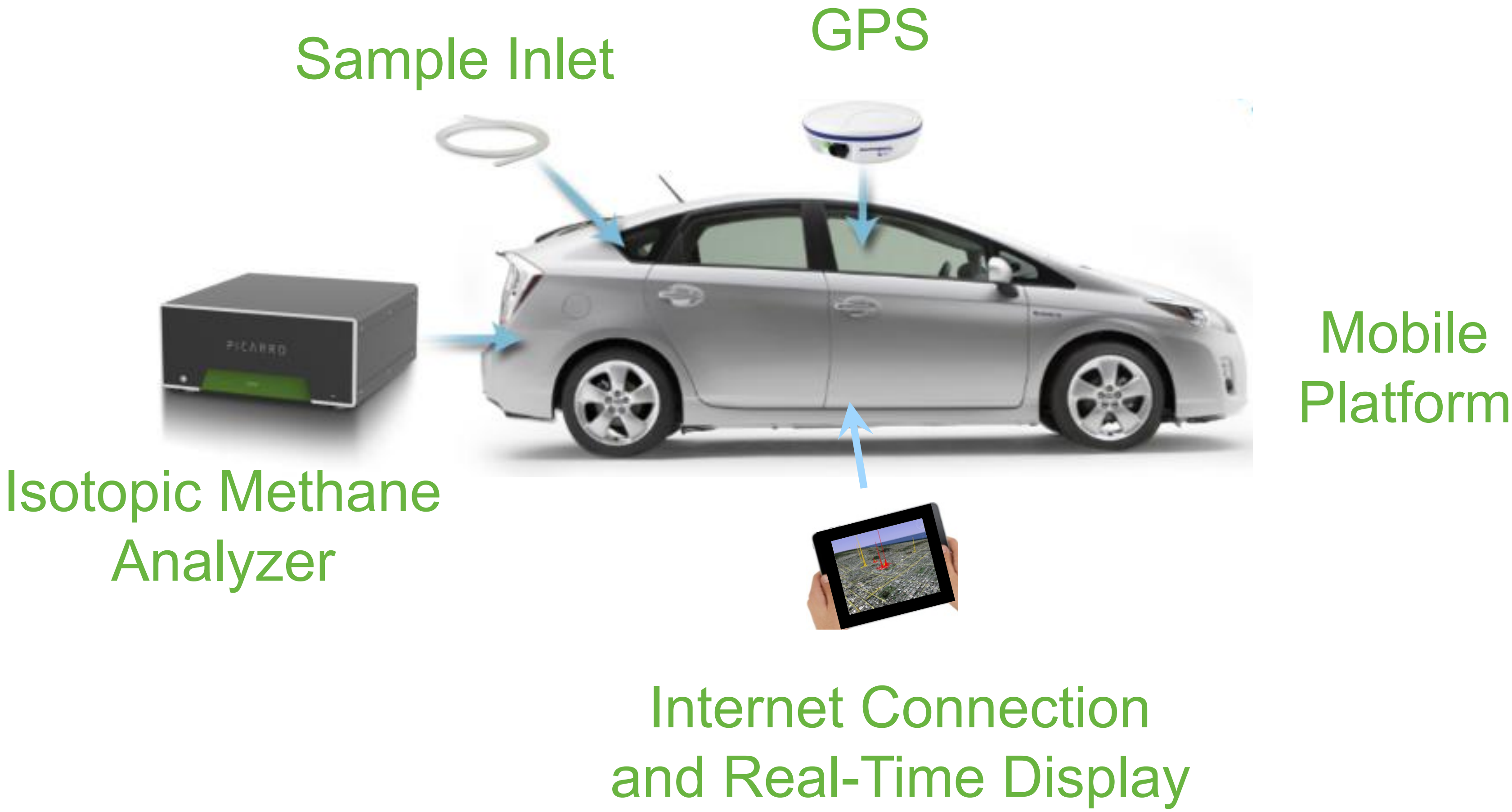
Enables the collecting of information using state of the art technology that the non-scientist can understand and utilize

