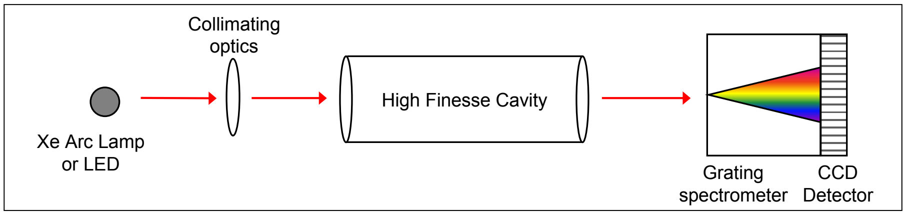
IBBCEAS



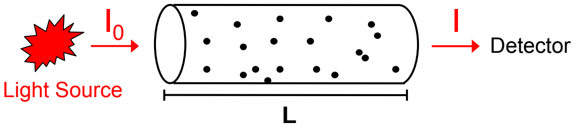
Incoherent Broadband

Cavity Enhanced Absorption

Spectrometer

CHEM 5161 – Nov 11 2008
Rebecca Washenfelder
rebecca.washenfelder@noaa.gov

Scientific Motivation



Beer's Law:

$$c = \frac{1}{\sigma L}\ln\left(\frac{I_0}{I}\right)$$

c = absorber concentration
σ = absorber cross-section
L = pathlength

Differential Optical Absorption Spectroscopy (DOAS)

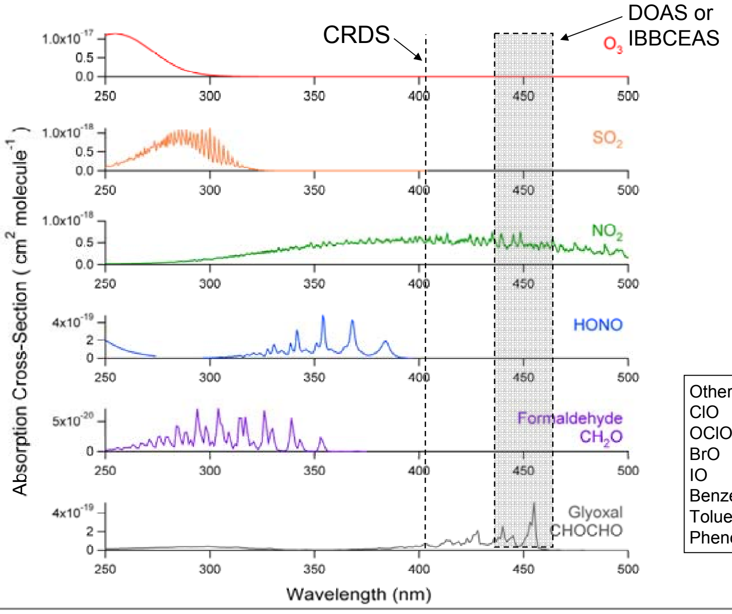
- **Broadband, incoherent, continuous light source**
- **Measure spectrally-resolved light**
- **Long pathlength (remote measurement)**
- **Appropriate for molecules with overlapping absorption spectra**

Cavity Ringdown Spectroscopy (CRDS)

- **Narrowband, coherent, pulsed light source**
- **Measure exponential decay of light in cavity**
- **Long effective pathlength (in situ measurement)**
- **Appropriate for molecules with non-overlapping absorption spectra**

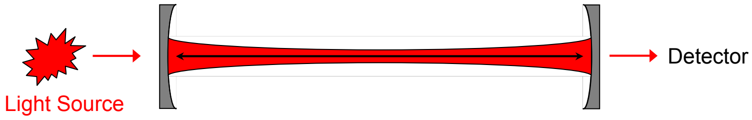
What is missing? A broadband, in situ technique with long effective pathlength.

