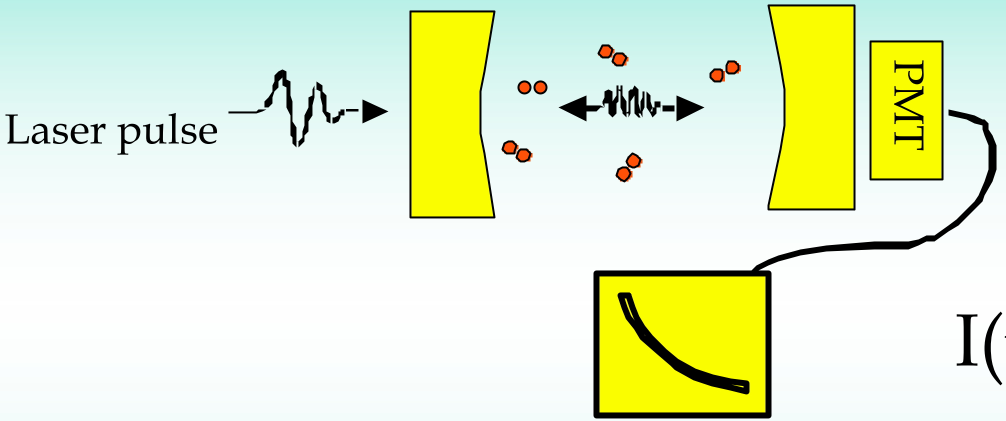
Novel Miniature Spectrometer for Remote Chemical Detection based on

Evanescent Wave Cavity Ring-down Spectroscopy (EW-CRDS)

Andrew C. R. Pipino
Process Measurements Division
National Institute of Standards and Technology (NIST)
Gaithersburg, Maryland 20899-8363

"Conventional" Cavity Ring-Down Spectroscopy



$I(t)=e^{-t/J(T)}$

- A "new" optical absorption technique.
- Photon decay time is very sensitive to cavity losses.
- Spectrum obtained as cavity loss vs wavelength.

Detection Limit in CRDS

$$J(T) = \frac{t_r}{L_0 + L_{abs}}$$

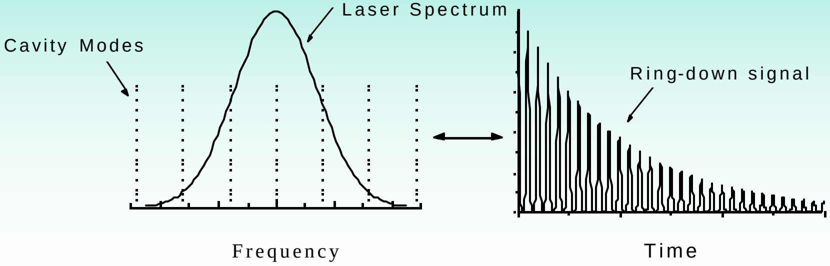
Round-trip time

Empty cavity loss

Sample absorption

- Min. Detect. Abs. (MDA) = L_0 *( ) **J**/**J**(T))$_{min}$
- L_0 depends on cavity design.
- () J/J)$_{min}$ depends on detection/digitization factors.
- Goal: Minimize L_0 and measure **J** precisely.

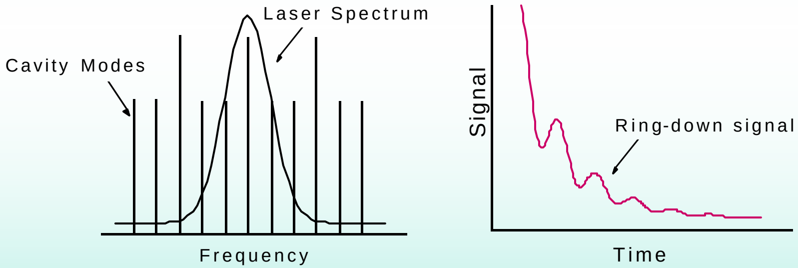
Cavity Mode Effects



Free-Spectral Range = c/(2*length)

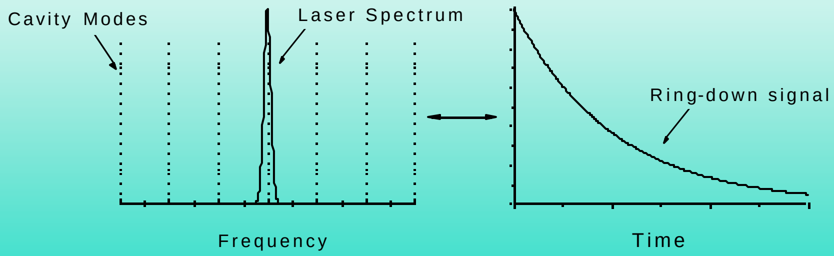
FSR < laser frequency spectrum

Multiple longitudinal modes excited



Transverse Mode-beating :

