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Miniature Chemical Sensor Combining Molecular Recognition with
Evanescent Wave Cavity Ring-Down Spectroscopy

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1. Executive Summary

A new chemical detection technology has been realized through EMSP Projects 60231 and 73844 that addresses DOE environmental management needs. The new technology is based on a variant of the sensitive optical absorption technique, cavity ring-down spectroscopy (CRDS). Termed *evanescent-wave cavity ring-down spectroscopy* (EW-CRDS), the technology employs a miniature solid-state optical resonator having an extremely high Q-factor as the sensing element, where the high-Q is achieved by using ultra-low-attenuation optical materials, ultra-smooth surfaces, and ultra-high reflectivity coatings, as well as low-diffraction-loss designs. At least one total-internal reflection (TIR) mirror is integral to the resonator permitting the concomitant evanescent wave to probe the ambient environment. Several prototypes have been designed, fabricated, characterized, and applied to chemical detection. Moreover, extensions of the sensing concept have been explored to enhance selectivity, sensitivity, and range of application. Operating primarily in the visible and near IR regions, the technology inherently enables remote detection by optical fiber. Producing 11 archival publications, 4 conference proceedings, 5 patents, 19 invited talks, a CRADA, and a patent-license agreement, Projects 60231 and 73844 realized a new chemical detection technology providing >100 times more sensitivity than comparable technologies, while also providing practical advantages.

At the beginning of Project 60231, EW-CRDS was only a concept supported by modeling studies and preliminary experiments. During FY98, the first demonstration of a miniature TIR-ring resonator for EW-CRDS was achieved using a square-ring design. The TIR-ring resonator provides a broad spectral bandwidth (~1000 nm) enabling multiple species to be probed with a single device. Also during FY98 a new optical resonator termed the monolithic folded resonator was designed and fabricated. During FY99, the TIR-ring resonator was thoroughly characterized for chemical detection sensitivity, polarization properties, bandwidth, stability, and alignment sensitivity. Both wavelength and polarization dependence were used for identification and quantification of a molecular species. In FY99 and FY00, the folded resonator and a sapphire hexagonal-TIR-ring resonator were characterized for chemical detection sensitivity, polarization properties, bandwidth, stability, and alignment sensitivity. Also during FY00, the use of diode lasers for CRDS measurements was explored together with a commercial partner.

During FY01, Project 73844 began with the addition of a broadly tunable, pulsed optical parametric oscillator (OPO) to the EW-CRDS laboratory, which enabled operation in the visible and near infrared regions between 440 nm and 1800 nm. Although the OPO installation and debugging process was unexpectedly time consuming, procurement of this new capability was essential to probe analytes of interest to DOE using overtones and combination bands in the near-IR region. The extremely low attenuation (<1 dB/km or 2.3 ppm/cm) of selected fused silica in the near-IR permitted exceptionally high-Q solid-state resonators to be realized over the course of the project, which provided exceptionally high sensitivity for EW-CRDS even when probing rather weak overtones and combination bands. FY01 activities also included preliminary studies of nanoparticle-enhanced CRDS detection and synthesis of a molecular recognition agent for selective detection of perchloroethylene (PCE). Further, a preliminary effort was

made to evaluate the use of EW-CRDS for humidity sensing in ultra-dry environments by probing the second OH stretching overtone of water adsorbed on a fused-silica folded resonator. During FY02, studies of nanoparticle-enhanced CRDS detection yielded successful results. In particular, the surface plasmon resonance (SPR) response of Au nanoparticles to trichloroethylene (TCE) and PCE was probed by CRDS, yielding detection limits in the 10^{-8} mol/L range for these small molecules. Also during FY02, direct detection of TCE in the near-IR was accomplished by probing the first C-H stretching overtone by EW-CRDS with a folded resonator. In addition, a preliminary demonstration of absolute surface coverage measurement of TCE by EW-CRDS was accomplished. During FY02, advancements were also made in the development of contamination-resistant coatings to enhance molecular recognition response and to prevent surface fouling. During FY03, a detailed study of direct detection of TCE, cis-, and trans-dichloroethylene (DCE) by EW-CRDS using the first C-H overtones of these species was completed, which included evaluation of sensitivity, selectivity, reversibility, and absolute coverage measurement. Further, a detailed comparison was made between EW-CRDS and comparable competing technologies for TCE detection. Moreover, during FY03 a new class of monolithic resonators was conceived to enable EW-CRDS in liquids, followed by the design, specification, and fabrication of a specific selection from this new class. While the previous designs could permit liquids to be probed by EW-CRDS, severe astigmatism along with rather inconvenient angular separation between input and output beams complicated realization of a liquid-phase device. During FY03, films containing molecular recognition agents were also characterized and the development of contamination resistant films continued. During FY04 the new liquid-phase resonator was characterized for sensitivity, bandwidth, polarization properties, and stability. Also, during FY04, Au-nanoparticle-enhanced CRDS was demonstrated to provide uniquely high sensitivity and selectivity for nitro-compounds including 2,4-dinitrotoluene (DNT), a common signature species for the explosive, TNT. Furthermore, EW-CRDS was demonstrated as a viable humidity sensing technology by probing a combination band of adsorbed water in the near IR, around 8000 cm^{-1} . Indeed the polarized combination band spectra for both surface SiOH and adsorbed water species were obtained with rather high signal-to-noise ratio, revealing an ordered, semi-crystalline layer at the surface of the amorphous fused-silica resonator.

