Novel Miniature Spectrometer for Remote Chemical Detection

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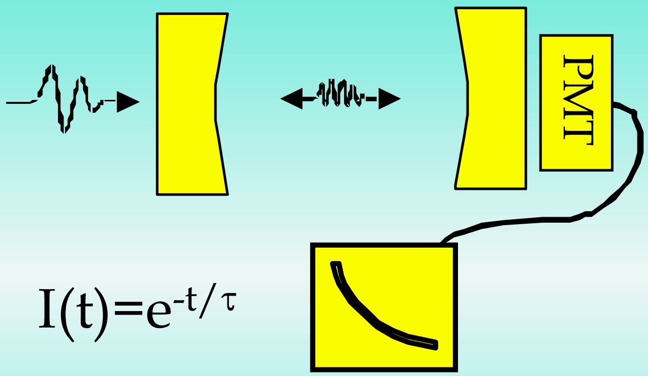
ABSTRACT

A novel miniature spectrometer is being developed that permits ultra-high sensitivity chemical detection in remote or hazardous environments. The technology employs a miniature total-internal-reflection-ring optical cavity to extend the cavity ring-down concept to condensed matter for the first time. A detailed theoretical model and two levels of prototyping have been successfully completed. The ultimate potential of the technology approaches single molecule detection at ambient temperature.

"Conventional" Cavity Ring-Down Spectroscopy



$I(t)=e^{-t/\tau}$

$$\tau(\omega) = \frac{t_r}{L_{mirrors} + L_{abs}}$$

Round-trip time

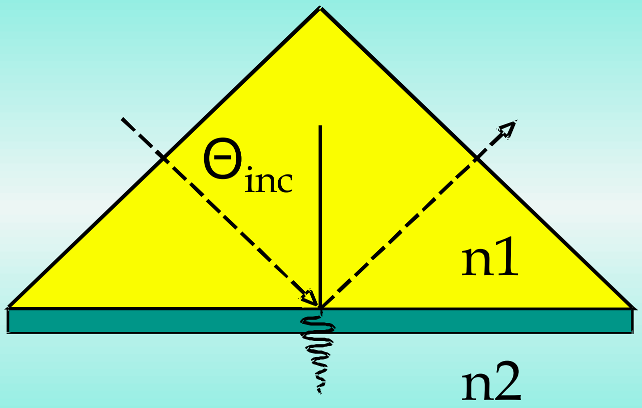
Mirror loss

Sample absorption

- New technique for measurement of optical absorption
- $(L_{abs})_{min} = L_{mirrors}$ * minimum detectable $\Delta\tau/\tau$
- **Gas-phase diagnostics only**

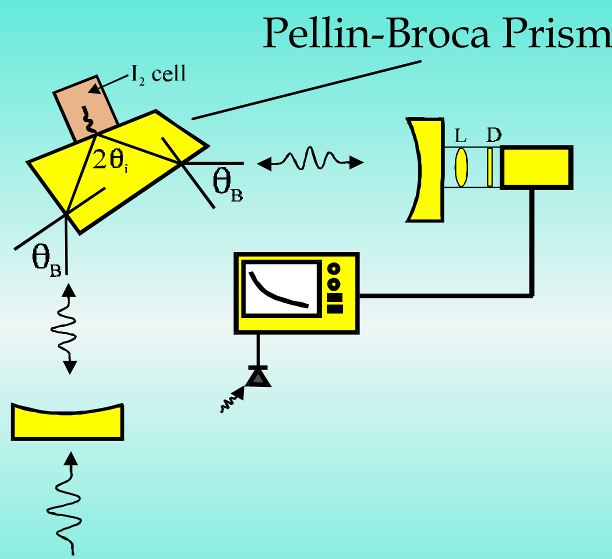
Extension to Condensed Matter

Use Total Internal Reflection

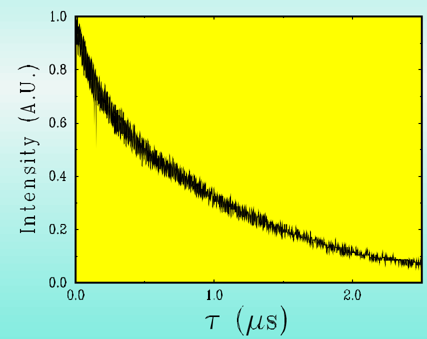


- Requires $\Theta_{inc} > \Theta_c = \sin^{-1}(n_2/n_1)$
- Ultra-high reflectivity
- Broadband
- Evanescent wave defines the sampled path length
- Can be used to probe adlayers, films, or bulk media