PICARRO

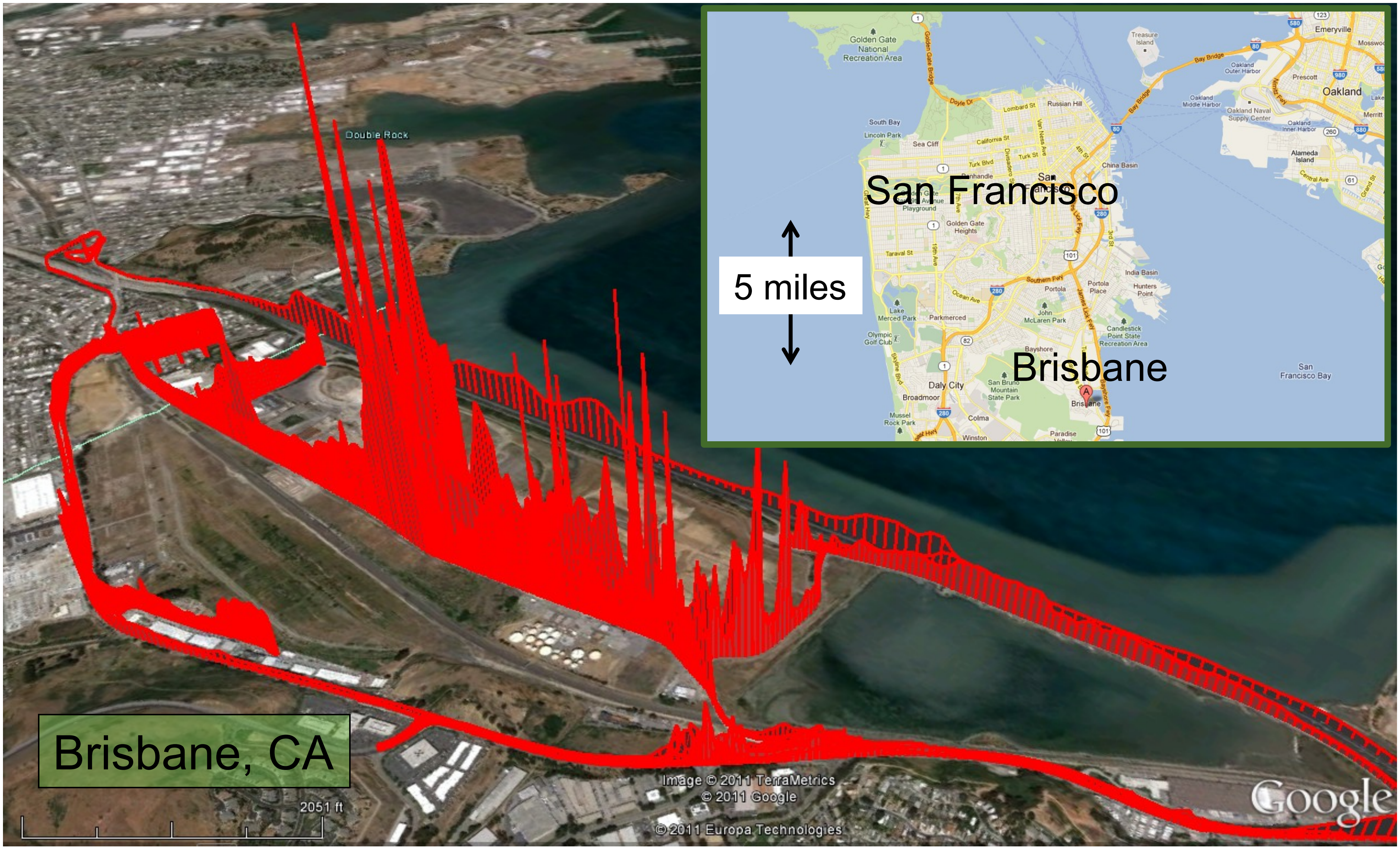
Problem Statement

PICARRO

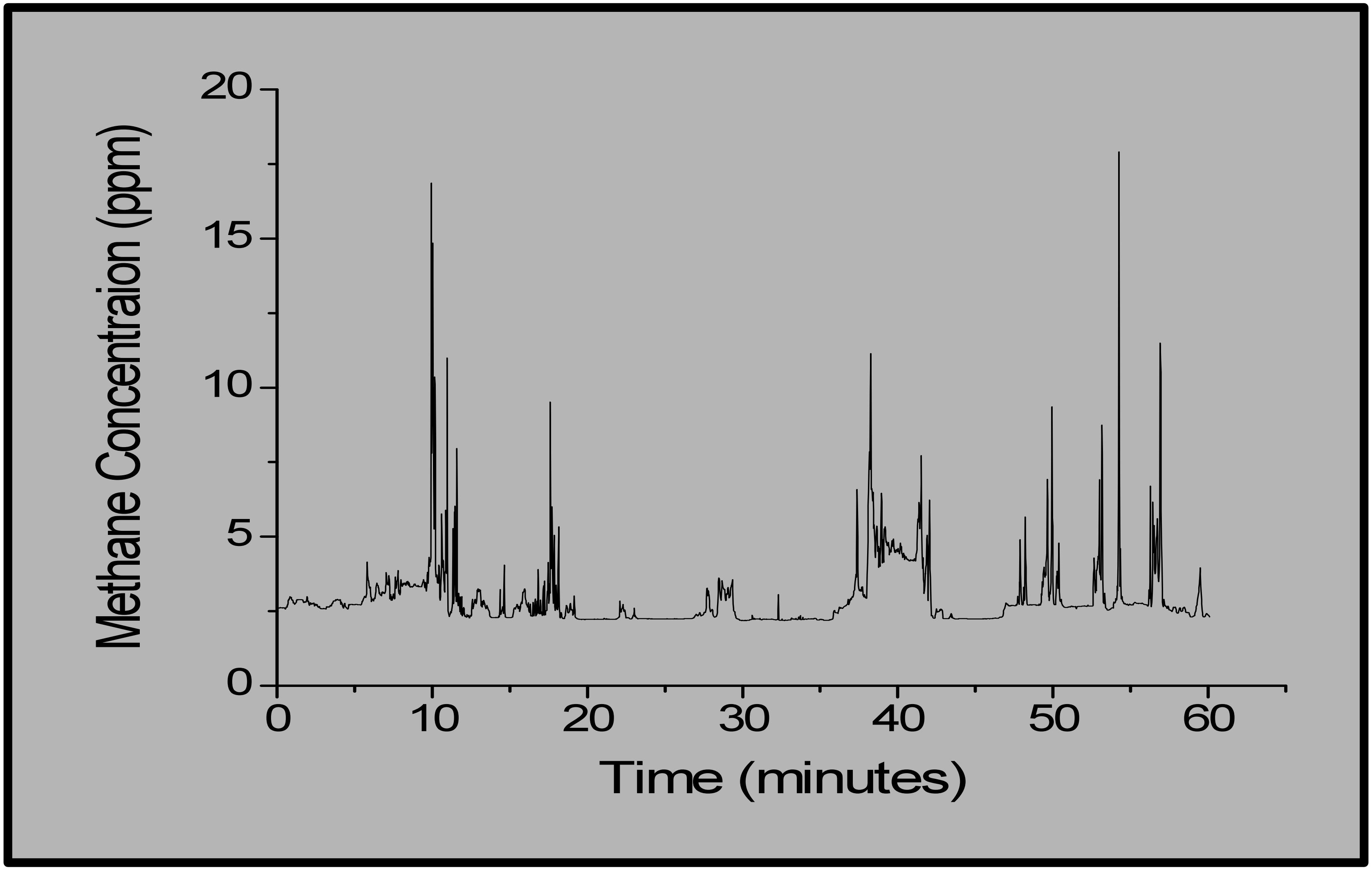
Proposed Solution



Application: Methane Mapping