Concerning relevance, impact, and technology transfer, the EW-CRDS technology has the potential to fulfill many DOE sensing needs by ultimately providing a sensitive, selective, and rugged *in-situ* chemical sensing technology that is patent-protected. While the development of EW-CRDS is in its infancy, application to TCE detection using a monolithic folded resonator has the greatest potential for near-term field trials. The resonator could be coating with a polysiloxane polymer to yield a sensitive, selective, and robust sensor for both remediation and long-term monitoring applications, where the polymer protects the sensing surface and enriches the TCE concentration in the evanescent wave region. While chemically selective films employing molecular recognition do not yet appear to be sufficiently robust for field applications, polysiloxane polymers, provide an enrichment mechanism based on simple partitioning and are currently used in many rugged environments. Furthermore, polysiloxane polymers have been applied previously for near-IR TCE detection with a waveguide sensing platform.

2. Research Objective

A new class of chemical sensors has been realized through EMSP Project 60231 and continuation Project 73844. New chemical sensing technologies are critically important for addressing many EM needs. Many *technology needs* were addressed by this research. For example, improved detection techniques are needed for non-aqueous phase liquids (NAPLs), such as PCE and TCE, which persist in the environment due their stable structures. Projects 60231 and 73844 have yielded a miniature, ultra-sensitive, selective, and potentially field-deployable detector, which could enable NAPL plumes to be characterized. Further, the miniature spectrometer developed could also provide accurate contaminant transport data, either in the field or the laboratory, for use in the development of transport models. The technology could also be used for long-term monitoring/long-term stewardship. Further, several *science needs* were also addressed, since the effort significantly advances the measurement science of chemical detection. Although much remains to be accomplished, the objective of these Projects was to realize a new chemical detection technology, which has been accomplished.

3. Methods and Results

A. Background

Chemical sensing can be accomplished by many strategies. In general, optical techniques offer significant advantages, including high sensitivity, cost-effectiveness, and remote detection. In the shot-noise limit, optical absorption spectroscopy has the potential to be the most sensitive optical technique, since the intrinsic molecular cross-sections are typically largest for absorption. Optical absorption is also the most general optical technique since all molecules absorb light at some frequency. However, to reach the ultimate potential of absorption spectroscopy requires the ability to detect a small power loss in a large optical signal. Some progress in this direction was made years ago with the development of modulation techniques^{1,2} in which the intensity or frequency of an optical beam was modulated and detected with a lock-in amplifier, which substantially reduced 1/f noise. A minimum detectable absorption of $\Delta I/I \sim 10^{-7}$ can be achieved with modulation techniques under laboratory conditions, which permits detection of a single molecule of a very strong absorber at very low temperatures³. However, modulation techniques are relatively expensive, involve complex instrumentation and data interpretation, and further improvements in sensitivity have not been realized.

Recently, with the development of cavity ring-down spectroscopy (CRDS)⁴⁻⁶, detection of absorption changes of $\sim 10^{-9}$ has been demonstrated⁷, with changes of $\sim 10^{-13}$ predicted to be possible⁸. Of equal importance, the extremely high sensitivity provided by CRDS is obtained with a comparatively simple measurement, using the intensity decay rate of light pulses injected into a low-loss optical cavity as the absorption-sensitive observable. Typically, the cavity is formed from a pair of ultra-high reflectivity ($R > 0.9999$) concave mirrors configured to form a stable optical resonator. Injected light pulses have a mean lifetime or “ring-down” time given by $\tau(\omega) = t_r / L(\omega)$, where the round-trip transit time in the cavity of length L and refractive index n_i is $t_r = 2n_i L / c$, and where the total round-trip optical loss is $L(\omega) = L_0(\omega) + L_{\text{spl}}(\omega)$, being composed of the intrinsic loss, $L_0(\omega)$, (typically arising from mirror reflectivity losses), and the sample loss, $L_{\text{spl}}(\omega)$. The ring-down time is determined by fitting the decaying transmitted light

intensity to an exponential function. Determination of absorption is thereby transformed from the measurement of an optical power ratio as in standard absorption spectroscopy to a measurement of time. A complete measurement is accomplished with a single light pulse, thereby eliminating errors introduced by light source fluctuations. The minimum detectable absorbance change is determined by the product of the intrinsic loss, $L_0(\omega)$, and the minimum detectable relative change in the ring-down time $\Delta\tau/\tau$, or $(\alpha L)_{\min}=L_0*\Delta\tau/\tau$. This form for $(\alpha L)_{\min}$ reveals the simplicity and challenge of CRDS: Minimize the intrinsic cavity loss and determine the ring-down time with the highest possible precision. While CRDS has been typically applied to gas-phase diagnostics using a large (~1 m) linear optical resonator, EMSP Projects 60231 and 73844 have led to miniaturization and extension of CRDS to surfaces, films, and liquids through the development of novel resonator designs that permit ambient sampling without introducing extraneous intrinsic losses which degrade sensitivity.

The product of Projects 60231 and 73844, evanescent wave cavity ring-down spectroscopy (EW-CRDS)⁹⁻¹⁹, extends CRDS to surfaces, films and liquids and miniaturizes the technique by using the unique properties of total internal reflection (TIR). For light incident on a perfectly smooth interface between two media with indices of refraction n_i and n_o , TIR occurs when the angle of incidence θ_i exceeds the critical angle, defined by $\theta_c=\sin^{-1}(n_i/n_o)$, which in theory provides a perfect ($R=1$), broadband mirror. In practice, the reflectivity is less than unity due to surface-roughness scattering and nonspecular transmission arising from the non-planar character of real wave fronts. Yet ultra-smooth polished surfaces with root-mean-square surface roughness of ~0.05 nm can be generated routinely, yielding $R=0.999999$ in the visible region of the spectrum. Furthermore, TIR generates an evanescent wave with a locally enhanced surface electric field at the TIR interface, which increases chemical detection sensitivity for molecules that are in the vicinity of the TIR surface. EW-CRDS uses miniature solid-state optical resonators that incorporate one or more TIR surfaces. The evanescent waves emanate from the TIR surfaces, sampling the surrounding medium. The utility of evanescent waves in chemical analysis forms the basis for attenuated total reflectance (ATR)²⁰ spectroscopy. While ATR solves many diagnostic problems that are intractable by ordinary methods, ATR typically lacks the sensitivity needed for ultra-trace chemical detection. In EW-CRDS, the ring-down time of a resonator sensitively responds to chemical species present in the evanescent wave thereby combining the advantages of ATR with the sensitivity of CRDS. Furthermore, the use of miniature solid-state resonators permits optimization of the sensitivity when compared to other strategies for implementation of EW-CRDS, while forming the basis for a rugged miniature chemical sensor for which the laser source and photo-detector can be located remotely by optical fiber.