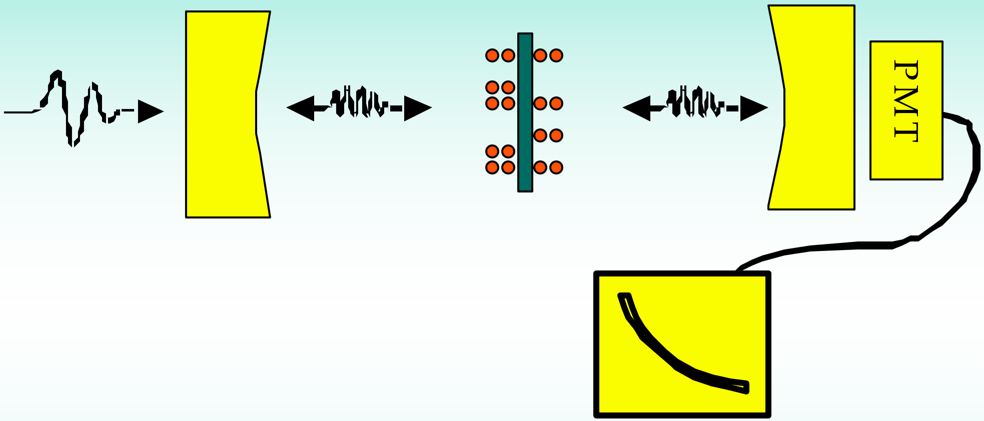
Non-exponential decay



Single Mode excitation :

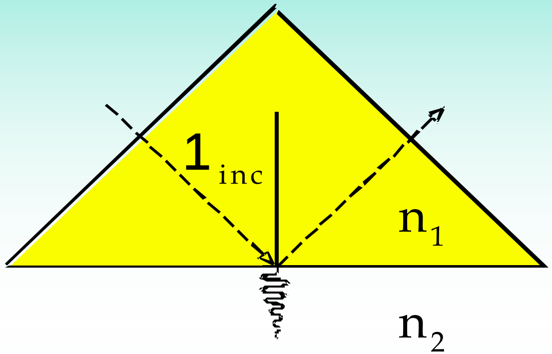
Pure exponential decay

Extension to Condensed Matter?



- Use of a cell or plate in the cavity increases L_0.
- Absorption/ring-down time equation is complicated.
- Multilayer, dielectric mirrors have narrow bandwidth.

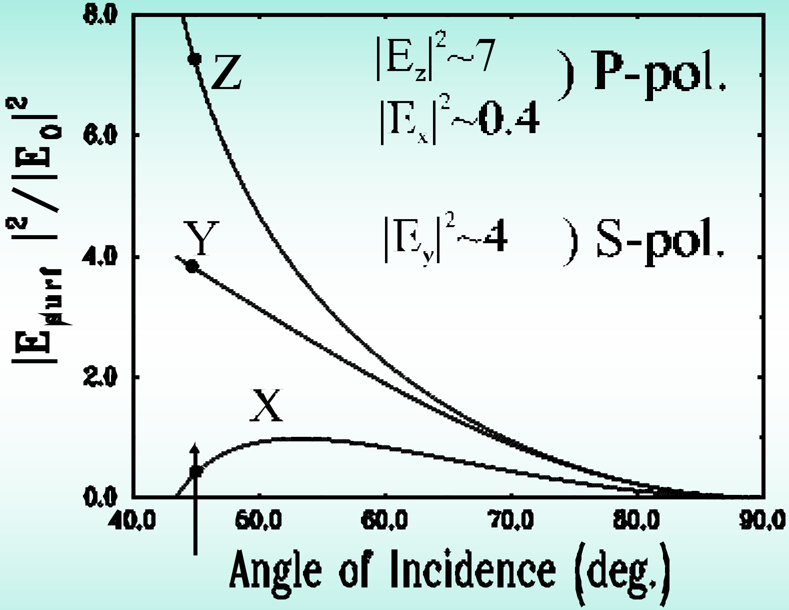
Total Internal Reflection: Nature's perfect mirror



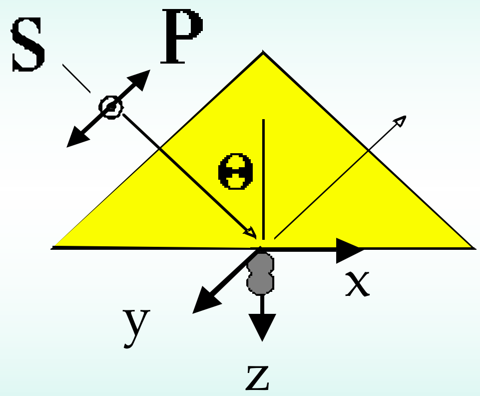
$$1_{inc} > 1_c = \sin^{-1}(n_2/n_1) \quad n_2<n_1$$

- Broadband
- **R** limited by surface scattering loss.
- **R**>99.9999 for a "superpolished" surface.
- Evanescent wave probes absorption as in ATR.
- Applicable to surfaces, films, or liquids.

More on TIR:
Surface Electric Field Enhancement

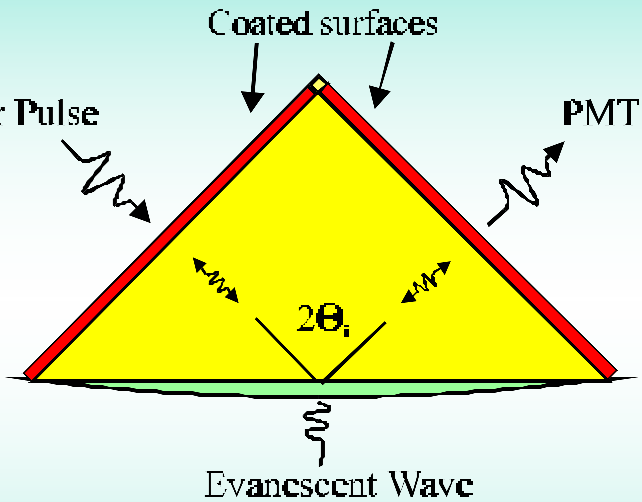


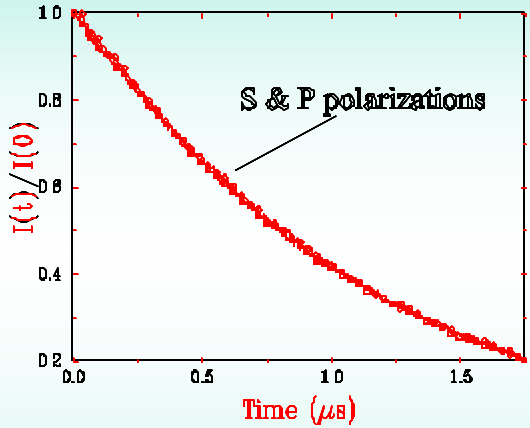
Results for a fused-silica/air interface



