# Novel Miniature Spectrometer for Remote Chemical Detection

Project ID: 60231

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## Research Objective

To develop a new optical technology for chemical detection that is highly sensitive, miniature, rugged, and permits remote sensing of hazardous gaseous, liquid, or semi-solid environments.

## Research Progress and Implications

This report, which summarizes work completed as of year 2.4 of a three year project, describes a novel chemical sensing technology that extends cavity ring-down spectroscopy (CRDS) to condensed phases. Applied mostly to gas-phase diagnostics previously, CRDS is an optical absorption technique that uses the photon intensity decay time or "ring-down" time of a low-loss optical cavity as the absorption-sensitive observable. Yet by employing intra-cavity total-internal-reflection (TIR) with monolithic, miniature, optical resonators, a novel variant of CRDS is achieved. TIR provides effective mirror reflectivities of R~0.999999 and generates an evanescent wave with an enhanced electric field at the TIR interface that permits absorption of an ambient condensed phase to be probed. Evanescent wave cavity ring-down spectroscopy (EW-CRDS) combines the advantages of evanescent wave spectroscopy with CRDS.

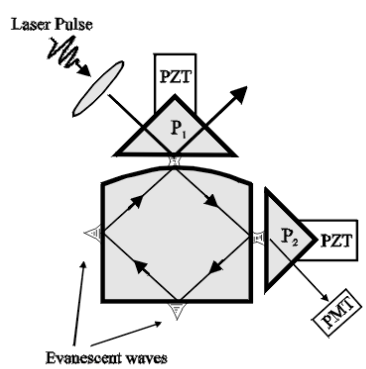


**Figure 1: TIR-ring cavity**

Several cavity designs for applying EW-CRDS have been realized. In Figure 1, a square, TIR-ring cavity is depicted with a convex facet that refocusses the internally circulating light beam. This cavity is an example of a more general class of polygonal TIR-ring resonators, which was explored theoretically in detail during the initial phase of this work[1]. The round-trip optical loss, $L_0$, can be made very small ($10^{-3} < L_0 < 10^{-7}$) by using ultra-pure optical materials, ultra-smooth surfaces, and optimized coupling. Photon tunneling across the junctions between the monolithic cavity and the coupling prisms $P_1$ and $P_2$ is used for input and output coupling, respectively. Evanescent waves emanate from the remaining facets to probe the absorption of an ambient medium. Figure 2a shows single-shot ring-down traces with decay times of 1.270 µs and 1.278 µs for s- and p-polarized cavity modes, respectively, obtained at 580 nm for a 7 mm x 7 mm x 5 mm fused-silica cavity with a 2.23 cm radius of curvature convex facet[2]. The inset in Figure 2a defines the surface coordinate system and shows the components of the electric field intensity of the evanescent wave as a function of

distance from the cavity facet. With knowledge of the field magnitude and direction, measurement of the ratio of s- to p-polarized absorptions can be related to the molecular orientation. Figure 2b shows ring-down traces for s- and p-polarized modes under identical conditions with Figure 2a, but a TIR facet has been exposed to $I_2$ vapor, which has a visible X-B transition dipole moment that is aligned with the molecular axis. Note that both s- and p-polarized modes show a change in ring-down time with $\tau_s$=0.497 μs and $\tau_p$=0.889 μs, but the s-polarized mode shows a significantly larger change, despite the smaller field enhancement associated with $E_y$, indicating that $I_2$ molecules are preferentially oriented with their molecular axes parallel to the surface. The measurement of molecular orientation is important for chemical sensing because molecules often have a preferential orientation on a surface and because oriented molecular films can be combined with EW-CRDS to increase selectivity. The estimated minimum coverage for detecting adsorbed $I_2$ is 0.006 % of a monolayer for this prototype, which is instrumentation-limited in these results. Improvements in sensitivity can be anticipated by reaching the shot-noise limit at high fluence and by further reducing round-trip cavity loss. The square fused silica cavity of Figure 1 permits adsorbed vapors to be probed from the near-UV through the near-IR spectral regions. A hexagonal, sapphire TIR-ring cavity has also been successfully fabricated and tested that allows liquid samples to be probed by direct immersion.

