Optical Cavities in Spectroscopy

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Talk Summary

- Review of Optical Cavities
- Review of Absorption Spectroscopy
- Molecular Beam Spec. with cavities
- Single atom detection with cavities
- Trace Gas Detection
  - FM Spectroscopy
  - Cavity Ring-Down Spectroscopy
  - NICE-OHMS
  - Intra-Cavity Laser Absorption Spectroscopy
Review of Optical Cavities
(a.k.a etalons)
Radii of Curvature: $R_1, R_2$

Length of Cavity: $L$

Mirror Transmission: $T$

Mirror Reflectivity: $R$

Mirror Loss: $A = 1 - R - T$
Higher order Gaussian Modes ($z = 0$ is focus)

$$E_{m,n}(x,y,z) \propto H_n\left(\frac{\sqrt{2}x}{w(z)}\right)H_m\left(\frac{\sqrt{2}y}{w(z)}\right)\exp\left(-\frac{x^2 + y^2}{w^2} - ik \frac{x^2 + y^2}{R_f} - ikz + i(m + n + 1)\eta(z)\right)$$

$$w(z) = w_0\sqrt{1 + \frac{z^2}{z_0^2}} \quad z_0 = \frac{n\pi w_0^2}{\lambda_0}$$

$$R_f(z) = \frac{z^2 + z_0^2}{z} \quad \eta(z) = \tan^{-1}\left(\frac{z}{z_0}\right)$$

When you “see” a TEM$_{00}$ the laser beam it has diameter $\sim 2w$

$R_f$ is radius of curvature; infinity at focus and $\sim z$ far from focus.

$z_0$ is confocal parameter; beam size increases by $\sqrt{2}$ for $z = \pm z_0$ from focus

An arbitrary electric field in any plane can be decomposed into TEM$_{m,n}$ modes and each component propagates as above.

All distances measured in “optical path length”, i.e. x index of ref.
Stable Optical Cavities

• For $R = 1$, modes exist which exactly reproduce themselves upon round trip.

• $0 < L < R_1$ or $R_2 < L < R_1 + R_2$ ($R_1 < R_2$)
  – If $R_2 - R_1, << L$, then $R_1 < L < R_2$ only weakly unstable

• Optic axis defined by line through centers of curvature of mirrors (or normal to flat mirror).

• Light rays will oscillate around optic axis for stable cavity

• For cavity made of equal radii mirrors, focus in middle with

\[
\omega_m = \left( \frac{\lambda L}{\pi} \right)^{1/2} \cdot \left( \frac{2L}{R_m} - \frac{L^2}{R_m^2} \right)^{-1/4}
\]

for $R_1 = R_2 = R_m$
• Radius of curvature of mode matches each mirror

• Confocal cavity: \( L = R_1 = R_2 \)
  – Smallest spot size on mirrors for fixed \( L \)
  – Unstable if \( R_1 \) not exactly equal to \( R_2 \)!

• Concentric: \( L = R_1 + R_2 \).
  – On edge of stability (but stable is \( L \) very slightly reduced)
  – Spot size very small in center but large on mirrors.

• If \( R_1, R_2 \gg L \). Mode is nearly uniform inside cavity
Cavity Transmission as function of Mirror Reflectivity, R, for ideal cavity and monochromatic radiation source

\[
F_{SR} = \frac{c}{2nL} = \frac{1}{\tau}
\]

\[
\text{Finesse} = \frac{\pi \sqrt{R}}{1 - R} = \frac{\text{FWHM}}{F_{SR}}
\]

\[
\tau = \frac{nL}{c \cdot (1 - R)} \quad \text{Ring-down Time}
\]

Quality factor: \( Q = 1/(2\pi\nu\tau) \)  
Cavity mode width: \( \Delta \nu_c = \frac{1}{2\pi\tau} \)
Peak Transmission of Cavity
For perfectly monochromatic Input radiation

Peak Intracavity Gain

MIRRORS WITH T, A ~ 5 ppm ARE AVAILABLE IN NEAR IR AND RED

INTRACAVITY POWER GAIN OF \( \sim 10^5 \) CAN BE REALIZED

FOR L = 40 cm, FSR = 250 MHz, (1-R) = 5 ppm
\( \tau = 400 \mu s \) BUT \( \Delta \nu_c = 250 \text{ Hz}! \)