- Enhanced field intensity enhances absorption.
- Direction and magnitude can be calculated.
- Average molecular orientation can be extracted.

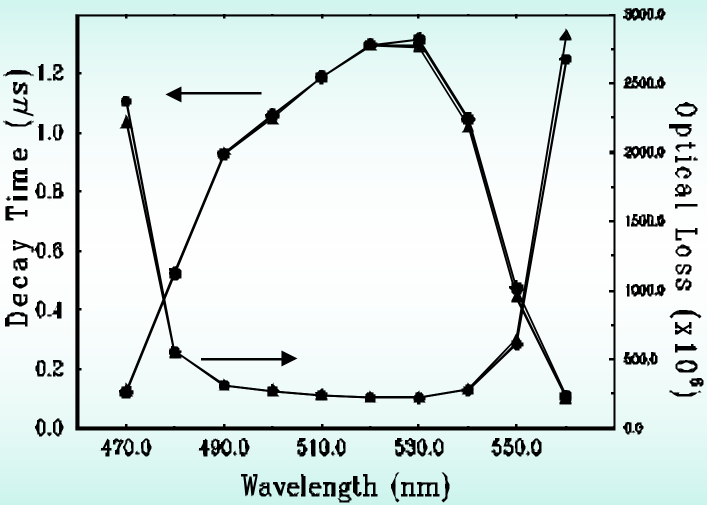
Monolithic, Folded Resonator



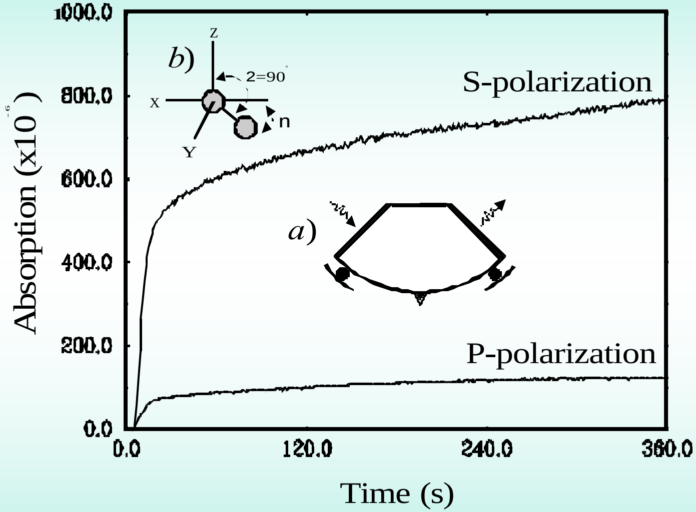


- Both polarization states resonate.
- Small (~1-3 cm) & Easily interfaced to experiments.
- BUT coated surfaces restrict bandwidth.