Molecules with Absorptions in the Visible and UV



Others:
ClO
OClO
BrO
IO
Benzene
Toluene
Phenol

Optical Cavities



Reflectivity > 99.99%
Effective Pathlength = 10 km for a 1-m long cavity

Types of Cavity Enhanced Absorption Spectroscopy:

1. **Cavity Ringdown Spectroscopy (CRDS)**
2. **Integrated Cavity Output Spectroscopy (ICOS)**
3. **Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS)**

Types of light sources:

1. **Pulsed lasers**
2. **Continuous wave (CW) lasers**
3. **Broadband sources such as arc lamps or LEDs**

Stable Optical Resonators

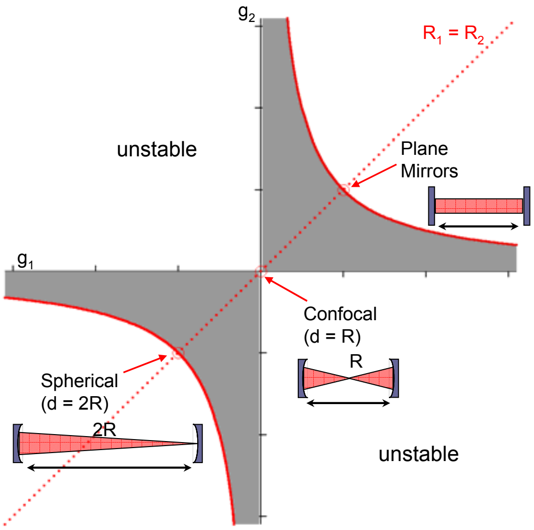
R = mirror radius of curvature
d = mirror separation

Stability is characterized by g:

$$g_{1,2} = 1 - \frac{d}{R_{1,2}}$$

Stability condition:

$$0 \le g_{1,2} \le 1$$



Longitudinal Modes in Optical Cavities

Resonant:

Not Resonant:

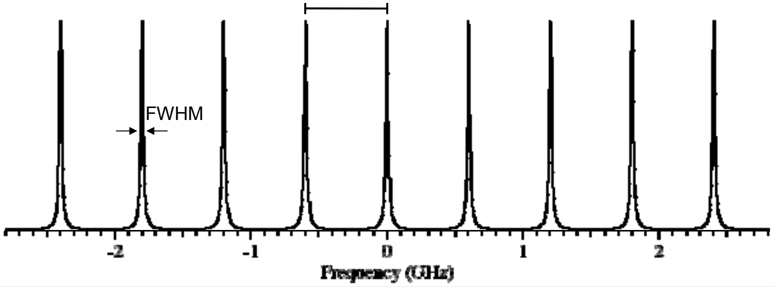
Integer numbers of wavelengths will be resonant:

$$\nu \frac{2d}{c} = \frac{2d}{\lambda} = integer$$

Free Spectral Range: $FSR = \frac{c}{2d}$

Full Width Half Max: $FWHM = \frac{c}{2d} \frac{1-R}{\pi\sqrt{R}}$

Cavity Transmission: $T(\nu) = \frac{(1-R)^2}{(1-R)^2 + 4R\sin^2\left(\frac{2\pi\nu d}{c}\right)}$



Pulsed Lasers used for CRDS

Examples: Nd:YAG lasers, excimer lasers, pulsed dye lasers, optical parametric oscillators (OPO)*

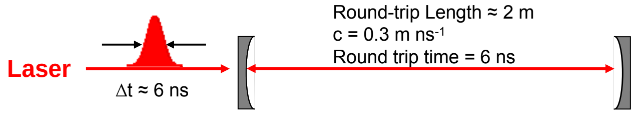
Advantages: Commercially available, broad wavelength tunability (e.g. dye lasers)

Disadvantages: Large, high power consumption, low repetition rates (10’s of Hz)

Key features:
- Pulse width (Δt) similar to cavity round trip time (t_R)
- Laser Linewidths ($\Delta\nu$) >> cavity free spectral range (FSR)

* Book recommendation:
Building Scientific Apparatus 4th Ed., available 2009, $80

Pulsed Lasers used for CRDS



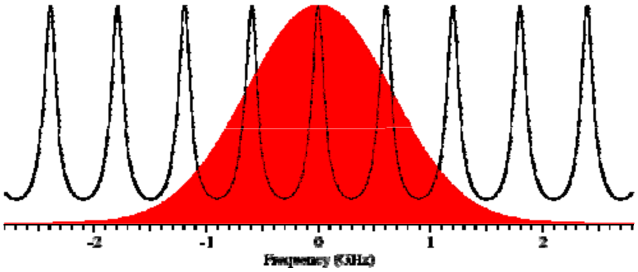
Round-trip Length ≈ 2 m
$c = 0.3$ m ns^{-1}
Round trip time = 6 ns