IF LINESWIDTH OF LASER IS MUCH LARGER THAN MODE, TRANSMISSION REDUCED BY FACTOR OF \( 1/(1 + 2 \pi \tau \Delta \nu_L) \)
Transverse resonance modes of Cavities

\[ \nu_r = \frac{c}{2L} \left( q + (m + n + 1) \cdot \delta_g \right) \]

\[ \delta_g = \frac{1}{2} \left( 1 + \frac{4}{\pi} \tan^{-1} \left( \frac{L - R_m}{L + R_m} \right) \right) \]

- q is the longitudinal mode index (# of half waves in cavity)
- m,n transverse mode numbers
  - Size of transverse modes increased by \((1 + m + n)^{1/2}\)

If \(\delta_g = M/N\), then we have rational cavity with periodic transmission spectrum. Arbitrary pulse inside Cavity will exactly reshape after N round trips -- such cavities are used for Herriott Cells.
For cavities made of 3 or more mirrors

Can be “linear” cavities with standing waves or “ring” cavities with Degenerate modes running clockwise and counter clockwise around cavity

Cavities will generally be astigmatic with $\text{TEM}_{00}$ mode no longer circular and two different transverse mode spacings

Because of polarization dependence of phase shifts when light reflects off of mirrors away from normal, modes with split by Polarization. If cavity is planer, one half of modes will be polarized in the plane (P) and the other perpendicular to that plane (S)

Stability conditions, mode spacings, and shapes can be determined using the ABCD matrix approach. (A. Siegman *Lasers*)
Are modes of cavities evenly spaced?

Important for coupling frequency combs into cavities.

Short answer is not exactly because of various sources of dispersion. This limits the width of the freq. comb that can be simultaneously coupled into cavity.

If we have any material in cavity, dispersion of medium will make modes not evenly spaced.

Dielectric mirrors have wavelength dependent phase shifts which also cause modes spacing to vary.

Ultrafast lasers often use mirrors with mirrors designed to cancel the dispersion of the gain medium.
Some Uses for Optical Cavities in Spectroscopy

- Control frequency and linewidth of lasers
- Monitor laser scan for calibration
- Laser linewidth is reduced by locking on to the transmission peak of a cavity
- Cavities are used to build up intensity
  - External c.w. second harmonic generators
  - Pump extremely weak transitions
- Used to enhance optical absorption
Review of Absorption of Light

\[ I_{out}(\nu) = I_{in}(\nu) \cdot \exp(-\alpha(\nu)L) \quad \text{Beer-Lambert Law} \]

\[ \alpha(\nu) = N_g \cdot \left(1 - \exp(-h\nu/kT)\right) \cdot \sigma(\nu) \]

\[ \sigma(\nu) = \frac{2\pi^2 \mu_{ge}^2}{3\varepsilon_0 hc} \cdot \nu \cdot g(\nu - \nu_{01}) = \frac{A_{01} \lambda^2}{8\pi} \cdot g(\nu - \nu_{01}) \]

\[ \int g(\nu - \nu_{01})d\nu = 1 \rightarrow g(\nu_{01}) \approx \frac{1}{\Delta\nu_{FWHM}} \]

\[ S = \int \sigma(\nu)d\nu = \frac{A_{01} \lambda^2}{8\pi} \]
Electronic vs. Vibrational

• $\mu = 10$ Debye
• $\nu \sim 50,000$ cm$^{-1}$
• $A = 10^8$ s$^{-1}$
• $S = 10^{-13}$ cm
• $\Delta \nu$ (liquid) = $10^4$ cm$^{-1}$

• 0.1 Debye
• $\nu \sim 1000$ cm$^{-1}$
• $A = 1$ s$^{-1}$
• $S = 10^{-18}$ cm
• $\Delta \nu$ (liquid) = 10 cm$^{-1}$
Sub-Doppler resolution infrared spectroscopy of vibrationally hot molecules

Experimental Apparatus

Nd:YAG Laser

Ar\textsuperscript{+} Laser

F-Centre Laser

150 MHz Etalon

1.5 µm fiber

Electro-optic modulator

0.8 µm fiber

MBR-110 Ti:Al\textsubscript{2}O\textsubscript{3}

Verdi

Nozzle

Skimmer

1.5 µm Cavity

0.8 µm Cavity

Bolometer
The anharmonicity of the v=2 level means that we need much less laser power to see the 2→6 transition than the 0→4 or 0→6 transitions.
Potential energy "surface"

\[ \text{H}_a - \text{C}_a \equiv \text{C}_b - \text{H}_b \rightarrow \text{C}_a \equiv \text{C}_b \rightarrow \text{H}_b - \text{C}_a \equiv \text{C}_b - \text{H}_a \]

\[ \sim 18,500 \text{ cm}^{-1} \]

\[ \sim 15,000 \text{ cm}^{-1} \]

\[ 6\nu(\text{CH}) \]

\[ 2\nu(\text{CH}) \]

\[ 1-5 \text{ kcal/mol} \]

\[ 350-1750 \text{ cm}^{-1} \]
Did not observe tunneling splitting -> rate < $10^7$ s$^{-1}$