B. Project 60231

Project Objective: To develop a new class of sensors for qualitative and quantitative, remote, real-time, optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases based on evanescent wave cavity ring-down spectroscopy (EW-CRDS).

1. A key outcome from Project 60231 was the first demonstration of a miniature spectrometer prototype based on EW-CRDS, whereas the previous proof-of-concept experiments employed a rather large cavity incorporating a Pellin-Broca prism¹⁰. As described in detail elsewhere^{11,12} the first miniature spectrometer prototype was based on a monolithic square-TIR-ring resonator fabricated from high purity fused silica, which is a specific example of a general class of polygonal, TIR-ring resonators. As the TIR-ring resonator uses photon tunneling to excite and probe cavity modes, the dependence of coupling efficiency and cavity round-trip loss on the tunneling junction gap width was investigated by using piezoelectric translators to provide precise (± 5 nm) control of the tunneling junction, while interferometry was used to determine the junction size. Furthermore, the bandwidth at fixed tunneling junction, the alignment sensitivity, and the ring-down time stability were also characterized.
2. Chemical detection using the square-TIR-ring resonator was demonstrated by detection adsorbed molecular iodine. The average orientation of adsorbed iodine on the resonator surface was determined from the polarized surface absorption, together with the calculated surface electric field intensities. Iodine served as a suitable probe molecule because the gas-phase peak absorption cross-section does not change substantially with physisorption. An estimated minimum detectable coverage of $\sim 0.006\%$ of a monolayer (1 monolayer = 4.5×10^{14} sites/cm²) was determined. The detection limit was based on a minimum detectable absorption of 1.9×10^{-7} as achieved for a 25 laser shot average, which provided an instrumentation-limited relative standard deviation in the ring-down time of 0.2%. It is interesting to note that this level of sensitivity previously achieved by double modulation techniques was sufficient to achieve single molecule detection³.
3. In addition to the fused-silica square-TIR-ring resonator, a sapphire hexagonal-TIR-ring resonator was also fabricated and tested. Allowing liquid samples to be probed by direct immersion, the hexagonal cavity has a 60° angle of incidence at the TIR surface. With a refractive index of sapphire as $n_i=1.78$ and assuming the angle of incidence exceeds the critical angle by at least 2° , rather dense liquids with a refractive index of up to $n_o=1.5$ can be probed with this resonator design. The c-axis of the sapphire crystal was orthogonal to the resonator plane, which results in separate refractive indices but identical beam paths for s- and p-polarizations. The resonator facets were super-polished to 0.05 nm rms roughness, which reduced the surface scattering loss to $\sim 1 \times 10^{-6}$ (1 ppm) per surface at 550 nm. However, several factors conspired to complicate the prototype hexagonal TIR-ring development. In contrast to fused silica, published bulk attenuation data for sapphire shows wide variation in transmission based on the crystal growth process. Further, for low-loss sapphire conventional absorption spectroscopy does not provide sufficient sensitivity to permit facile characterization of the material to allow rapid selection by suppliers. Moreover, because a large difference exists between the critical angle at an air/sapphire interface ($\sim 34^\circ$) and the angle of incidence for the hexagonal resonator, a very small tunneling junction ($\ll \lambda$) is needed when an air-filled gap is employed for input- and output-coupling.

Although input coupling at the apex of the convex surface was easily achieved, output coupling required two macroscopic (25 mm^2) flat surfaces to be positioned with a small fraction of a wavelength of each other, which was difficult to achieve due to the limited resolution of the manual positioning hardware that controlled other degrees of freedom (tilt, rotation, *etc.*). To circumvent this problem, a low refractive index material was used to fill the coupling junction in order to extend the evanescent wave by reducing the index discontinuity of the junction, which could be readily incorporated into the fabrication of a field-deployable instrument. Also, additional engineering eventually allowed consistent coupling without the use of a liquid in the coupling junction. However, the bulk intrinsic loss of sapphire was found to be rather large and not well controlled or characterized by the supplier compared to fused silica. Un-doped YAG was also tested as a possible material for a low-loss hexagonal TIR-ring resonator, having no birefringence. Yet un-doped YAG also showed rather large bulk losses. Therefore, a new class of resonator designs was conceived as discussed below under Project 73844.