Folded Resonator Performance

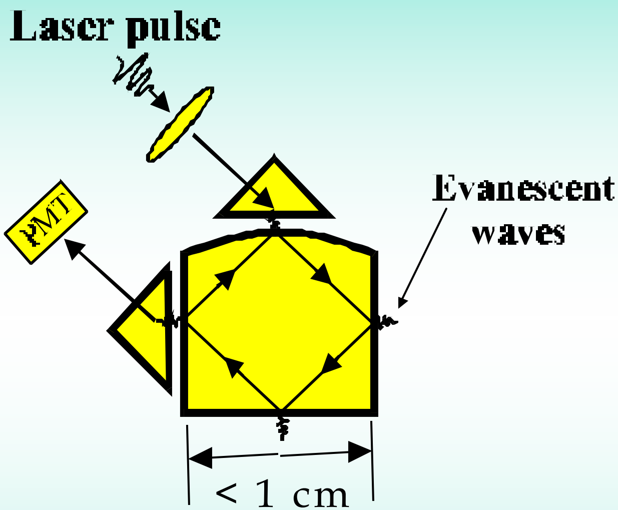


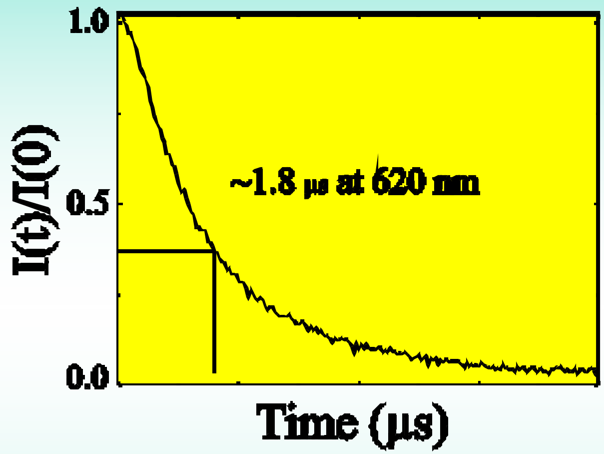
Bandwidth



Response to I_2

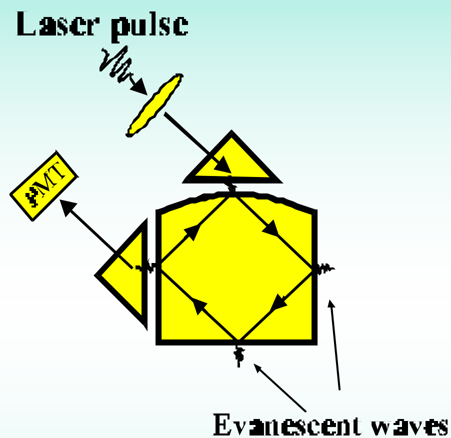
Miniature TIR-ring cavity





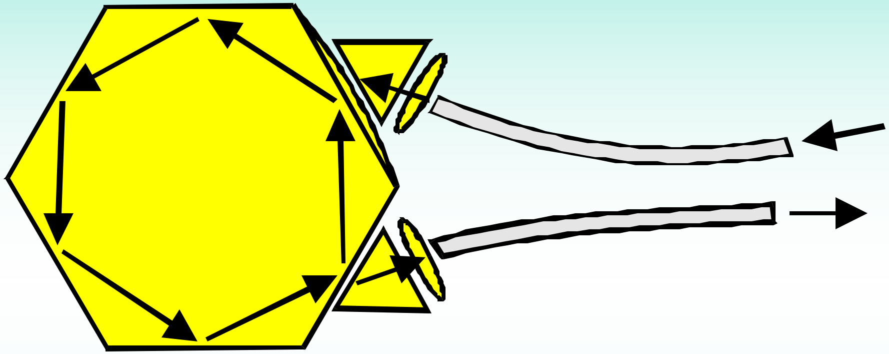
- Monolithic polygonal solid forms the cavity.
- # of sides determines the angle of incidence.
- A single convex surface results in a stable resonator.
- Light enters/exits the ring by photon tunneling.
- Evanescent waves probe absorption at remaining facets.

TIR-ring Cavity Advantages



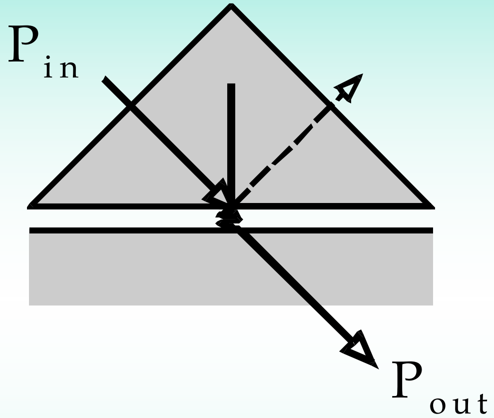
- Miniaturizable to ~ 10 um
- Extremely small loss ($10^{-7} < L_0 < 10^{-3}$)
- Single-mode excitation is easy
- Broad spectral bandwidth (1000 nm+)
- Both polarizations: orientation measurements
- Wide T and P range.
- With optical fiber, forms a remote, miniature spectrometer.

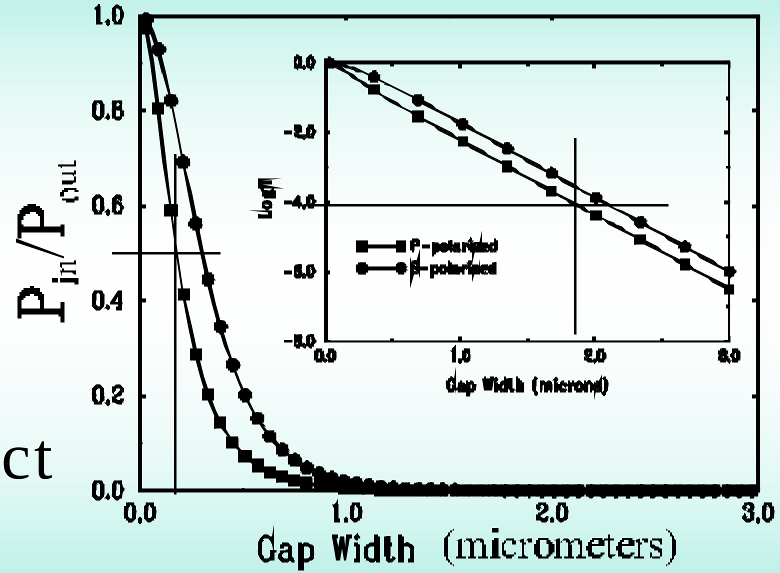
Cavities for Liquids and Other Spectral Regions



- Sapphire Hexagonal cavity : UV to Near-IR for liquids
- Undoped YAG Hexagonal cavity : Mid-IR for liquids
- Fluoride glass Square cavity: Thin films in the Mid-IR