- Can also think in terms of *coherence length* vs. cavity length
- Mode overlap

FSR = c/2d = 0.15 GHz

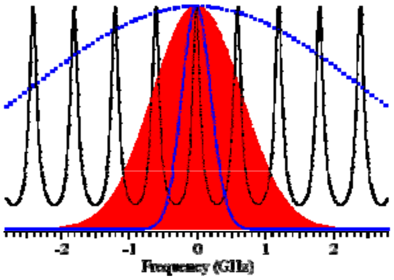
$\Delta\nu_{pulsed} \geq 3$ GHz

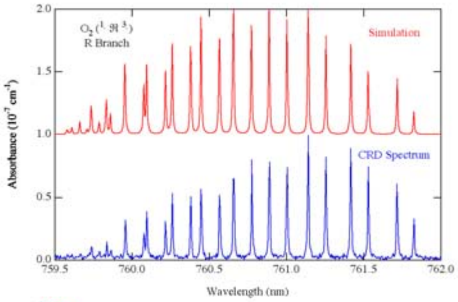
$\Delta\nu/\mathrm{FSR} \geq 20$

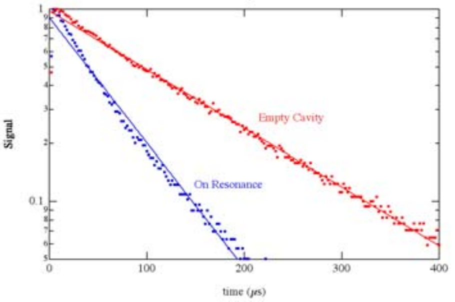


Net Result: *Passive coupling* between laser and cavity

Pulsed Lasers used for CRDS







$$I(t) = I_0 \sum_i \exp[-(1/\tau_0 + c\alpha_i)t] \neq I_0 \exp[-t/\tau]$$

- Decays are *not* single exponential

- Limits applicability of pulsed CRDS to discrete spectroscopy - e.g. rovibrational lines in small molecules

- Effect can be corrected for small absorptions - e.g., $\alpha < 10^{-8}$ cm^{-1}

Continuous Wave (CW) Lasers used for CRDS

Examples: Diode lasers, HeNe lasers, Ar-ion lasers, Nd:YAG

  Many ways to generate CW light

  Spectral coverage from visible to mid-infrared

  Recent advances in telecommunications have made high-performance infrared diodes cheaply available.

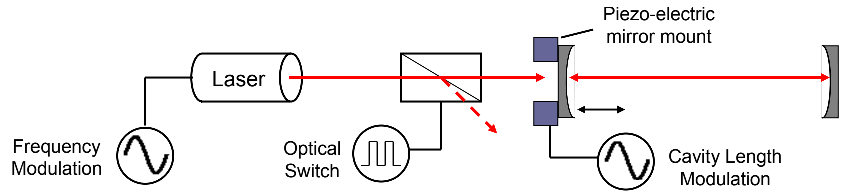
Advantages: Lightweight, lower power consumption, may be inexpensive.

Disadvantages: Limited wavelength tunability (e.g. temperature tuning of diode lasers)

Key features:

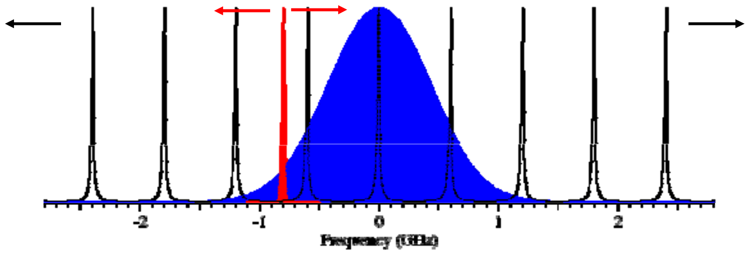
  - Coupling between laser source and cavity must be *active*
  - Fast switch is required to shutter light source and record ringdown signal