4. Since the polygonal, TIR-ring resonators employ only TIR mirrors, a broad spectral bandwidth is accessible. However, because photon tunneling is required to excite and detect the cavity modes, coupling prisms must be employed, which require precise positioning and mounting. Yet many applications require only a limited bandwidth and would benefit from simple, direct coupling through a coated mirror as in standard CRDS. Therefore, another monolithic resonator was designed for EW-CRDS termed the monolithic, folded resonator¹⁴. The folded resonator employs both ultra-high reflective coatings and TIR. Although a restricted bandwidth results from the use of reflective coatings, the design has several advantages including direct excitation through a coated surface, high finesse for all polarization states, excellent stability, and simplicity of operation. The folded design is formed from a monolithic solid of ultra-low-loss optical material having a refractive index n_i with two planar ultra-high-reflective coated surfaces and a convex TIR surface. The sample absorption is also probed by the evanescent wave emanating from the TIR surface.
5. A specific folded resonator design was selected, fabricated, characterized, and tested for chemical detection sensitivity. The selected design had a 3 cm per-pass length, a 7.5 cm radius of curvature for the TIR surface, and was coated for a center wavelength of 520 nm. The folded resonator provided a bandwidth of approximately 90 nm with the minimum intrinsic loss of 220 ppm occurring at 530 nm, where the maximum ring-down time was 1.3 μs . Molecular iodine was used to characterize the chemical detection sensitivity, allowing a direct comparison to the TIR-ring results. Molecular orientation measurements of adsorbed iodine yielded identical results for both resonator types, as expected since both were fabricated from fused silica. By averaging 25, individually acquired ring-down times, a relative uncertainty in the ring-down time of 0.20 % was obtained, which yielded a minimum detectable absorbance of $(L_{\text{abs}})_{\text{min}} = 4 \times 10^{-7}$, providing a minimum detectable coverage for adsorbed iodine of 0.004% of a monolayer. This estimate uses $L_{\text{abs}} = 2\Gamma\sigma(\omega)N_s/\cos\theta_i$, where N_s is the surface

density, Γ is the field enhancement factor, and $\sigma(\omega)$ is the surface-species absorption cross section. An increase in sensitivity has since been realized by working in the near-IR region where the bulk loss is smaller and by reducing the size of the resonator, as discussed under Project 73844.

6. To facilitate the development of a portable, inexpensive sensing technology based on EW-CRDS, the use of diode laser sources was examined in collaboration with a commercial partner. The use of a narrow line width source such as a diode laser also facilitates single mode excitation and increases light throughput as the laser line width approaches the cavity line width. Improved sensitivity can be obtained through single mode excitation by improving ring-down time measurement precision. However, the laser diode must be optically isolated from the cavity to prevent optical feedback, which frequency shifts and distorts the diode output. Using a linear CRDS cavity, we achieved extremely efficient (58:1), lowest-order mode (TEM_{00}), excitation 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 time-averaged line width, which provided ample cavity output intensity ($\sim 5 \mu\text{W}$) for detection. These results indicate that a cost effective sensing system based on EW-CRDS can be produced. Furthermore, this excitation strategy could be miniaturized and packaged on a chip. The knowledge gained in this investigation of diode laser CRDS facilitated the development of a prototype commercial instrument²¹.
7. The combination of EW-CRDS with chemically selective films that show molecular recognition for a particular class of molecules was also briefly examined during Project #60231. Working with collaborators at LANL, we are examining cyclodextrin films, which show selectivity for toluene, DNT, and TNT. Initial light scattering and CRDS measurements indicate that these films, which form rugged, well-ordered monolayers on super-polished surfaces, show low-scatter loss and low total attenuation. The measurements were performed using a single, coated optical flat, tilted at Brewster's angle in a linear CRDS cavity. These important preliminary results demonstrate that super-polished surfaces can be chemically modified with an organic layer without introducing large losses due to surface restructuring or contamination. The rms surface roughness of the organic layer seems to reflect the underlying substrate. These layers are in fact quite durable and can be cleaned by the same procedure used for the native fused-silica surface. Therefore, functionalizing the surfaces of EW-CRDS resonators to increase selectivity was found to be potentially feasible.

C. Project 73844

Project Objective: 1) To demonstrate the spectroscopic selectivity of EW-CRDS by using polarized near-IR "fingerprint" spectroscopy, 2) To increase the range of application by extending EW-CRDS to liquids and by combining EW-CRDS with the unique optical properties of nanoparticles, and 3) To enhance selectivity and contamination resistance of EW-CRDS measurements through chemical modification of the sensing surface.

I. Optical Technique Advances

1. To enable vibrational overtones and combination bands to be probed by EW-CRDS a tunable near-IR laser source was required. Therefore, a new laser system was specified, procured, installed, and debugged. The system consisted of an optical parametric oscillator (OPO) and optical parametric amplifier (OPA) combination in which two beam-walk-compensating beta-barium-borate (BBO) crystals forming the OPA were pumped by a 10 Hz, frequency-tripled, injection-seeded-Nd:YAG laser, which also pumped a 0.075 cm^{-1} line width OPO that seeded the OPA at the signal wavelength. Although this system was a commercial instrument, considerable time and effort were required to achieve stable operation.
2. The surface plasmon resonance (SPR) of Au nanoparticles under optical excitation generates a strongly enhanced local electric field at the particle surface, which leads to enhancement of optical observables. Although the SPR has long been used to enhance chemical detection sensitivity of optical measurements, the combination with CRDS had not yet been attempted. Therefore, we sought to combine advantages of SPR with CRDS. The initial challenge was to generate Au nanoparticles in such a way that a reproducible surface coverage could be achieved having a sufficiently low optical loss to permit use inside a CRDS cavity, while providing a sensitive response to relevant DOE analytes. Several strategies were attempted including the use of solution-phase-deposition of nanospheres, sputter-deposition of Au films through size-selecting grids, and sputter-deposition of ultra-thin films. In the latter case, we found that the natural granularity of the ultra-thin film yielded a monodisperse distribution of small nanoparticles. Having a mean diameter of 4.5 nm as determined by AFM, the nanoparticle distribution was reproducible, provided a strong response to DOE analytes, and incurred a modest intrinsic loss.
3. The SPR response of the Au nanoparticle distribution to PCE and TCE was thoroughly characterized¹⁷. The short-time response (30s) yielded high sensitivity, showing detection limits of 2×10^{-8} mol/L and 7×10^{-8} mol/L for PCE and TCE, respectively, where the higher sensitivity for PCE likely arises from the higher refractive index. The response of the Au nanoparticles was modeled using extended Mie theory, which accounted semi-quantitatively for some features of the optical response. From theory, a trend toward higher sensitivity was expected for nanoparticles of decreasing size. The observed response was consistent with this expectation, since a 10^{-8} mol/L detection limit is low for these small molecules.
4. Using the newly installed OPO/OPA system the detection of trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and trans-dichloroethylene (t-DCE) was examined by probing the first C-H overtones for these species occurring in the near-IR around 6050 cm^{-1} (1650 nm). Polarized absolute surface spectra were obtained by EW-CRDS using a fused-silica monolithic folded resonator having a finesse of 28,500 at 6050 cm^{-1} . A measure of the average molecular orientation of these species on the surface was derived from the polarization anisotropy of the surface spectra. Conventional CRDS was also employed to measure the absolute absorption cross sections for the gas-phase species. Given the surface and gas-