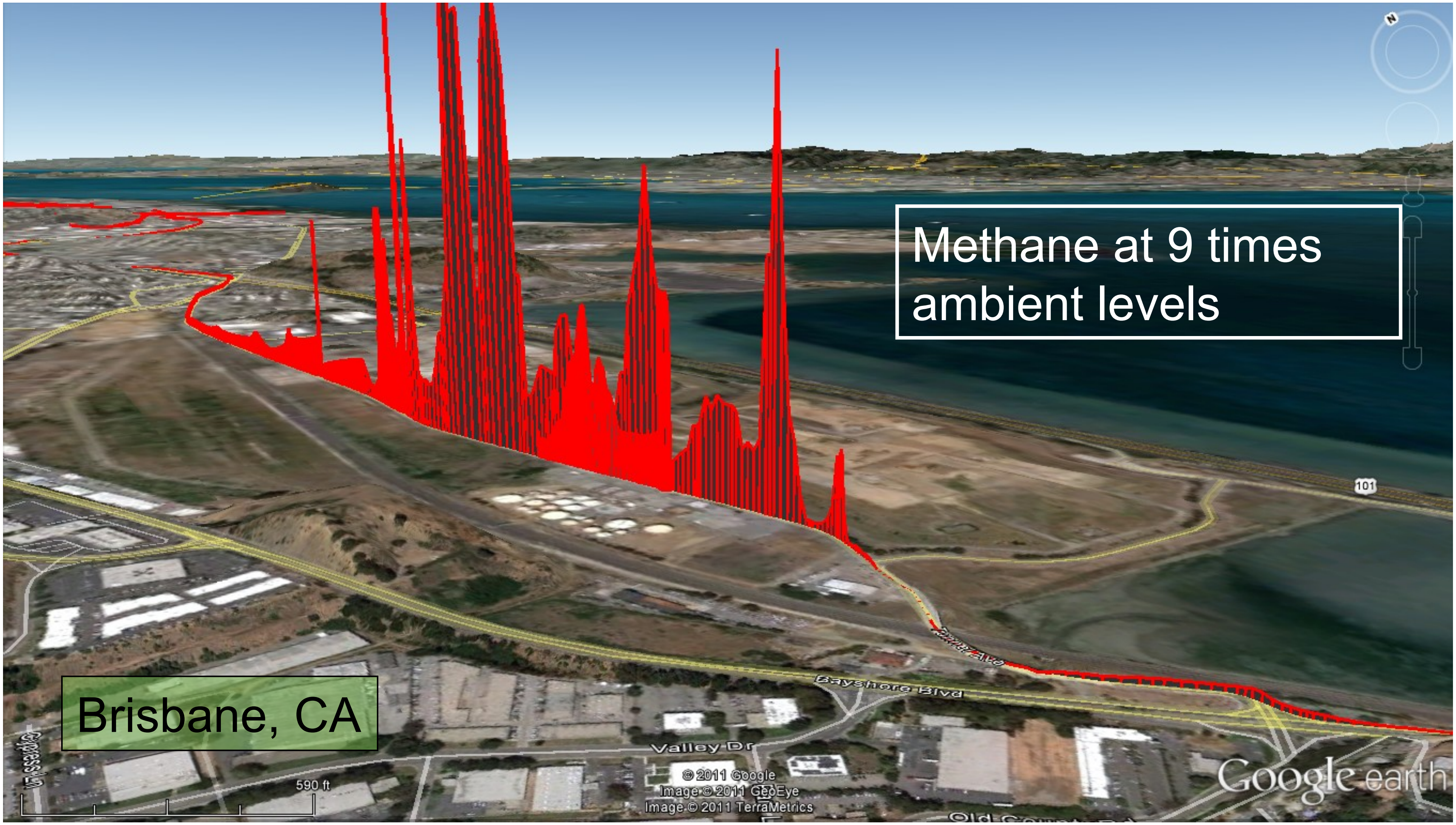


Speed is Everything

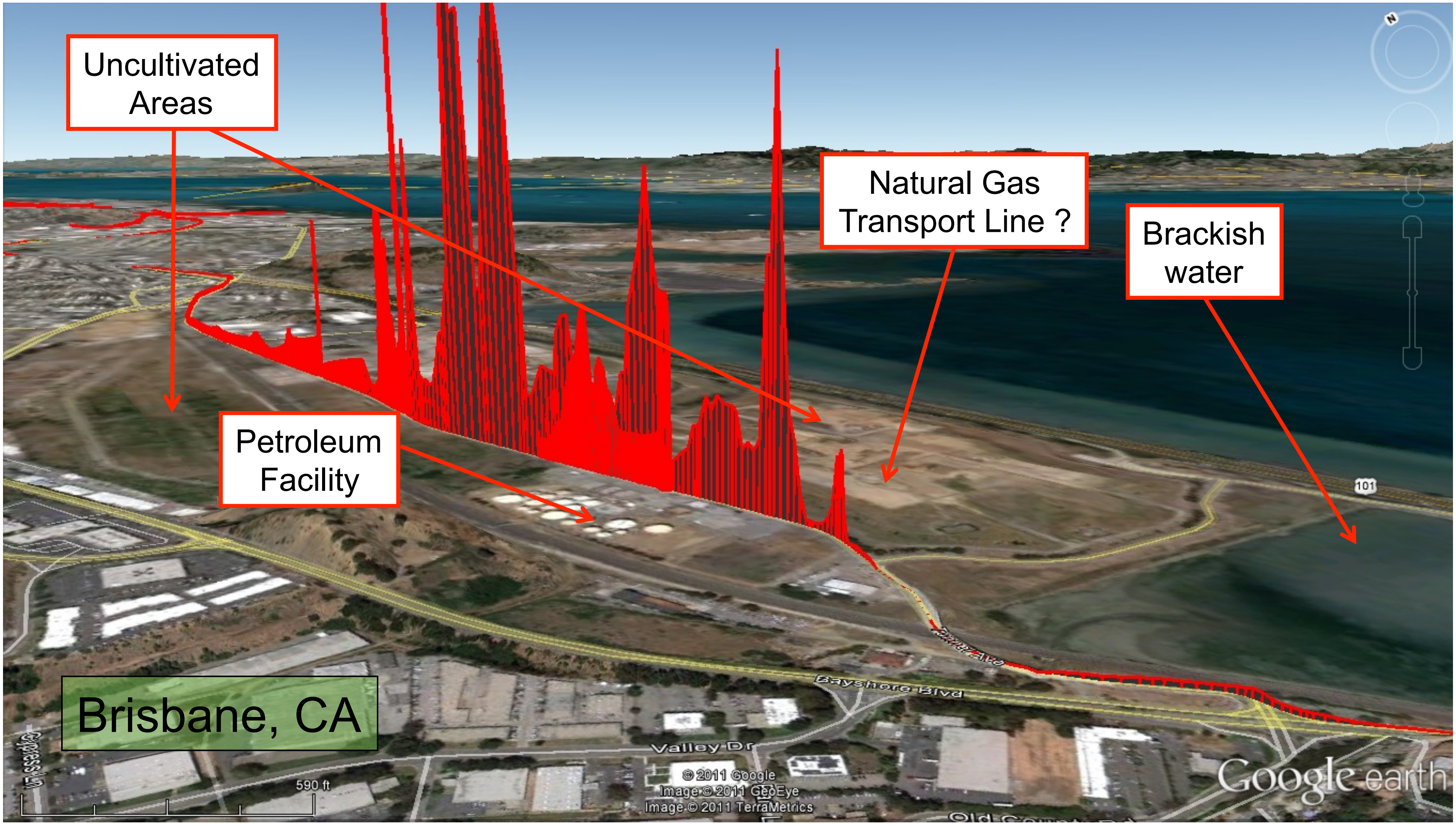


PICARRO

Many Sources Distributed Over ~2 miles



What is the Source?