Continuous Wave (CW) Lasers used for CRDS

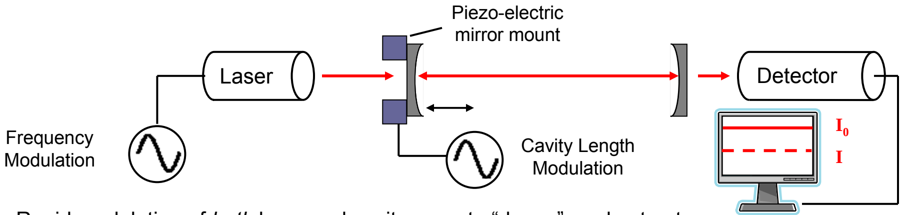


Two choices for coupling the laser into the cavity:
1. Modulate laser through at least one FSR of cavity
2. Modulate cavity length through at least one FSR

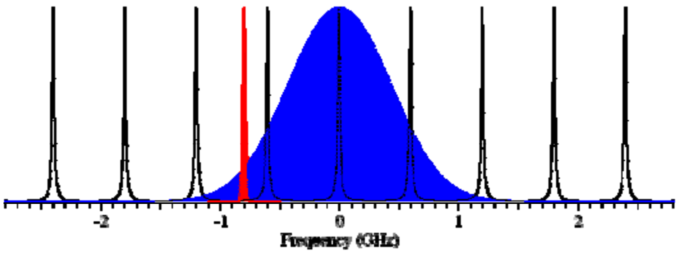
For either method, monitor output intensity and then switch input away when it reaches a predefined threshold



Continuous Wave (CW) Lasers used for ICOS



- Rapid modulation of *both* laser and cavity - create “dense” mode structure
- Average over modes - frequency independent transmission



Not an absolute method (pathlength unknown!)

Calibrate by measuring ring-down transients *or* by addition of a trace gas standard.

Broadband light sources used for IBBCEAS

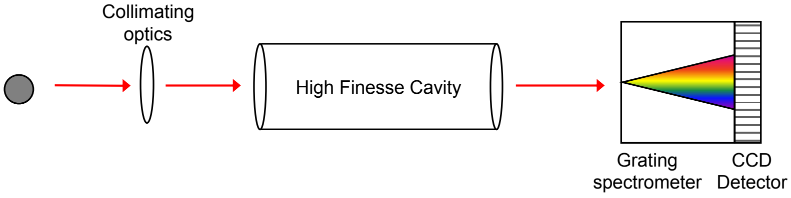
Examples: Xenon arc lamps, light emitting diodes (LEDs)

Advantages: Commercially available, simple, inexpensive, bright.

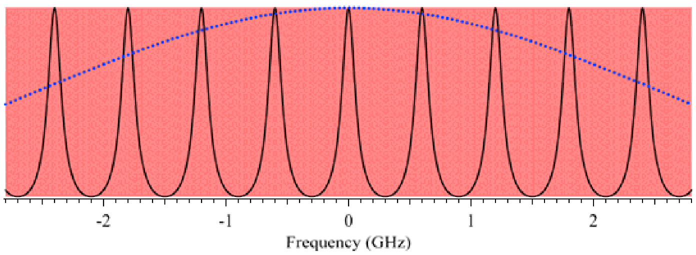
Disadvantages: Difficult to image

Key features:
- Broad light source is used to excite a large number of cavity modes
- Output is spectrally-resolved

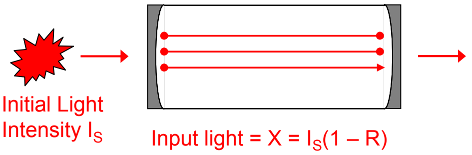
Broadband light sources used for IBBCEAS



- Similar to the concept of Integrated Cavity Output Spectroscopy (ICOS).
- Multiple wavelengths are measured simultaneously.
- *Not* an absolute method (pathlength unknown!)



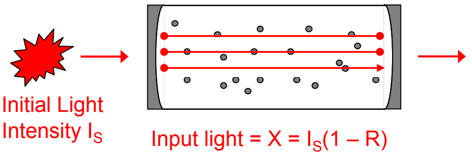
Extending Mathematics of CRDS to IBBCEAS



R = Reflectivity
α = Absorption coefficient
d = Cavity length
L = cavity loss due to absorber

Light Inside Cavity	Light Measured at Detector
X	
XR	X(1-R)
XR^2	
XR^3	$XR^2(1-R)$

Extending Mathematics of CRDS to IBBCEAS



R = Reflectivity
α = Absorption coefficient
d = Cavity length
L = cavity loss due to absorber

At each step, the change in light intensity depends on the current light intensity. This is the first-order differential equation describing cavity ringdown!