Photon Tunneling: Single gap

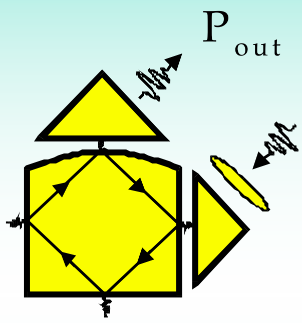


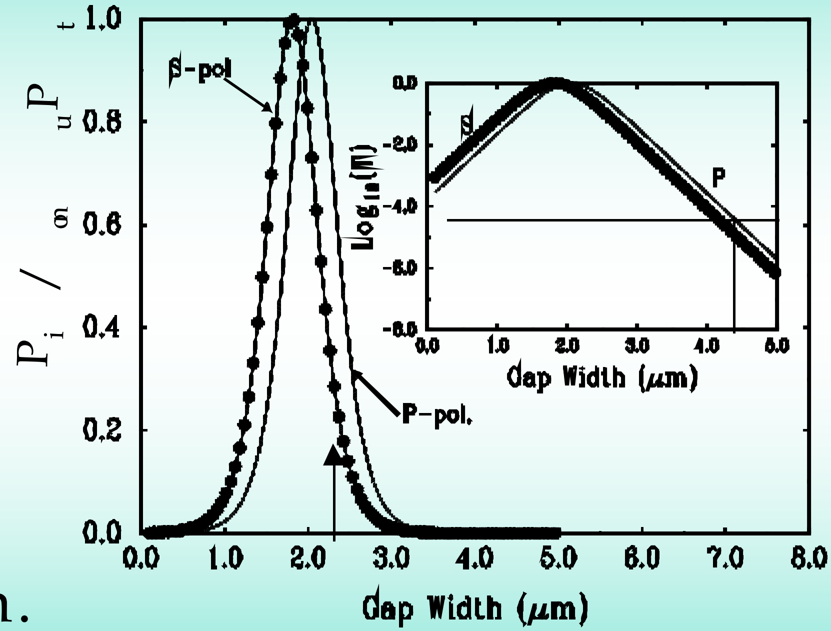


- 100 % T only at contact
- T=50 ppm ~ 2 μm.

(633 nm; 45°; fused silica)

Photon Tunneling: Cavity Transmission





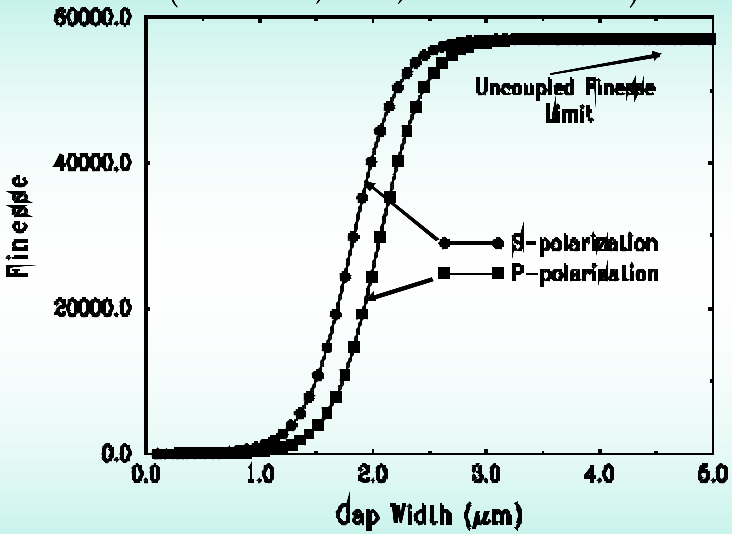
- ~100% **T** at ~2 μm.
- ~50 ppm **T** at ~4 μm.
- L_{coup} = ~50 ppm at 4 μm.

(633 nm; 45°; fused silica)

Coupling and Cavity Finesse

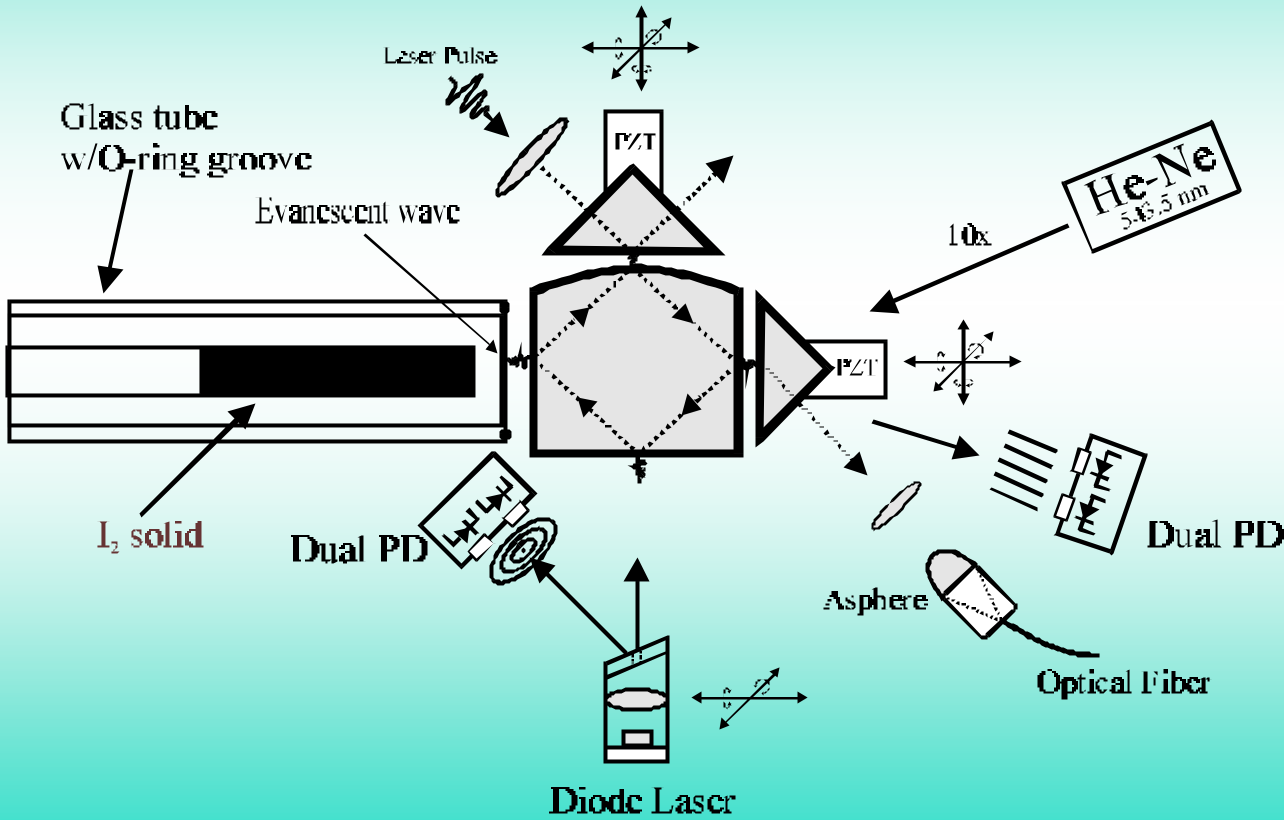
- At 4 μm, $L_{coup} \sim L_{bulk}$.
- Plenty of signal w/50 ppm .
- At 3-4 μm, F --> F_{max}