- phase data, absolute surface coverage determinations were possible for TCE, cis-, and trans-DCE, based on conservation of the integrated cross-sections. Further, the three chloroethylenes gave distinct overtone spectra, thereby demonstrating spectroscopic selectivity¹⁸.
5. To assess the potential for environmental sensing, we compared our EW-CRDS results to those obtained using optical waveguide techniques. Specifically, we compared the detection capability of EW-CRDS to previous efforts in which evanescent wave near-IR absorption of the first C-H overtone was employed for TCE detection. Ache and co-workers^{20,23} extensively studied the detection of TCE with the first C-H overtone using a long-effective-path-length planar waveguide, which provided improved sensitivity over their previous optical-fiber sensor²⁴ by a factor of 120. Polysiloxane coatings were employed with these devices to reversibly enrich the local concentration of TCE in the evanescent wave. The chemical composition of the polysiloxane polymers was also varied to identify optimal conditions for sensing as determined by the TCE partition coefficient and polymer refractive index²⁵. Furthermore, it was shown that competing absorption from C-H groups of the polymer could be essentially eliminated through efficient deuteration of the polymer²⁵. The gas-phase detection limit for TCE obtained using the optimized planar waveguide with a polysiloxane coating was found to be ≈ 0.1 mmol/L or ≈ 2 parts-per-thousand in the gas phase at atmospheric pressure. By comparison, EW-CRDS also provides an equivalent detection limit determined by the minimum detectable absorption of 1×10^{-7} based on a 0.1 % relative decay time precision (1σ for ensembles of 25 averaged laser shots per point) and a 1×10^{-4} /pass intrinsic loss. Yet this detection limit is obtained by EW-CRDS *without a TCE-enriching polymer*. Moreover, the EW-CRDS response to adsorption of TCE on the silica surface of the folded resonator was found to be fully reversible with a response time of seconds. The addition of an enriching polymer layer to an EW-CRDS-based TCE detection scheme could lower detection limits significantly. The use of a low-scatter-loss, deuterated polysiloxane film should permit a low intrinsic loss to be maintained²⁵. The polysiloxane layer, which can be thick relative to the evanescent wave decay length for an appropriate resonator design, should also serve to protect the sensing surface and eliminate interference from particulates. A significant additional improvement in sensitivity can be realized by reducing the resonator intrinsic loss relative to that found in the present work by the use of a smaller resonator that is fabricated from lower bulk-OH-content fused silica. Furthermore, it is worth noting that the monolithic resonator design improves in sensitivity through a reduction in size, whereas planar waveguides require an increase in length to increase sensitivity (through an increase in sample path length).
 6. In addition to the C-H overtones, several OH overtones are found in the near-IR, which could be used to detect OH-containing species with water being the simplest. Under ambient conditions, the native surface of a fused-silica monolithic resonator is partially or fully hydroxylated (i.e., covered with silanols, SiOH), which can be exploited to increase selective binding of an OH-containing analyte, providing in some sense a natural molecular recognition interaction. Using EW-

CRDS we have obtained vibrational combination band spectra of surface SiOH and adsorbed water on ultra-smooth amorphous silica in the 8000 cm^{-1} region²⁶. Remarkably, we find evidence for crystalline character for both SiOH and adsorbed water layers, where the latter suggests the formation of an ice-like structure at room temperature. The combination band spectra for the $2\nu\text{OH} + \delta\text{OH}$ mode of surface SiOH under dry $\text{N}_2(\text{g})$ shows two SiOH bands, which are both *highly polarized*. The p-polarized (8118 cm^{-1}) band indicates a mean orientation for the transition dipole that is perpendicular to the surface plane, while the s-polarized (8152 cm^{-1}) band indicates a parallel transition moment. Such spectra are consistent with the existence of a crystalline surface phase, similar to the (100) facet of β -cristobalite. Furthermore, four adsorbed-water peaks are observed, which are also highly polarized. For the “dry” surface (under dry $\text{N}_2(\text{g})$, no previous heating), adsorbed water peaks are still observed due to rather strong H-bonding with the surface SiOH groups. When exposed to 10% RH, the water bands show a strong increase in intensity, indicating EW-CRDS can be used to sense humidity in dry environments. When exposed to 50% RH, the water bands show only a slight additional increase by contrast, suggesting the observed bands arise from unique surface species associated with the first monolayer of surface coverage. Furthermore, as the SiO_2 surface is ubiquitous in science, technology, and the environment, our results demonstrate that EW-CRDS provides a unique diagnostic probe of this important surface, which can be employed for a plurality of pure and applied investigations.