Sources of Hydrocarbons in the Air

Storm Drains

Natural Gas Vehicles

Inefficient Vehicles

Sewer Systems

Petroleum Facilities

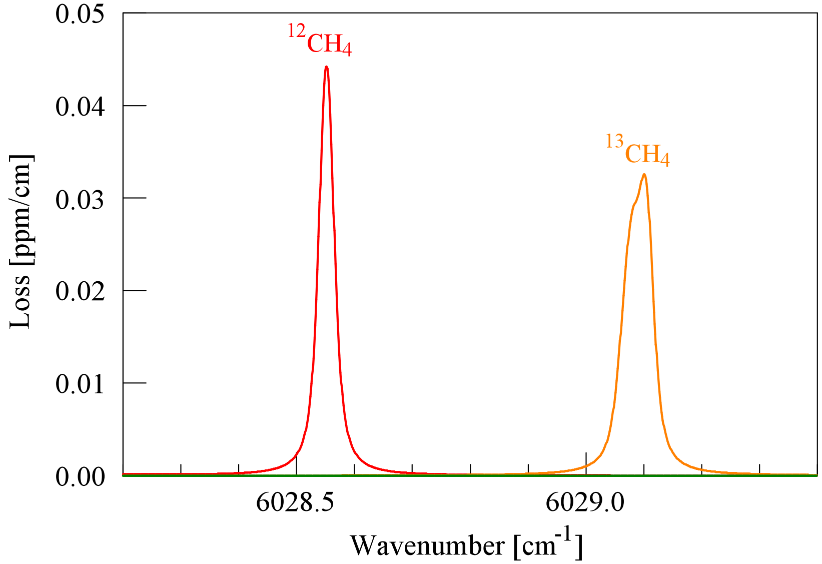
Landfills

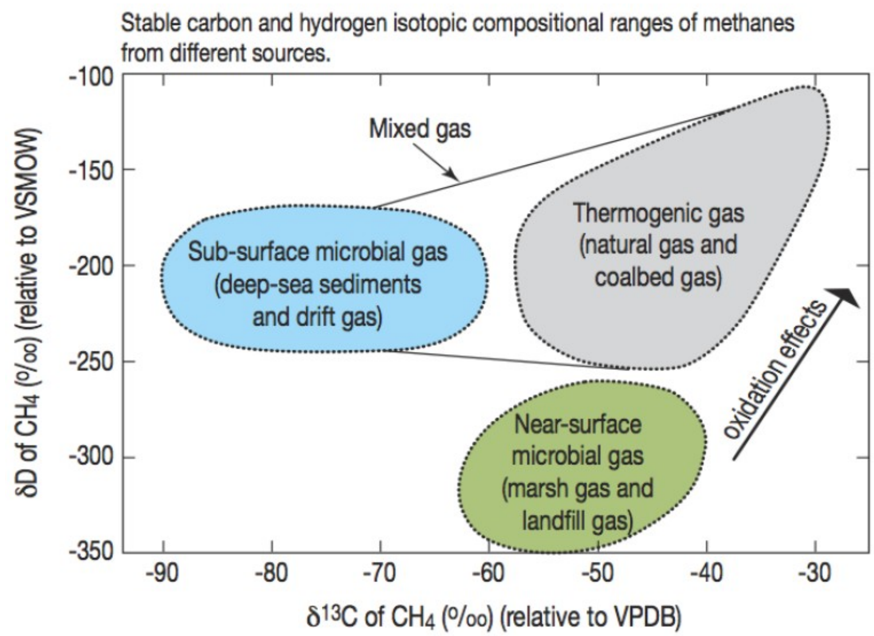
Natural Gas Leaks

Specificity: Carbon-13 Measurements

- Methane's carbon-13 and deuterium content depends on how the gas was created, typically reported as a delta:

$$\delta \equiv 1000\left(\frac{R}{R_{st}} - 1\right), R = \frac{^{13}CH_4}{^{12}CH_4}$$

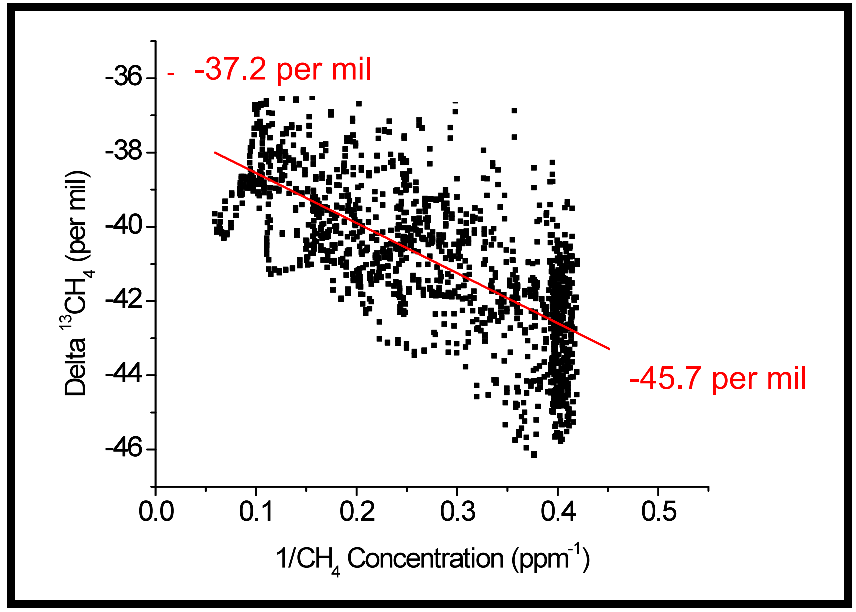




After Coleman and others (1993) based on the data set of Schoell (1980)