> $10^4$ times slower than prediction of RRKM theory
Real-time detection of individual atoms falling through a high-finesse optical cavity

Fig. 1. Schematic diagram of the experiment. The cesium MOT lies 7 mm above the cavity axis, the mirror substrate diameter is 3 mm, and the cavity length is 108 μm.

1-R = 15 ppm for Mirrors used

H. Mabuchi et al., Optics Letters 21, 1393 (1996)
Fig. 2. Time-varying cavity transmissions after a cesium MOT is dropped, normalized to probe power $P_0$ transmitted through the empty cavity. For these data $P_0$ corresponds to $\approx 2$ photons in the empty cavity, and $\omega_A = \omega_C = \omega_L$ (see text). Inset: histogram of atom arrival times compiled from 450 consecutive trap-drop cycles.
Trace Species Detection

• Need high Sensitivity
• Need high Selectivity
• Maximize Speed of response
• Minimize Sample preparation
• Minimize Cost
• Maximize Reliability
Spectroscopic Methods for trace detection

• Ionization & time of flight mass spect.
  – Most sensitive if can be saturated since one can detect every single ion produced.
  – Requires high vacuum.
  – Fragmentation can compromise selectivity

• Laser Induced Fluorescence
  – Can detect single molecules in some cases
  – Requires good emission yield.

• Absorption based techniques

• Photoacoustic and other thermal methods.

• Transient Grating techniques (CARS)
Sensitivity Limits in Absorption Spectroscopy

\[ \alpha_{\text{shot\_noise}} = \frac{1}{\text{Path\_Length} \sqrt{\frac{h \nu}{\text{Intensity}}}} \]

Real Lasers have orders of magnitude higher amplitude noise at low frequency. However, they often come close to shot noise limit for detection frequencies above \( \sim 10-100 \text{ MHz} \)

How can we modulate absorption at such high frequencies?
Frequency Modulation (FM) spectroscopy

Low Pressure Gas

RF

DC Drive

E

ω_{RF}

ω_0

RF

Mixer

DAS

Absorption

time

V

FM

ω
FM spectroscopy

- Requires fast detector (reduces sensitivity)
- Fastest response, can measure absorption in nsecs (used for transient species)
- Measures derivate of spectrum, which reduces sensitivity for broad lines by ratio of $\Delta \nu$ / optical transition linewidth.
- Real phase modulators introduce small amplitude modulation as well, introducing low frequency noise of laser into detection
  - Can be removed in some cases by double modulation.
Can we use optical cavities to improve sensitivity for absorption?

- Transmission of cavity decreases by ~2-4 times if loss per pass equals mirror loss, which can be ~10 ppm.
- Transmission is very noisy unless laser linewidth is << band pass of cavity (~1/2πτ)
- Easier to excite cavity and measure decay time of cavity-- Cavity Ring-Down
- Common Optical Filters
Cavity Ring-Down Absorption Spectroscopy

Where:
- $c$: speed of light
- $L$: length of cavity
- $R$: mirror reflectivity
- $\sigma$: absorption cross section
- $N$: number density (concentration)
- $L_{\text{eff}} = \frac{L}{1-R}$

Absorption

$$I(t) = I_0 \exp\left[-t\left(\frac{c}{L} \ln R + c \cdot \sigma(\lambda) \cdot N\right)\right]$$
Cavity Ring-Down Decay

\[ \tau = 295.82 \pm 0.20 \, \mu\text{sec} \]
Ring Down Cavity Technique

First Developed by O’Keefe and Deacon
Theory: Romanini and Lehmann

- Use a passive optical cavity formed from two high reflective mirrors (T~1-100 ppm)
- Excite cavity with a pulsed laser to ‘fill’ with photons
- Detect exponential decay of light intensity inside resonator
- Decay rate reflects:
  - Loss due to mirrors (slowly changing with wavelengths)
  - Absorption of gas between mirrors
Advantages of Ring Down Cavity Method