7. To extend EW-CRDS to liquids, a new class of optical resonators was conceived, designed, fabricated, and tested. The new resonator designs are achieved using optical-contacting in which two optical components fabricated from identical material and having ultra-smooth surfaces are bonded together (e.g., under pressure) to form a single monolithic element such that the bond between components is optically indistinguishable from bulk material. Using this design strategy, unique stigmatic, weakly astigmatic, and astigmatic Gaussian mode resonators and whispering gallery mode resonators can be formed having otherwise-unachievable properties. In particular, liquid-immersible sensors with little or no astigmatism, can be fabricated from low-refractive-index optical materials such as fused silica. Further, resonators with vicinal input and output ports can be realized, which facilitates the construction of compact distal probes where input and output beams can be introduced and accessed in spatial proximity. In addition, multiple input and output ports may be employed in parallel in a single device such that multiple spectral regions can be probed simultaneously. An arbitrary angle of incidence at a TIR surface can also be achieved through optical contacting, thereby allowing an optimum selection of incident angle for a given application. Based on model calculations, a specific example of this new class of resonators was selected for fabrication and characterized for stability, bandwidth, and sensitivity. The astigmatism-free design has a 4.59 cm per-pass length and five TIR surfaces. The 90 nm spectral range of the resonator is centered at 550 nm where the polarization-independent intrinsic loss is 165 ppm, providing a minimum detectable optical loss of <1 ppm.

Detection of a laser dye (R6G) has so far been demonstrated with the new design²⁷.

8. In addition to detection of PCE and TCE, the optical response of Au nanoparticles probed by CRDS was used to detect nitro-containing species²⁸. In particular, detection of NO₂, C₆H₅NO₂, and 2,4-dinitrotoluene (DNT) by SPR-CRDS was explored. A uniquely sensitive response, which appears characteristic of the -NO₂ group, was observed using the previously characterized nanoparticle distribution. Detection limits of 1.2 nmol/L, 7.6 nmol/L, and 0.17 nmol/L, were found for NO₂, C₆H₅NO₂, and DNT, respectively. The unique response could arise from the formation of a Au O,O'-nitrito bidentate-chelate complex, although more detailed studies will be required to fully elucidate the nature of this selective interaction. However, our SPR-CRDS studies suggest the unique sensitivity for NO₂ does extend in a general way to other nitro-containing species with an increased degree of analyte nitration apparently resulting in higher sensitivity. As a major impurity and decomposition product in production-grade TNT (1,3,5-trinitrotoluene) but having a higher vapor pressure than TNT, DNT in particular is a prevalent signature species in TNT-based explosives detection. Hence, SPR-CRDS could yield a novel detection mechanism for nitro-based explosives.

II. Advances in Selectivity through Molecular Recognition Chemistry

9. To enhance the selectivity of EW-CRDS and to permit the technique to be used in a complex matrix, we sought to engineer a sensor surface that specifically binds a chosen analyte while resisting adsorption of contaminants. The inhibition of non-specific contaminant adsorption is particularly important to the analysis of complex aqueous samples like soil extracts or ground water that will contain small compounds and surface-active biomaterials such as proteins. Since proteins in particular are notorious for showing a high degree of non-specific adsorption at inorganic surfaces, we chose to use proteins as a prototype contaminant. To this end, our chemical strategy was to synthesize and study (a) a "molecular recognition" agent (resorcin [4] arene) for selective binding of PCE and (b) to develop contamination resistant surfaces based on the use of an oligo(ethylene oxide)(OEO)-matrix, which is well known to exhibit remarkable resistance to non-specific adsorption of proteins.
10. The molecular recognition agent, resorcin[4]arene, also termed a molecular "cavitand", was chosen on the basis of a recent report suggesting that it showed selective adsorption of PCE²⁹. Synthesis of the resorcin[4]arene was accomplished as described in the literature³⁰, with some modification of the purification procedures. The molecule has a bowl-like shape and had been proposed to form a host-guest complex with PCE based on complementary size and symmetry. However, in a slight variation of the literature synthetic procedure, resorcin[4]arene was prepared using butanal instead of undecanal in the initial condensation step. Recrystallization from 20% ethyl acetate/hexanes afforded crystals whose ¹H NMR showed a 1/1 ratio between the protons of the resorcin[4]arene and ethyl acetate, suggesting formation of a host-guest complex.