Initial Prototype Design

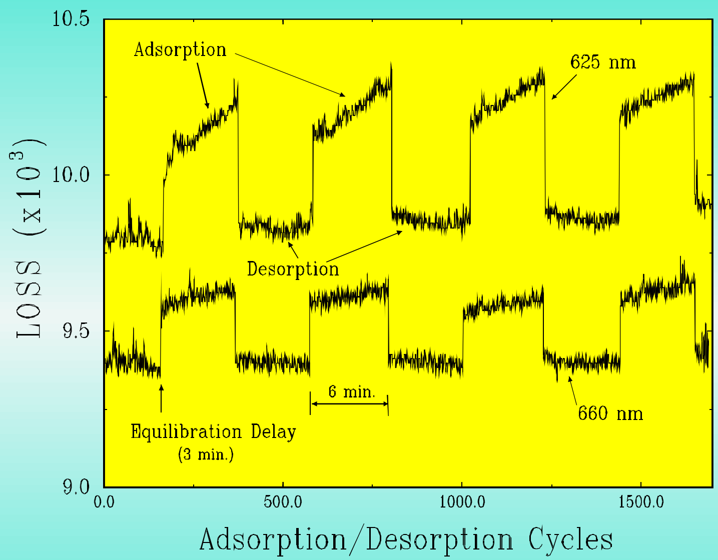


$$\tau(\omega) = \frac{t_r}{L_{mirrors} + L_{bulk} + L_{surf} + L_{pol} + L_{abs}}$$



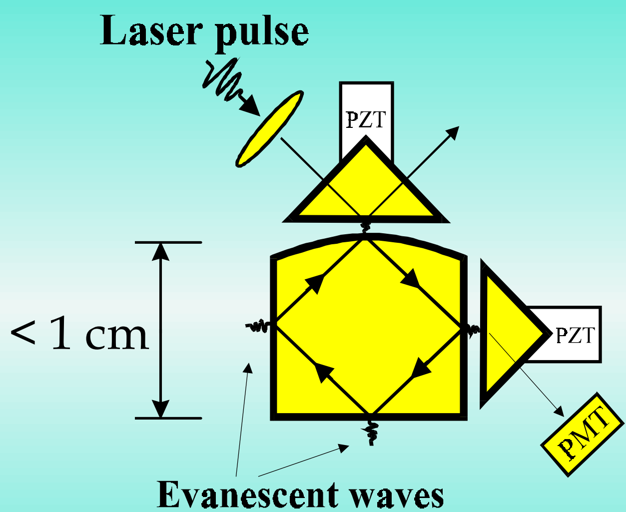
- First application of CRDS to a condensed phase
- Intra-cavity Pellin-Broca prism with ultra-smooth surfaces
- Low-loss (high finesse) for only one polarization component

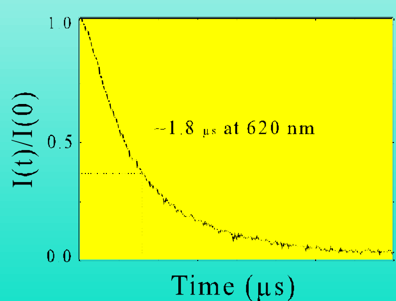
Initial Prototype Results



- Surface adsorbed I_2 used for calibration
- Detection limit: 4% of a monolayer at 625 nm
- Peak absorption at 520 nm for this moderate absorber

Optimum Cavity Design



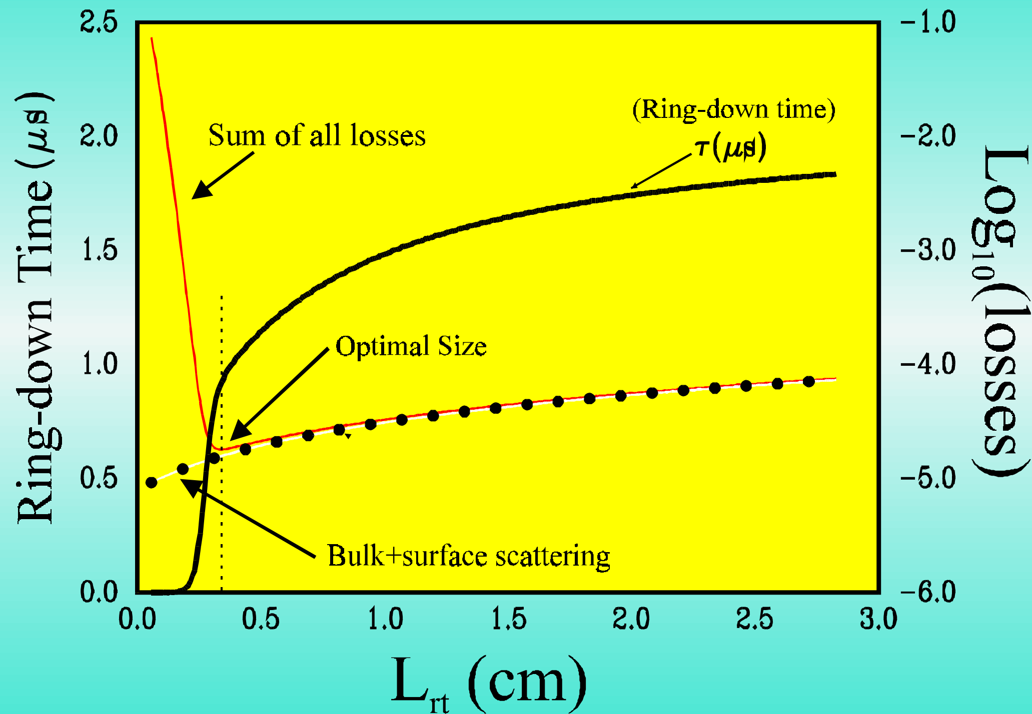


$$\tau(\omega) = \frac{t_r}{\underbrace{L_{bulk} + L_{surf} + L_{diff} + L_{coup}}_{\text{Intrinsic losses}} + L_{abs}}$$