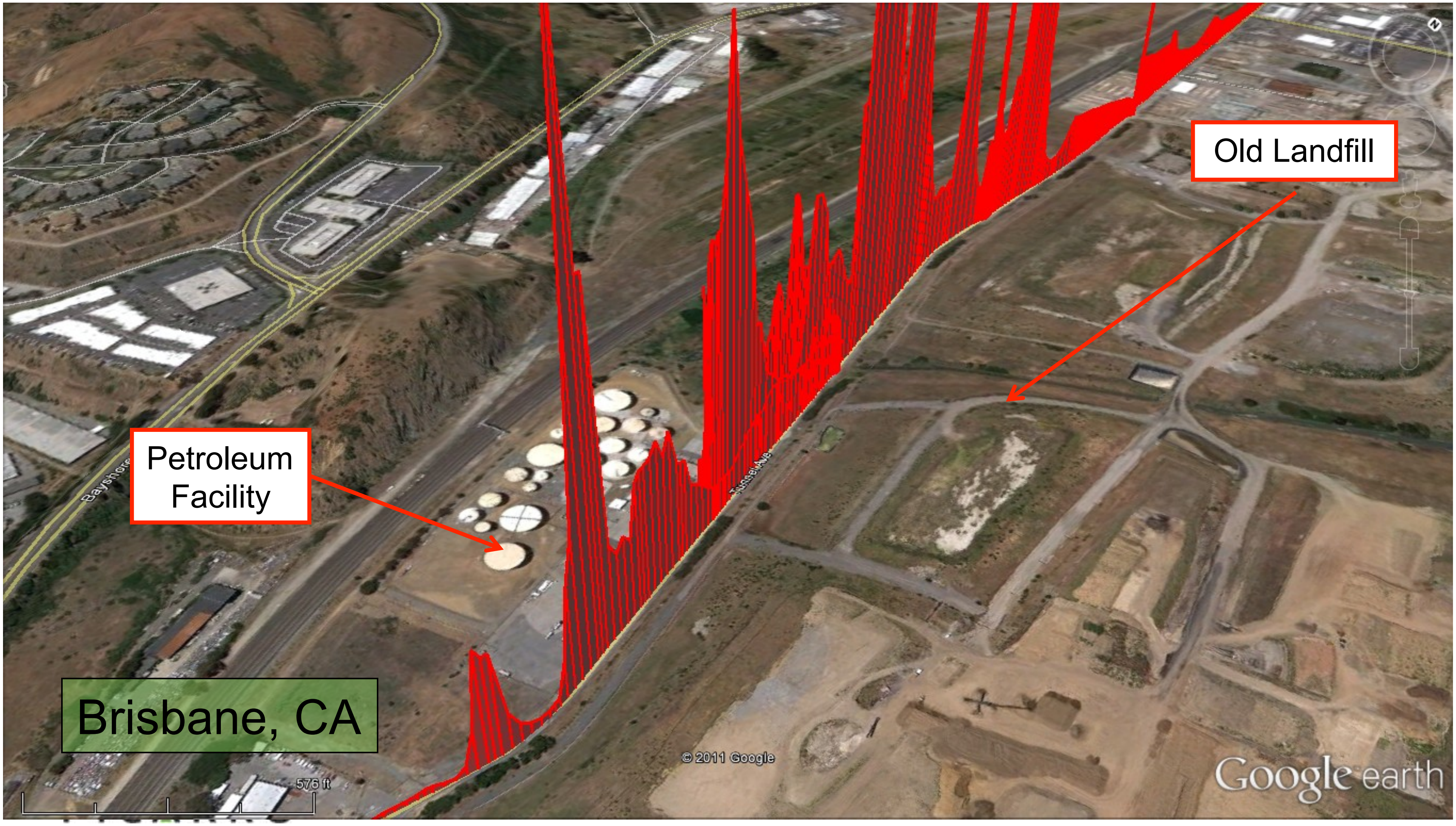
PICARRO

Specificity: Keeling Plots

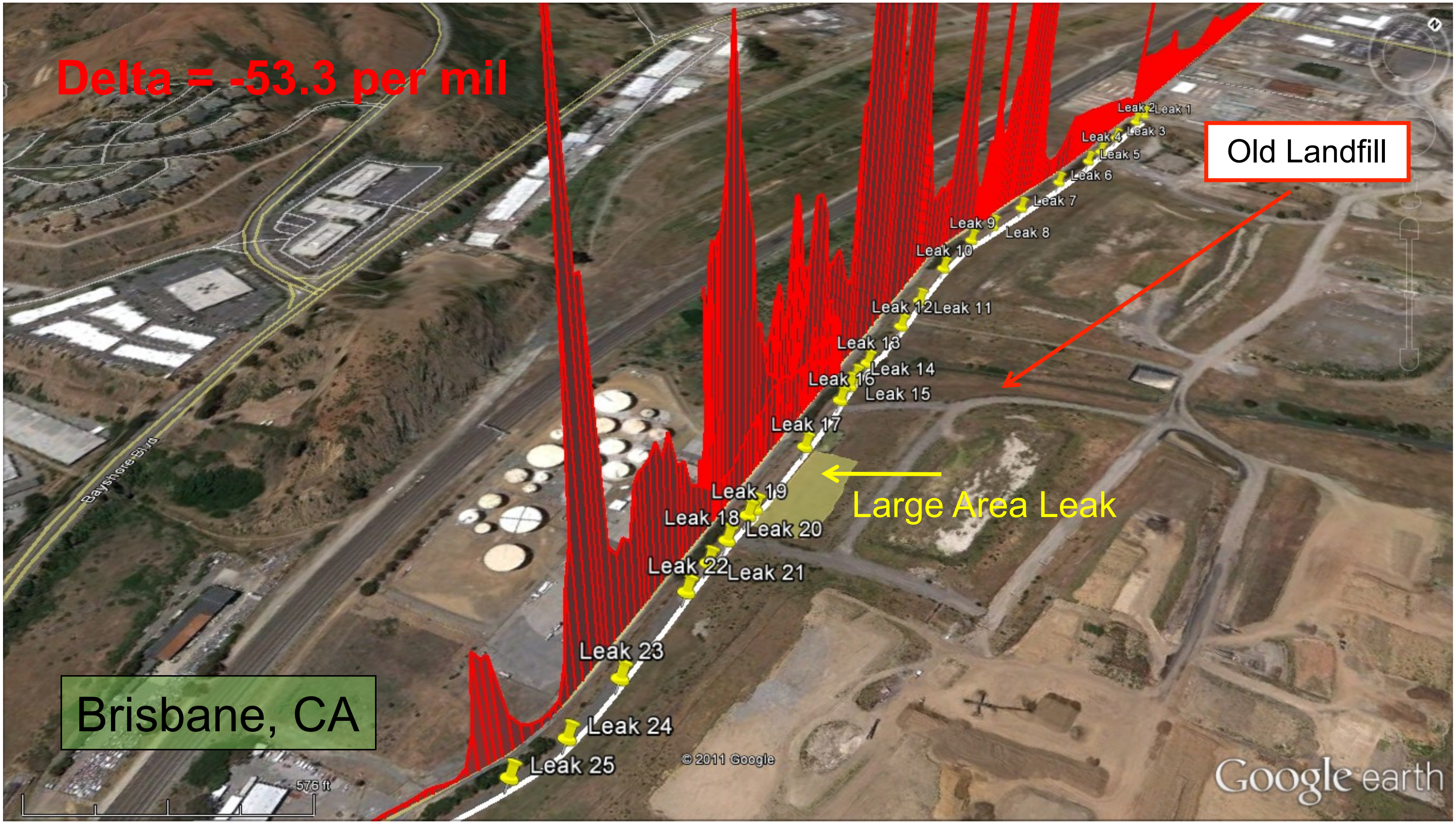


PICARRO

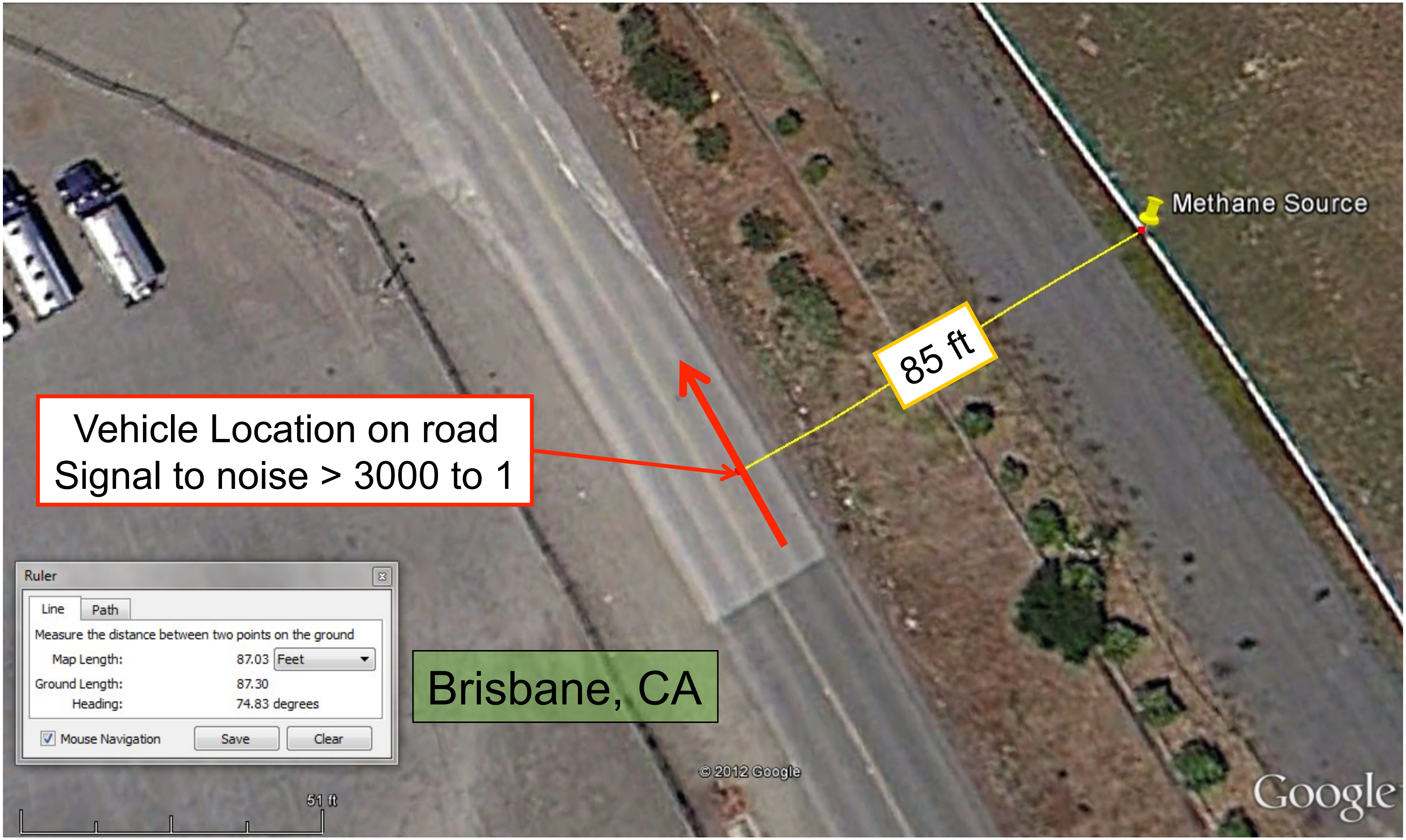
Back to the Brisbane Site



Methane Capture System is Leaking



Don't Need to be On Site



Brisbane Conclusion:
Old Landfill is Releasing Methane