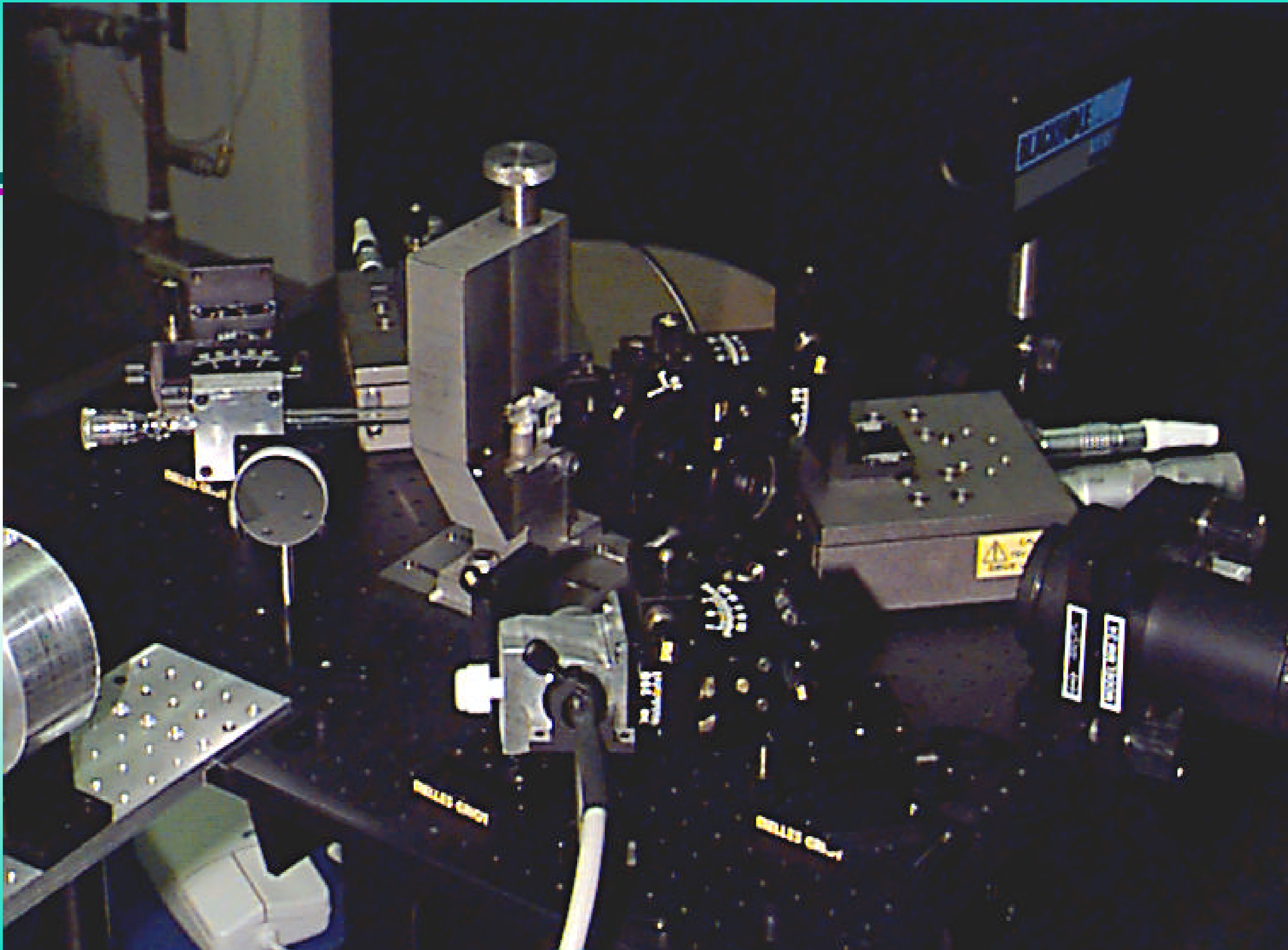
(633 nm; 45°; fused silica)



- Finesse is stabilized w/respect to changes in gap width.