- RDC allows much longer pathlengths than traditional multipass cells
- RDC only sensitive to loss between mirrors
- Beer’s Law holds for all pathlengths; pathlengths determined by time
- RDC cell is very compact; light contained in narrow spot of ~ 1 mm²
- RDC cell insensitive to vibration since it is a stable optical cavity
- Amplitude noise of laser not important
- Light can be coupled in and out with optical fibers
- Simple and low cost compared to ICLAS
Trace gas detection with cavity ring down spectroscopy
Rienk T. Jongma, Maarten G.H. Boogaats, Iwan Holleman, and Gerard Meijer
Department of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED, Nijmegen, The Netherlands

Hg: 7 ppt
(n = 1.7 × 10^8 cm\(^{-3}\))

O\(_2\): A\(\rightarrow\)X(7,0) N = 19
(n\(_i\) = 7 × 10^{16} \text{ cm}^{-3}\)
Diode Laser Advantages

• Low cost, compact, all solid state
• Low power requirements
• Wide electronic frequency tuning
• Single mode diodes in the near-IR are becoming available for sensing apps.
  – H₂O, C₂H₂, CH₄, CO₂, NO₂, NH₃, etc.
Other Advantages of c.w. Excitation:

- Observe cavity decays at much higher rate (~1-10 kHz), reduces dynamic range of detection system
- Couple only one resonate mode of cavity
- Increased spectral resolution
  - Time of flight through laser focal spot ~ 100 kHz
- Light intensity inside cavity increased ~$10^4$ - $10^5$
  - Calculations indicate that we should be able to saturate allowed Doppler free two photon transitions
- Diode lasers greatly reduces system cost and size
Stability of Ring-Down Rates

Ensemble Standard Deviation:

10 pts: 201.384 ±0.139 µs 0.069%
100 pts: 201.378 ±0.165 µs 0.082%
1000 pts: 201.304 ±0.146 µs 0.073%

This translates, with averaging ~100 decays, to a noise equivalent Absorption of ~10^{-11} cm^{-1} or 1 part per billion per pass of cell.

This is still a couple orders of magnitude above theoretical limits.

A commercial trace gas instrument was developed with Tiger Optics
Variations on CRDS Method

- CRDS (a.k.a. CRLAS, RDCS, cavity leak-out spectroscopy)
  - pulsed CRDS
  - cw CRDS
  - phase shift CRDS
  - Fourier Transform CRDS
  - broad band CRDS
  - evanescent wave CRDS
  - fiber optic CRDS, fiber loop CRDS
  - Cavity Ring-down polarimetry
  - Optical feedback CRDS
  - Saturation absorption CRDS (SCAR)
• Cavity Enhanced Absorption Spectroscopy (CEAS) - Englehn, Meijer, et al.
  – a.k.a Integrated cavity output spectroscopy (ICOS) - O’Keefe
  – Frequency chirped CEAS
• Noise Immune Intracavity optical heterodyne method (NICE-OHMS)
• Intracavity laser absorption spectroscopy (ICLAS)
• Intracavity photoacoustic spectroscopy
  – attractive with optical locking!

Prism Ring-down Resonator

Input

Output

P-polarization

6 meter radius of curvature
Advantages of Prism Cavity

• Wide spectral coverage - Simultaneous detection of multiple species
• Compact ring geometry (optical isolation)
• No dielectric coatings (harsh environments)
• Coupling can be optimized for broadband
Broadband system using white light from photonic crystal fiber

Fig. 1. Schematic of the ultra-broadband cavity enhanced absorption spectrometer showing the major components of the spectrometer: the broadband supercontinuum source, the broadband Brewster’s angle retroreflector prism cavity, and dispersive grating spectrograph.
Supercontinuum Output
Cavity Loss from

\[ \text{Loss} = \frac{A}{\lambda^4} + 2 \left( \frac{n^4 - 1}{4n^6} \left( \delta \theta_1^2 + \delta \theta_2^2 \right) \right) \]

**Fig. 6.** Observed round trip cavity loss, as determined from the ring-down time, as a function of wavelength, with 2\(\sigma\) error bars from the ring-down fit indicated. Also shown is the Fresnel and scattering loss of the prisms vs. wavelength as determined by a fit of the loss to Eq. 3. The resulting fit parameters are given in the text.
Cavity enhanced spectroscopy

• Measure time integrated intensity

\[ \alpha(\nu) = \left( \frac{I_o(\nu)}{I(\nu)} - 1 \right) \frac{1 - R}{l} \]