- X-ray crystallographic analysis of the crystals (Travis Holman, Georgetown University) showed that the ethyl acetate was indeed associated in the “bowl”. The orientation of ethyl acetate in the bowl is not explainable from symmetry arguments as for PCE. Instead, the complexation and orientation of ethyl acetate may be the result of insertion of the most hydrophobic end (the ethyl group) into the hydrophobic part of the “bowl” [the lower part] coupled with a coordination of the carbonyl group with one or more of the “upper rim” oxygens. Hence, we observe a host-guest interaction between the molecular cavitand and a molecule that does not present complementary size, shape, or symmetry corresponding to the bowl-like structure of the cavitand, which is contrary to the original claims of small-molecule selectivity for the molecular cavitand, a concern also raised by others³¹. However, our results using ethyl acetate do show unambiguously that a host-guest interaction can occur with molecular cavitands.
11. It is well known that surfaces coated with long chain poly(ethylene oxide) (PEO) or self-assembled monolayers (SAMs) terminated with shorter OEO exhibit remarkable resistance to non-specific adsorption and are promising candidates for creation of fouling-resistant surfaces. However, the molecular basis of the protein resistance of PEO- and OEO-modified surfaces is not well understood. Structural variation and packing density of the films have been shown to be important in performance. Therefore, we have studied film structure and packing density effects on the contamination resistance of these films. The structures of the SAMs of the series $\text{HS}(\text{EO})_x\text{CH}_3$, where $x = 3 - 6$, were found to vary with x . Highly ordered, helical, SAMs were found for $x=5$ and 6 and disordered, amorphous SAMs were found for $x=3$ and 4 . Electrochemical impedance spectroscopy data indicates that all SAMs, $x < 6$, are rapidly penetrated by water under aqueous conditions while water penetration into the helical $x = 6$ SAMs is slow. The significant difference between the experimental and calculated specific capacitance values for $(\text{EO})_5$, coupled with the observation of SAM variability, suggests that the helical $(\text{EO})_5$ is less robust than $(\text{EO})_6$. This, coupled with the absence of any helical structure for $(\text{EO})_4$, indicates that $(\text{EO})_5$ is the shortest segment capable of forming a helical conformation.
 12. Using reflection-adsorption infrared spectroscopy (RAIRS) and spectroscopic ellipsometry (SE), SAMs of $\text{HS}(\text{CH}_2)_3\text{O}(\text{EO})_x\text{CH}_3$, where $x = 3$ to 9 , were studied, showing variation in structure and order. Highly ordered SAMs are obtained for $x = 5$ to 7 which were found to be isostructural with the OEO segments oriented normal to the substrate, in a $7/2$ helical conformation of the folded-chain crystal polymorph of PEO. The $x = 5$ to 7 SAMs order as a function of immersion time faster and over a wider range of assembly conditions, including assembly from 100% water. Our data suggests that the $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ (C_3) segment facilitates OEO segments to adopt the helical conformation and allows both the film coverage and protein adsorption components of INSPA experiments to be carried out in water. The identification of isostructural films, in this series, (thickness range 2.1 to 2.7 nm) provides possible metrology materials/standards for surface science measurement and instrument calibration in ~ 0.3 nm increments.

13. We found that the protein adsorption reaches a minimum (a) at coverages where the opposing conditions of effective screening of the underlying substrate and significant conformational mobility of the bound oligomers are both present and (b) corresponds to coverage ranges in which the onset of self-rejection of OEO itself is observed. We have further confirmed that EO surfaces, optimal in the inhibition of non-specific protein adsorption, also exhibit inhibition of non-specific adsorption of small molecules. For example, surface plasmon resonance data show that neither PCE nor TCE adsorb to EO surfaces grown on Au. Our data also supports the idea that the mechanism of protein resistance of PEOs and OEO-SAMs is similar. Further, the relatively low surface coverage of OEO required for maximal resistance to non-specific adsorption suggests that it should be possible to retain the general rejection properties of the surface in the presence of specific guest-host (or molecular recognition) sites, which could be anchored among the rejecting OEO matrix. In that way, nonspecific adsorption might be minimized in a straightforward and general manner for EW CRDS.
14. Molecular dynamics simulations were used to study a set of surface-tethered methyl 1-thiahexa(EO)s [HS(EO)₆CH₃] to provide visualization of the monolayer structure that relates to non-specific adsorption properties. We found spontaneous helix formation and helix morphology depend on charge partitioning ascribed to oxygen and the methylene (CH₂) groups. The effects of varying surface coverage as well as chain-surface interaction strength indicated, in accord with infrared spectroscopic studies, a set of approximate 7/2 helical structures oriented predominantly normal to the surface at near full coverage. Thermal fluctuations in chain morphology in the vicinity of the terminal methyl groups lead to exposure of the oxygen atom to the external environment. We also found that the persistence of compact helix-containing domains at partial surface coverage results in the formation of well-defined cavities or void regions that expose the bare surface, even in the presence of strong chain-surface attractive interactions. These voids appear at approximately the same coverage at which the surface becomes self-rejecting (i.e., rejection of further surface binding of EO itself), thus supporting the model of protein resistance proposed.
15. Characterization of molecular recognition chemistry on surfaces and/or nanoparticles requires methods to characterize selectivity and binding constants. Because protein chemistry essentially defines true molecular recognition, we investigated a method to measure binding constants based on measurement of the extent of amide hydrogen/deuterium exchange. The ability to exchange hydrogen for deuterium in protein is related to the protection from the incoming deuterium, afforded by the tertiary structure of the protein. If the protein has bound ligand, the protection of some of its amides to exchange has been further enhanced. By comparing the extent of this protection in proteins versus proteins bound to ligands, with and without tertiary structure, a measure of protein binding constant is achieved. We obtained results for trypsin bound by benzamidine inhibitors system because this system is a model of toluene/*o*-xylene monooxygenase in *Pseudomonas stutzeri* OX1, which is used for bioremediation of PCE and TCE³².