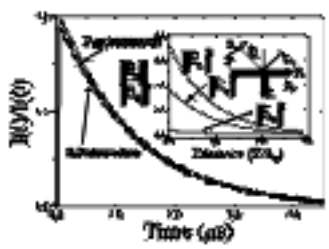

**Figure 2a. No adsorbed $I_2$**

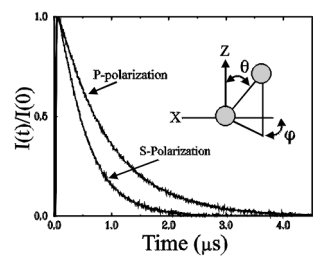


**Figure 2b: w/adsorbed $I_2$**

Since the TIR-ring cavity uses only TIR mirrors, a broad spectral bandwidth is accessible. However, photon tunneling is needed to excite and detect the cavity modes, which requires precise positioning of the coupling prisms. Another monolithic resonator design for EW-CRDS is shown in Figure 3 that employs both ultra-high reflective coatings and TIR[3]. Although a restricted bandwidth (~80 nm) results from the use of reflective coatings, this resonator provides high-sensitivity, excellent stability, and facile operation for single wavelength monitoring applications. Light is injected into the cavity through one of the coated facets, along the folded optic axis. The single convex TIR surface imparts stability (refocussing) and generates an evanescent wave. Figure 4 demonstrates the detection of iodine at 530 nm with a fused-silica resonator having an unfolded cavity length of L=3.0±0.1cm, a radius of curvature $R_C$=7.5±0.1 cm, and $\Theta_i$ =45.0°±0.08°, which employs an ultra-high-reflective coating centered at ~520 nm with an estimated loss of $L_C$=1.2x$10^{-5}$ per reflection. An excimer-pumped dye laser was used without mode matching as the laser source. The transmission through surface $S_3$ was monitored with a photomultiplier tube and an 8-bit digital oscilloscope. The time dependence of the signal arises from the slow reaction of $I_2$ with adsorbed water and surface hydroxyl groups. The sensing surface can be easily interfaced to a sample chamber by O-ring seal, as indicated in the inset a of Figure 4.

In order to develop a portable, inexpensive sensing technology based on EW-CRDS, the use of diode laser sources has been examined in collaboration with our commercial partner. In order to obtain the best possible ring-down time measurement precision, which optimizes sensitivity, single mode excitation is required. Furthermore, the laser diode must be optically isolated from the cavity to prevent optical feedback, which shifts and distorts the diode output, rendering single mode matching impossible. Having resolved these issues, we are now able to achieve extremely efficient (58:1), single, lowest-order mode ($TEM_{00}$), excitation of CRDS cavities with a standard, off-the-shelf diode laser (not an extended cavity diode laser system). These experiments used a 685 nm diode with a 15±5 MHz linewidth, which provided ample cavity output intensity (~10 μW) for detection. These results indicate that a cost effective sensing system based on EW-CRDS can be produced. Furthermore,

the sensing element (the resonator) can be remotely located from the source and detector by optical fiber or all three miniature elements could be packaged on a chip.

Finally, we are examining the combination of "smart films", which show molecular recognition for a particular molecule or class of molecules, with EW-CRDS. Working with collaborators at LANL, we have tested cyclodextrin films which show selectivity for toluene. Initial results indicate that these films, which form rugged, well-ordered monolayers on superpolished surfaces, show low-scatter loss and low total attenuation. Therefore, functionalizing the surfaces of EW-CRDS resonators to increase selectivity should be feasible.

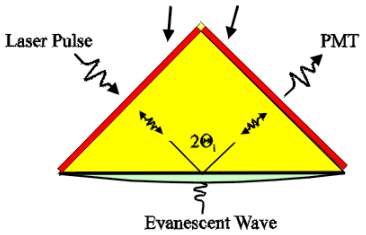


**Figure 3: Folded, monolithic cavity**

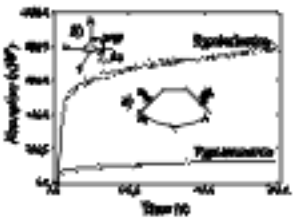

**Figure 4: $I_2$ detection**

## Planned Activities

During the remaining months of FY 2000, we anticipate continuing our investigation of the combination of EW-CRDS with smart films. We will also employ diode laser excitation with several EW-CRDS cavity designs. Experiments on bulk liquids will also be explored.

## Information Access

1) A. C. R. Pipino, et al. Rev. Sci. Instrum. **68** (8), 2978-2989, (1997).
2) A. C. R. Pipino, Phys. Rev. Lett. **83** (15), 3093-3096, (1999).
3) A. C. R. Pipino, Appl. Opt. March 20, 2000.
4) Also see patents: US5835231, US5943136, US5986768