1. Pipe connectors leak.
2. Methane capture system is failing in one area of landfill.

In a very short time, we are able to identify specific problems that can be acted on by landfill owner or city officials.

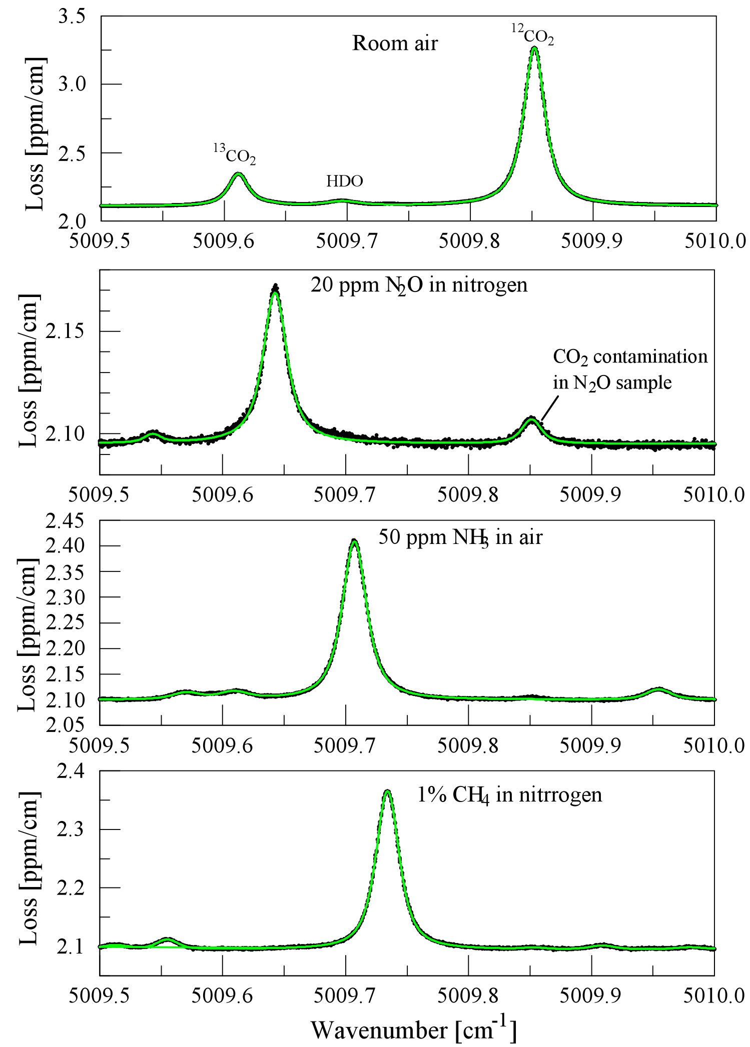
The Modern World-Class Laboratory

(Courtesy of Prof. Benson, Stanford U.)