A synergistic combination

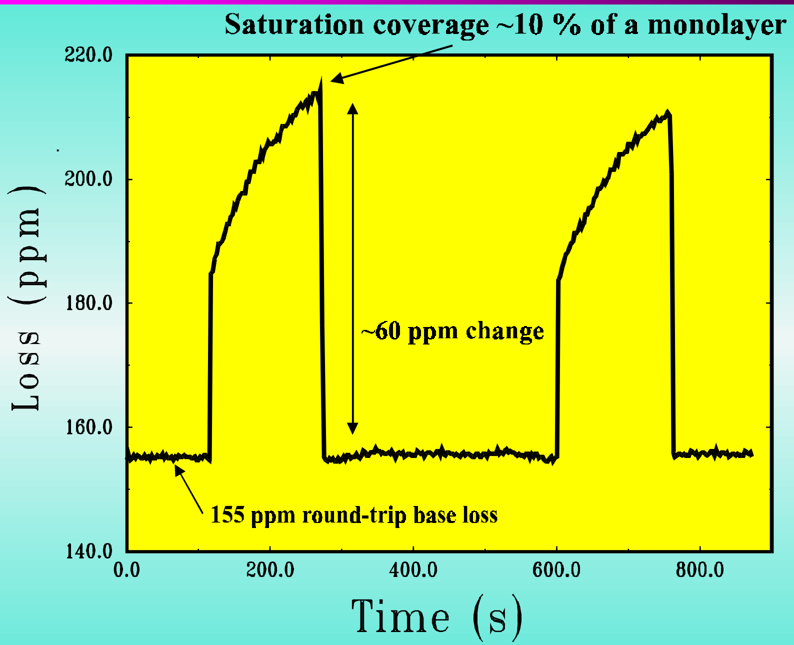
- Ultra-high sensitivity
- Broadband
- Wide T and P range
- Single point sampling
- Miniaturizable
- Potential on-chip sensor

Theoretical Model



- Permits the optimum cavity size to be identified
- Optimum size arises from a competition between losses

The Experiment

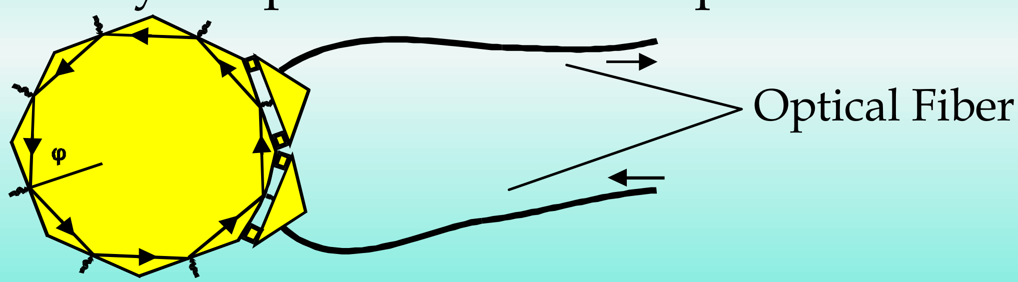


- Gaps controlled piezoelectrically/monitored interferometrically
- Detection limit of ~40 ppm of a monolayer of I_2
- Final form can be packaged w/fiber optics

Other Geometries

For fused-silica cavities (visible and near-IR) :

- ✦Square geometry is optimal for thin-film diagnostics
- ✦Octagonal geometry is optimal for bulk aqueous solutions



Other materials exist for other spectral regions:

- ✦Fluoride and chalcogenide glasses for the mid-IR
- ✦Sapphire for the UV

Summary of Achievements

- A fundamentally new technology for chemical sensing has been:
  - conceived
  - elucidated theoretically through a general model
  - realized experimentally (quantitative agreement with theory!)
  - patented and published
- The technology has important properties for the EMSP mission:
  - spectroscopic detection/characterization
  - sensitivity approaching single molecule detection
  - miniaturizable
  - broadband
  - rugged and chemically inert
  - wide temperature and pressure range
  - can be remotely located with optical fiber

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).

Condensed matter cavity ring-down spectroscopy with miniature optical cavity,
A. C. R. Pipino, in preparation.

Intra-cavity total reflection for high sensitivity measurement of optical properties,
A. C. R. Pipino et al., U. S. Patent Application Serial No. 08/962,170, pending.

Broadband intra-cavity total reflection chemical sensor,
A. C. R. Pipino, U. S. Patent Application Serial No. 08/962,171, accepted.