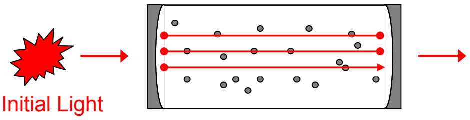
Light Inside Cavity	Light Measured at Detector
X	
X(1-L)R	X(1-L)(1-R)
$X(1-L)^2R^2$	
$X(1-L)^3R^3$	$X(1-L)^2R^2(1-R)$

$$\frac{dI_{in}}{dx} = \left(-\frac{(1-R)}{d} - \alpha_{Rayleigh} - \alpha_{Mie} - \sum \alpha_i\right) I_{in} \qquad \begin{aligned} x &= ct \\ dx &= c\,dt \end{aligned}$$

$$\frac{dI_{in}}{dt} = c\left(-\frac{(1-R)}{d} - \alpha_{Rayleigh} - \alpha_{Mie} - \sum \alpha_i\right) I_{in}$$

Next consider a continuous light source: $\frac{dI_{in}}{dt} = c\left(-\frac{(1-R)}{d} - \alpha_{Rayleigh} - \alpha_{Mie} - \sum \alpha_i\right) I_{in} + ck_s I_s$

Extending Mathematics of CRDS to IBBCEAS



Initial Light Intensity I_S

Input light = X = $I_S(1 – R)$

R = Reflectivity
α = Absorption coefficient
d = Cavity length
L = cavity loss due to absorber

Next consider multiple wavelengths:

0 at steady-state

$$\cancel{\frac{dI_{in}(\lambda)}{dt}} = c\left(-\frac{(1-R(\lambda))}{d} - \alpha_{Rayleigh}(\lambda) - \alpha_{Mie}(\lambda) - \sum \alpha_i(\lambda)\right) I_{in}(\lambda) + ck_s I_s(\lambda)$$

Define I_0 as an empty cavity with no absorbers.

Solve the equation to find:

$$\sum \alpha_i(\lambda) = \left(\frac{(1-R(\lambda))}{d}\right)\left(\frac{I_0(\lambda) - I(\lambda)}{I(\lambda)}\right)$$

We know the cavity length. We will measure $I_0(\lambda)$ and $I(\lambda)$.

But two unknowns remain: *R(λ)* and *α(λ)*.

IBBCEAS Calculation of Mirror Reflectivity

$$\alpha_{Rayleigh}(\lambda) = \left(\frac{(1-R(\lambda))}{d}\right)\left(\frac{I_0(\lambda) - I(\lambda)}{I(\lambda)}\right)$$

Both mirror reflectivity (*R*) and concentration (*α*) are unknown.

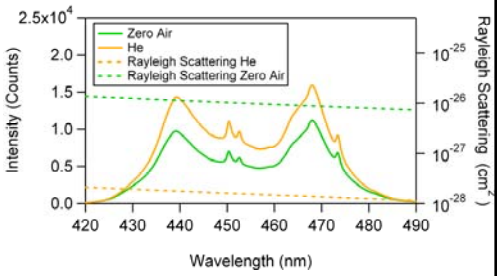
Unlike CRDS, ICOS and IBBCEAS are not absolute techniques.

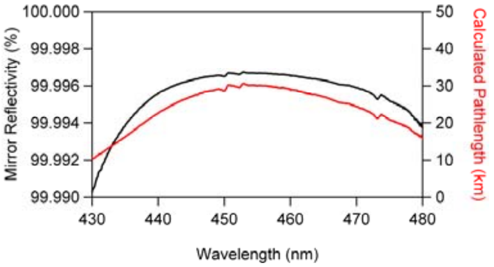
Methods for determining R experimentally:

•Introduce a known absorber concentration, such as NO_2 or O_3.