All Cavities Have Optical Loss

- Mirror loss
  - Scattering
  - Transmission through mirrors
  - Absorption by the materials that comprise the mirror

- Loss from optical absorption by the sample



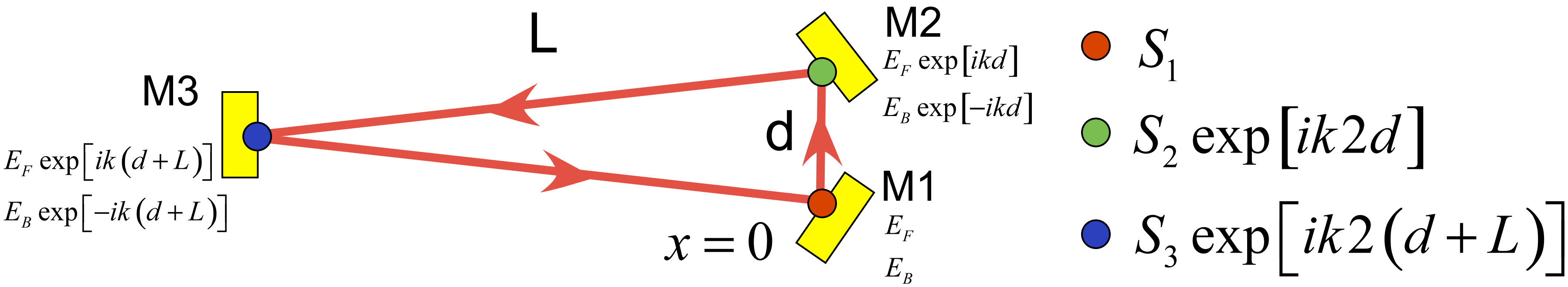
Frequency Dependence of Backscattering

- Coupling η indicates how much a forward wave increases the backward wave amplitude and vice versa

$$\frac{dE_F}{dt} = -\gamma E_F + i\eta E_B + \varepsilon$$

$$\frac{dE_B}{dt} = -\gamma E_B + i\eta E_F$$

- Backwards wave results from the superposition of scattering interactions, potentially at all three mirrors – these can interfere:

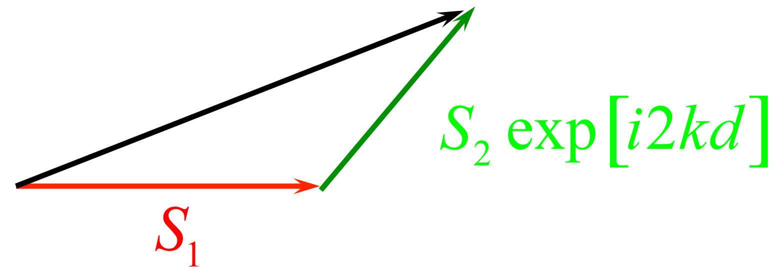


PICARRO

$$E(x) = E_F \exp(ikx) + E_B \exp(-ikx)$$

Frequency Dependence of Backscattering

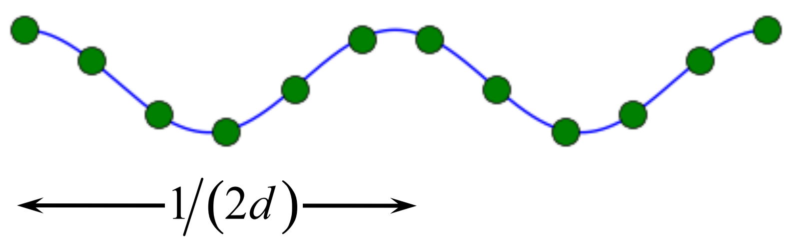
- Consider two scatterers on **M1 and M2**. Coupling depends on $S_1 + S_2 \exp\left[ik2d\right]$



- Depending on k and hence on laser frequency $\bar{\nu}$, interference causes coupling to vary, with "period" $\Delta k = \dfrac{\pi}{d}$

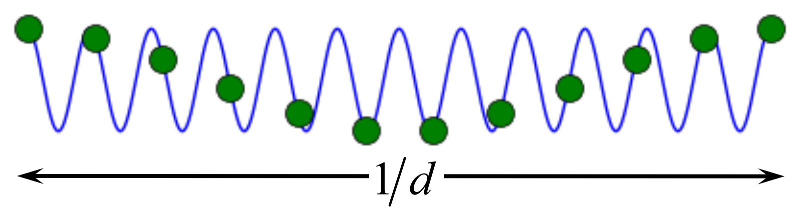
- Since coupling strength affects fitted loss and shot-to-shot, this gives a baseline ripple with wave-number period