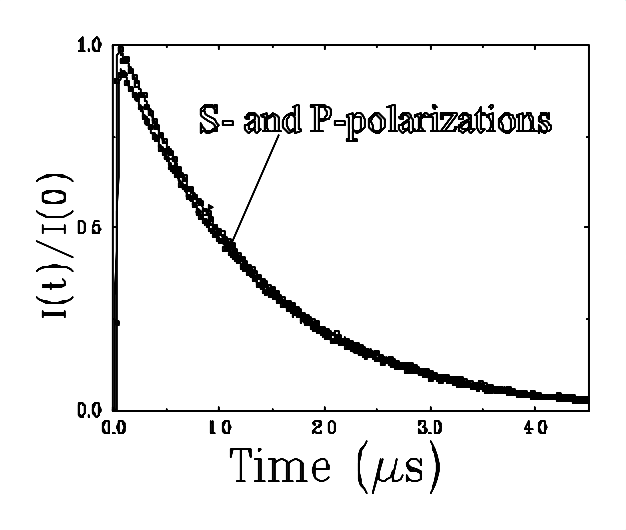
The Experiment



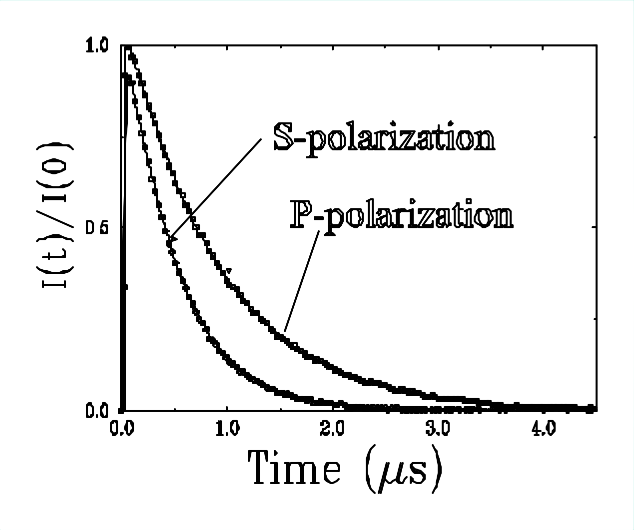


Measuring Molecular Orientation at the Surface

Before I_2 adsorption



After I_2 adsorption



- Large difference in decay times for S- vs P-polarization.
- **E**-field direction and magnitude are known.
- Results indicate I_2 molecules lay flat on average.

Estimating Sensitivity

Field Enhancement ~ 4

$$MDA = \text{'}_y N_s F_s(T) = 1x10^{-7}$$

- S-polarized absorption identified as physisiorbed I_2.
- Knowing orientation provides the correct field enhancement.
- Estimated detection limit: 60 ppm of a monolayer.

Reaching the Shot-noise Limit

Now 10^{-3} but 10^{-5} is possible

- Single Mode excitation
- 16-Bit digitizer
- Analog Detection

Now 10^{-7} but 10^{-12} is possible

$$\text{MDA} = L_0 *(\ )J/J)_{min}$$

Now 80×10^{-6} but $<10^{-7}$ is possible

- Other optical materials
- Different spectral regions
- Smaller cavities

- Limiting shot-noise uncertainty ~ $N^{-1/2}$ (N= #photons detected)

Single Molecule Detection?

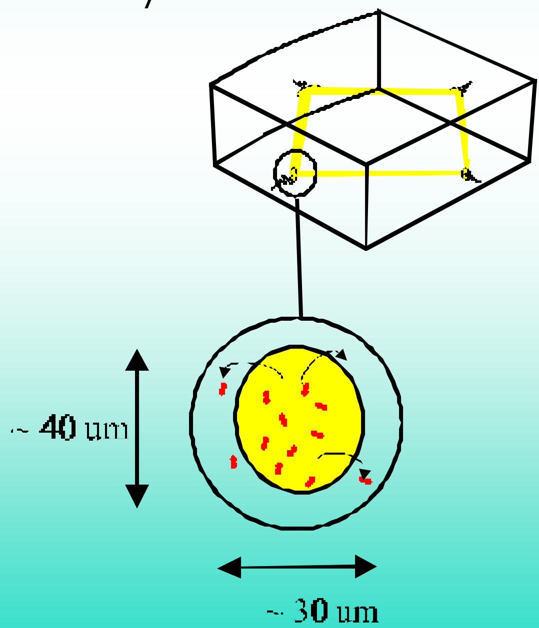
- Achieved at 2 K with double-modulation (~10^{-7})
- At 2 K, pentacene cross-section is ~ 10^{-11} cm^2/molecule
- For an MDA ~ 10^{-12},