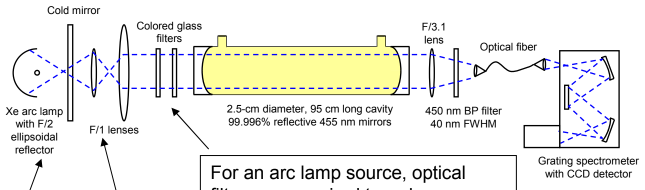
•Rayleigh scattering

•O_2-O_2 absorption





IBBCEAS Instrumental Choices



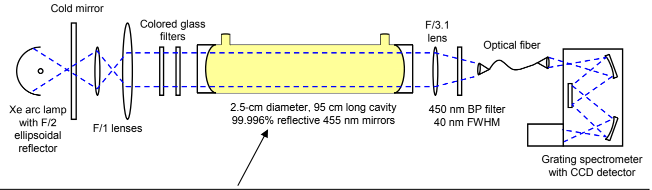
For an arc lamp source, optical filters are required to reduce spectral intensity outside of the measurement region.

LEDs are cheap, compact, and power efficient light sources. However, wavelength choices are limited.

Arc lamps are brighter light sources with very broad spectral output. They consume more power and generate more heat.

In theory, an optical point source can be collimated with a single lens with the source is placed at the focal length of the lens. A higher F-number lens will capture more light. In reality, no optical source is a true point source and efficient collection of the light requires several optics.

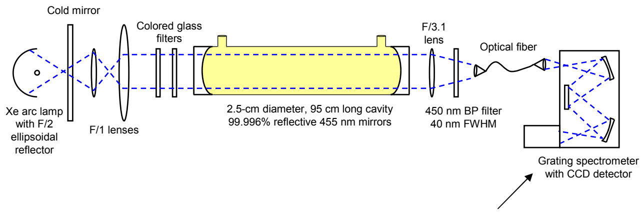
IBBCEAS Instrumental Choices



Two choices of sampling – open cell or closed cell

Extinctions for an open cell:	**Extinctions for a closed cell:**
Rayleigh scattering	Rayleigh scattering
Mie scattering by aerosol	–
Absorption by gas-phase species	Absorption by gas-phase species
Advantages:	Advantages:
No walls!	Fewer unknowns
	Absolute retrievals are possible

IBBCEAS Instrumental Choices



A grating spectrometer contains a diffraction grating consisting of a series of grooves that are identical in size, parallel, and equally spaced.

Characteristics of grating spectrometers:

Linear dispersion is ability to separate different wavelengths, expressed in nm / mm:

D^{-1} = grating spacing / (diffraction order x focal length)

Resolving power is ability to separate adjacent images

R = $\lambda / \Delta\lambda$ = (diffraction order x number of grooves)

Light-gathering power

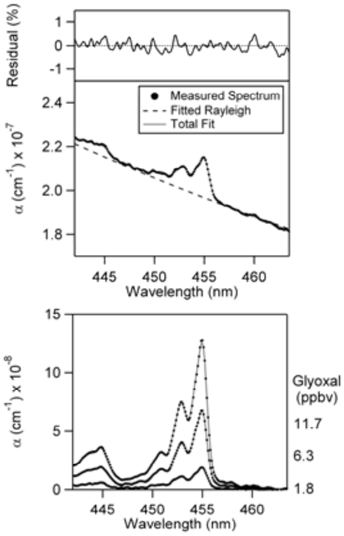
F-number = focal length of collimating mirror / diameter

Entrance and exit slit width

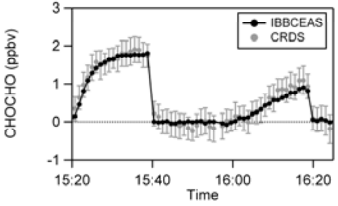
IBBCEAS NO_2 and CHOCHO Instrument

New field instrument:

Laboratory spectra:



Laboratory comparison of CRDS and IBBCEAS:



Other Applications of IBBCEAS

- Measurement of NO_3 and NO_2 at 645 – 705 nm using an LED (Ball et al., 2004; Venables et al., 2006)

- Measurement of HONO and NO_2 at 360 – 380 nm using an arc lamp (Gherman et al., 2008)

- Measurement of I_2, OIO, and IO at 525 – 555 nm and 420 – 460 nm using an arc lamp (Vaughan et al., 2008)