I(\nu) = time integrated intensity with absorbing species
I_o(\nu) = time integrated intensity of empty cavity

• Advantages
  – Relatively high sensitivity
  – Simpler set up

• Sensitivity limitations
  – Residual mode structure
  – Laser noise

$\alpha \text{ (cm}^{-1}) \times 10^6$

**Experiment**

**HITRAN**

Wavenumber (cm$^{-1}$)

O$_2$ SPECTRUM IN AIR
Combining FM Spectroscopy with low loss cavities: NICE-OHMS

- Use extremely narrow linewidth laser such that most light is coupled into cavity
- Put side bands a spacing to exactly match cavity free spectral range.
- Detect modulation in cavity transmission.
Fig. 5. Experimental configuration for NICE-OHMS. An external stabilizer (AOM–EOM) is employed to widen the frequency servo bandwidth. Sidebands at \(\delta/2\pi = 4\) MHz are used for reflection lock to cavity; sidebands at \(\Delta =\) cavity FSR are used in transmitted light as local oscillators for heterodyne detection of saturated gas absorption inside the cavity. DBM’s, double-balanced mixers; PD’s, photodiodes; R, concave reflector; other abbreviations defined in text.
Fig. 6. Precision scanning NPRO–HCCD spectrometer, referenced to an I$_2$-stabilized NPRO. rf offset between the two laser systems is implemented by a phase-locked loop. PD's, photodiodes; APD, avalanche photodiode.
Lamb Dip of $\nu_2 + 3\nu_3$ transition of HCCD 10^-6 times as strong as C-H IR fundamental

$\alpha_{\text{noise}} \approx 1 \cdot 10^{-14} \text{ cm}^{-1} / \sqrt{\text{Hz}}$

Only 30% above shot noise limit!
Sample spectrum of light $t_g$ after laser pumping is started. Spectrum will show gain narrowing and absorption from narrow Absorption peaks. Effective pathlength = $c \times t_g \times$ fill factor.

Maximum $t_g$ limited by mode coupling and spontaneous emission. For low gain solid state lasers, $t_g \sim 10$ ms can be used.
$t_g = 500 \mu s \quad \text{Pathlength} = 60 \text{ km} \quad \alpha(\text{min}) = 10^{-9} \text{ cm}^{-1}$

A. Garnache, A. Campargue *, A.A. Kachanov, F. Stoeckel

CRDS vs. ICLAS

• Both use long effective pathlengths
• Beer’s Law holds only approximately for ICLAS
• ICLAS has higher noise, but detects many wavelengths at once.
• ICLAS requires laser integrated as part of detection system
CRDS vs. ICLAS

• ICLAS requires:
  – Broad bandwidth laser
  – Very high resolution spectrograph
  – Array detector
  – Can only detect ‘narrow’ spectral

• CRDS requires:
  – Very high reflective mirrors
Dual Etalon Frequency Comb (DEFCOMB)
Cavity Ring Down Spectroscopy

David W. Chandler and Kevin E. Strecker
Sandia National Labs
Schematic of How Dual Etalon Frequency Comb (DEFCOMB) Apparatus Works. Many Versions are Possible!

Use two ~300 MHz etalons and a 2 GHz Dye laser (or OPO, or ASE, or Femtosecond pulse)

Etalons create frequency combs that when combined create the cross beats between 0 and 150 MHz contain the spectrum with 300 MHz (.0003 cm⁻¹) spectral resolution. (this requires about a 30 microsecond ring down time).


D. W. Chandler, K. E. Strecker
The frequencies expected in the combined etalon signal have cross beats that are ordered in a manner to allow one to perform spectroscopy.
By Fourier Transforming the Interferogram in Segments and Plotting the Intensity of Each Cavity Mode Separately one can do Multiplexed Cavity Ring Down Spectroscopy and Get Resolution of .

\[ \lambda = 15897.37 \text{ cm}^{-1} \]

\[ \lambda = 15904.5 \text{ cm}^{-1} \]

Photodiode voltage

Time (µs)

0.00
0.05
0.10
0.15

Time (s)

0.00
2.0x10^{-5}
4.0x10^{-5}
6.0x10^{-5}

Intensity (ARB)

Relative Frequency (MHz)

D. W. Chandler , K. E. Strecker
Preliminary Cavity Ring Down Spectra of O₂ for hindered \( \Sigma^+ \leftrightarrow \Sigma^- \) and H₂O \( 4\nu + (115, 000) \) Overtones have been Recorded. Single Shot Measurements are Shown at Bottom of Spectra.