Area=1.2×10^{-5} cm^2

F.E.~3

' (N/A) $F_s = 1 \times 10^{-12}$

10^{-18} cm^2

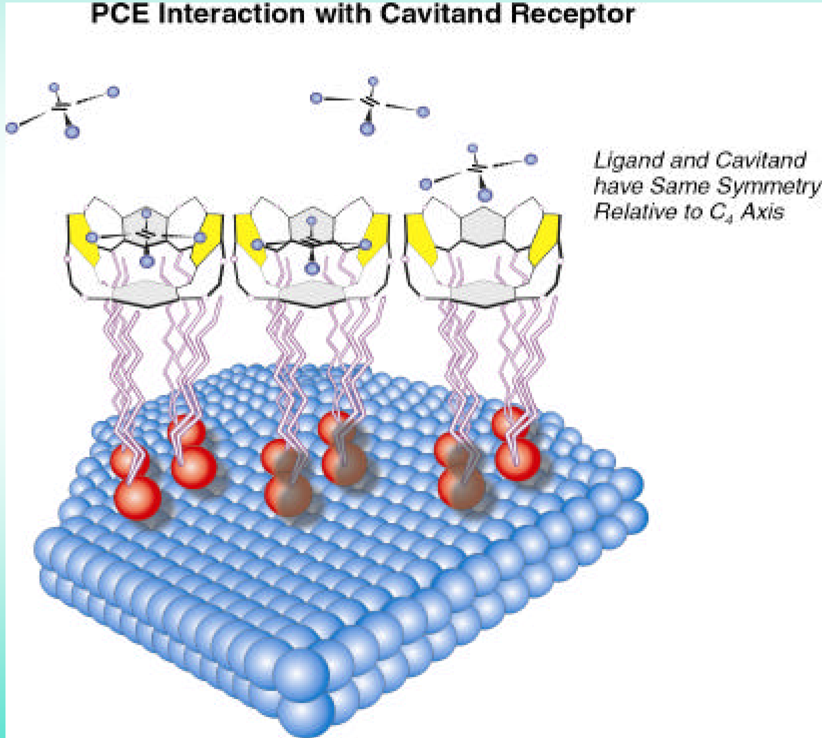


- **N ~ 4 molecules**

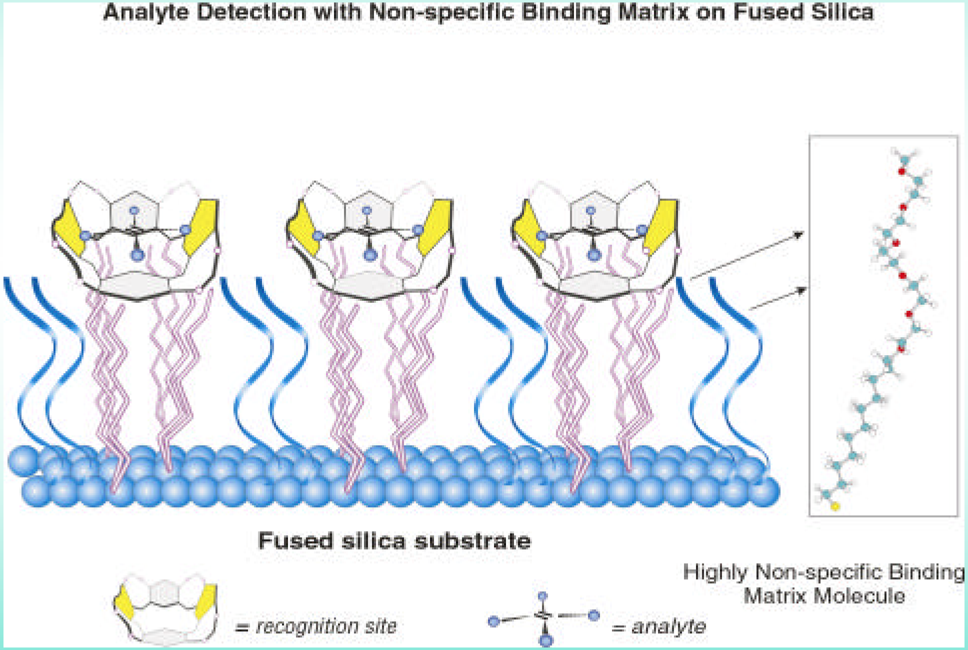
DOE Needs Addressed

- Technology Needs:
  - Rugged, miniature spectrometer
  - Detection of TCE, PCE, PB, Cs, and others
  - Characterize plumes
  - Long-term monitoring/stewardship
  - Headspace analysis
- Science Needs
  - Advances fundamental measurement science
  - New platform for Molecular Recognition

The Future: Molecular Recognition



MR surfaces with resistance to non-selective adsorption



Latest Developments

- A hexagonal TIR-ring sapphire resonator is operational for liquids
- Single mode excitation with a standard diode has been achieved
- Superpolished surfaces have been functionalized with cyclodextrins
- Functionalized surfaces show extremely low loss
- CRADA and licensing agreement with Informed Diagnostics Inc.

Publications and Patents

Evanescent wave cavity ring-down spectroscopy with a total-internal-reflection-ring minicavity,
A. C. R. Pipino et al., Rev. Sci. Instrum. **68** (8), 2978, (1997).

Evanescent wave cavity ring-down spectroscopy as a probe of surface processes,
A. C. R. Pipino et al. , Chem. Phys. Lett. **280**, 104, (1997).

Ultra-sensitive surface spectroscopy with miniature optical resonator,
A. C. R. Pipino, Phys. Rev. Lett. 83, 3093, (1999).

Monolithic folded resonator for evanescent wave cavity ring-down spectroscopy,
A. C. R. Pipino, Appl. Opt. 39, 1449, (2000).

Broadband intra-cavity total reflection chemical sensor,
A. C. R. Pipino, U. S. Patent No. 5,835,231.

Intra-cavity total reflection for high sensitivity measurement of optical properties,
A. C. R. Pipino, U. S. Patent No. 5,986,768.

Intra-cavity total reflection for high sensitivity measurement of optical properties,
A. C. R. Pipino et al., U. S. Patent No. 5,943,136.

A. C. R. Pipino in Advanced Sensors and Monitors for Process Industries and the Environment.,
W. A. De Groot, ed., Proc. SPIE 3535, 57-67, (1998).

A. C. R. Pipino in Advanced Materials and Optical Systems for Chemical and Biological Detection.,
M. Fallahi and B. I. Swanson, eds., Proc. SPIE 3858, 74-82, (1999).