$$\Delta\bar{\nu} = \frac{1}{2d} \approx 0.06\ \mathrm{cm}^{-1}$$



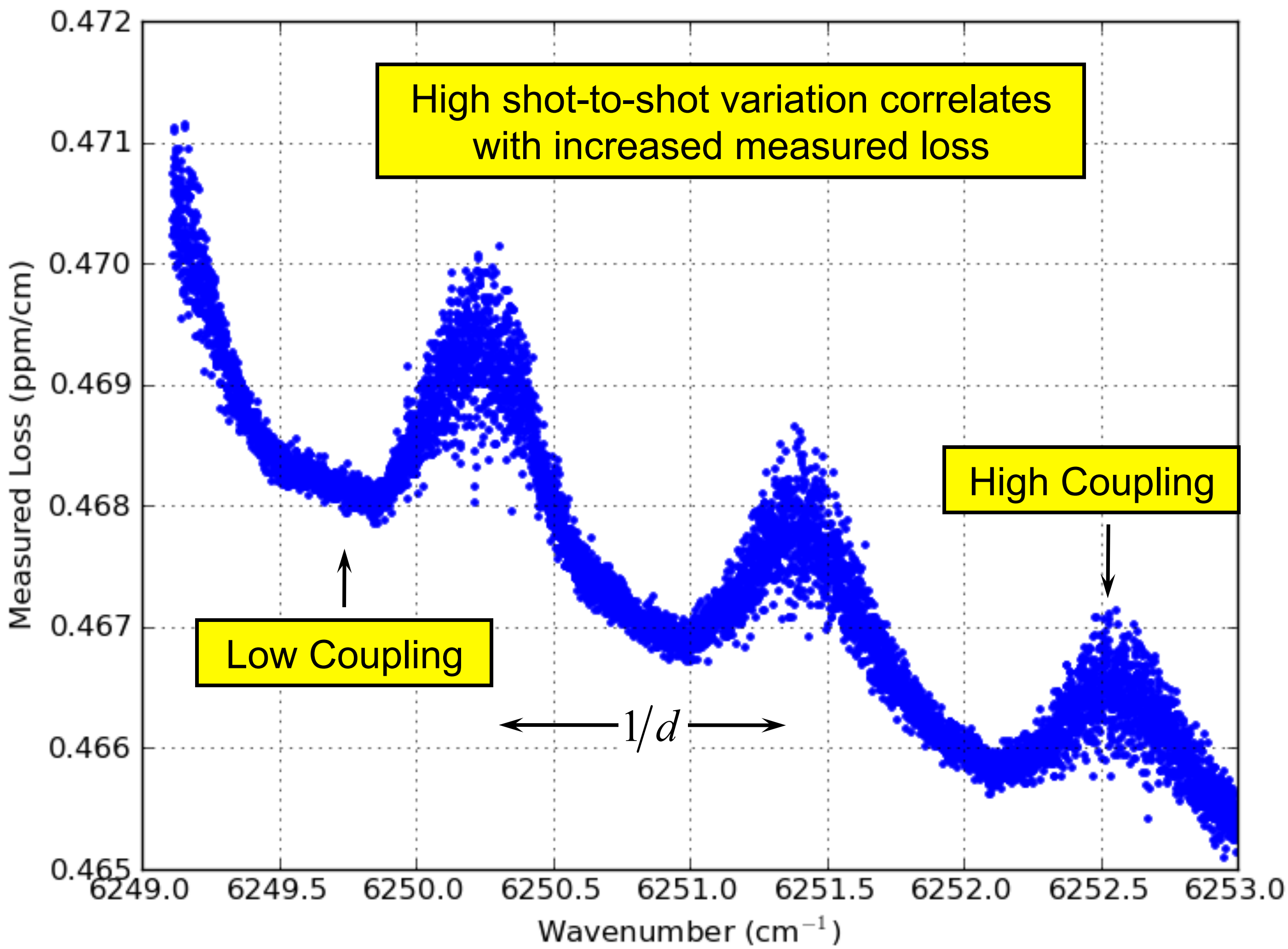
Frequency Dependence of Backscattering

- Consider two scatterers on **M1 and M3**. Coupling depends on $S_1 + S_3 \exp\left[ik2\left(d+L\right)\right]$
- The associated baseline ripple should have wave-number period
$$\Delta\bar{\nu} = \frac{1}{2\left(d+L\right)}$$
- However, this ripple is only "sampled" at the cavity modes which are at $\bar{\nu} = \frac{n}{2L+d}, \quad n \in \mathbb{Z}$



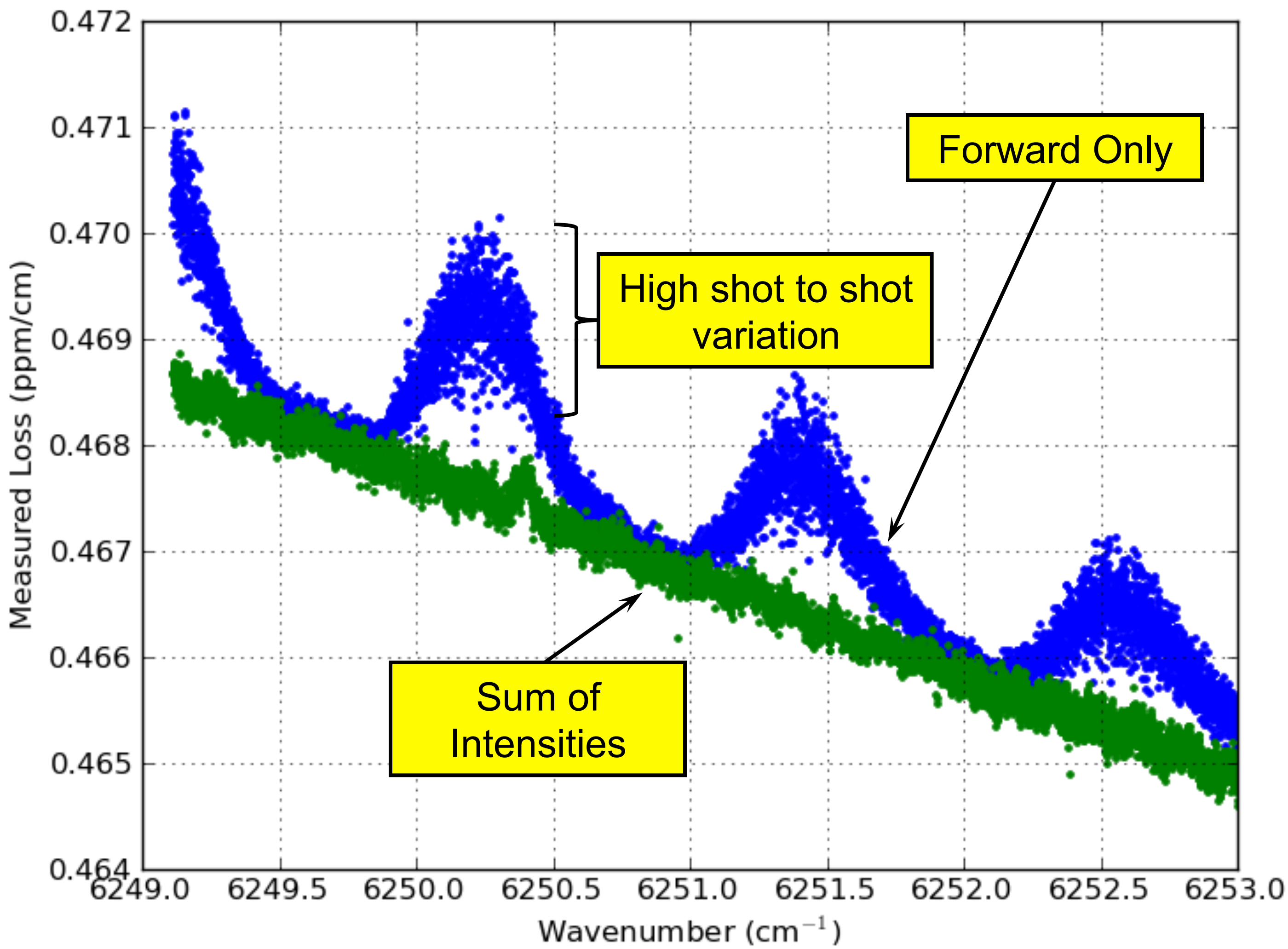
- Aliasing gives an apparent baseline ripple period of
$$\Delta\bar{\nu} = \frac{1}{d} \approx 1.2\ \text{cm}^{-1}$$

Empty Cavity Spectral Scan



PICARRO

Empty Cavity Spectral Scan
Fitting to Intensity Sum



PICARRO