4. Relevance, Impact, and Technology Transfer

- a. Project #60231 has yielded a new chemical sensing technology that could be applicable to a wide range of DOE environmental management problems.
- b. Improved technologies and clean-up approaches may result from availability of new chemical characterization data at DOE sites. Clean up costs could be reduced by having an in-situ probe rather than performing sample extraction followed by ex-situ analysis. Risk reduction could result from the creation of a chemical sensing probe that can be interrogated remotely from the contaminated site. A new sensing technology that could support long-term monitoring could also help DOE comply with agreed upon regulations. Finally, this project yields a new approach to characterizing chemically selective films that could be used by DOE.
- c. The basic research performed under Project 60231 has been basic *measurement science* underlying the EW-CRDS technology. Therefore, it forms the basis for all future applications of the technology.
- d. As a general chemical sensing technology, EW-CRDS could be used by many researchers in academic, government, or industrial research laboratories and could eventually become commercialized. There are at least four universities currently applying the EW-CRDS technique. Further, this work has contributed to the development of contamination resistant surfaces, which broadly impacts the field of chemical sensing.
- e. The project has made a fundamental impact since a new technology has been realized. More basic research is needed before a large-scale trial is justified.
- f. Several collaborations have evolved from this project. Working with a guest researcher (Johan Hoefnagels) from the group of Richard van de Sanden at the Eindhoven University of Technology (TU/e) in the Netherlands, high sensitivity detection and absolute coverage measurements of TCE, cis-DCE, and trans-DCE by EW-CRDS were completed. We also collaborated on the SiOH/H₂O studies, which have yielded a unique scientific outcome as well as a humidity sensing technology for dry environments. The TU/e group is also engaged in applying EW-CRDS to thin-film growth studies, which could produce more rugged and/or responsive sensors. Working with the group of Ulrich Heiz at the University of Ulm, we seek to expand EW-CRDS to studies of catalytic systems using both the monolithic folded and TIR-ring resonator designs. In particular, a TIR-ring resonator is being applied for broadband studies by adapting piezoelectric couplers for in-vacuum control. Furthermore, a CRADA with Informed Diagnostics Inc. (IDI) facilitated the development of a commercial prototype instrument based on gas-phase diode laser CRDS²¹.
- g. Projects #60231 and 73844 have opened up a new and rich area of research since a new tool has been developed that permits extreme sub-monolayer detection of adsorbed molecules on an important surface without the need for ultra-high vacuum. The work has

demonstrated that the cavity ring-down concept can be applied to such problems. In particular, we have shown that overtones and combination bands in the near-IR can be used to probe sub-monolayer chemistry, which is a unique contribution to surface science. Furthermore, new fundamental knowledge has been obtained on the creation of contamination resistant surfaces.

h. EW-CRDS is still in its infancy. More basic research investigations are needed to design rugged sensing surfaces. For example, atomic layer deposition techniques could be used to grow hard Al₂O₃ coatings on the comparatively “soft” silica surface. Further, polymer coatings could be used to provide analyte enrichment in the evanescent wave while providing protection of the ultra-smooth silica surface from contamination or physical damage.

i. Information was sent to DOD and DTRA in response to their request. A licensing agreement with Informed Diagnostics Inc. (Sunnyvale, CA) was negotiated, although IDI has since dissolved. Analytical Specialties Inc. (Houston, Texas) and Tiger Optics Inc. (Warrington, PA) have expressed interest in EW-CRDS. Additional information on licensing activity can be obtained from Terry Lynch at NIST (301-975-2691)

5. Project Productivity

Project 60231 demonstrated the feasibility of EW-CRDS through several working prototypes, which obtained or exceeded proposed sensitivity levels. Further, much of the fundamental measurement science underlying EW-CRDS was elucidated, which is critical for a newly developing technology. Project 73844 extended EW-CRDS to the near-IR where DOE-relevant species were detected with high sensitivity. Further, Project 73844 yielded a new class of resonators for optimal application of EW-CRDS to liquids. In addition, Project 73844 contributed to our understanding of molecular recognition and the development of contamination resistant surfaces. Overall, the accomplishments of Projects 60231 and 73844 have produced a new chemical sensing technology and a unique basic research tool.

6. Personnel Supported

During the first year of Project 60231, Dr. Andrew C. R. Pipino and Dr. Jeffrey W. Hudgens were supported, whereas during FY99 and FY00 only Dr. Pipino was supported, as the Principal Investigator. Dr. Pipino continued as the Principal Investigator throughout Project 73844. Within the Biotechnology Division, Drs. John T Woodward, Vitalii Silin, David Vanderah, and Curtis Meuse were all supported to varying degrees under Project 73844.

7. Publications

1. A. C. R. Pipino, “Monolithic optical resonator for evanescent wave cavity ring-down spectroscopy of liquids”, in preparation.
2. I. M. P. Aarts, A. C. R. Pipino, J. P. M. Hoefnagels, W. M. M. Kessels, and M. C. M. van de Sanden, “Highly Ordered Water Layer on a Smooth Amorphous-Silica Surface”, in preparation.

3. A. C. R. Pipino and Vitalii Silin, "Gold nanoparticle response to nitro-compounds probed by cavity ring-down spectroscopy", submitted.
4. A. C. R. Pipino, J. P. M. Hoefnagels, and N. Watanabe, "Absolute surface coverage measurement using a vibrational overtone", *J. Chem. Phys.* 120 (6), 2879, (2004).
5. A.C. R. Pipino, J. T. Woodward, C. W. Meuse, and V. Silin, "Surface-plasmon-resonance-enhanced cavity ring-down detection", *J. Chem. Phys.* 120 (3), 1585, (2004).
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8. D. J. Vanderah, T. Parr, V. Silin, C. W. Meuse, R.S. Gates, H. La, "Isostructural Self-Assembled Monolayers. 2. Methyl 1-(3-Mercaptopropyl)oligo(ethylene oxide)s, *Langmuir* 20, 1311, (2004) .
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15. A. C. R. Pipino in *Advanced Sensors and Monitors for Process Industries and the Environment*, W. A. De Groot, editor, Proc. of SPIE, Vol. 3535, p 57, Boston, Mass. 1998.
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8. Interactions

1. "Using cavity ring-down spectroscopy to characterize OH-content and absolute loss in silica glass", December 17, 2003, Heraeus-Tenevo, Hanau, Germany.
2. "Using cavity ring-down spectroscopy to probe adsorbed molecules and nanoparticles", December 15, 2003, Universität Ulm, Abt. für Oberflächenchemie und Katalyse, Ulm, Germany.

3. "Characterization of a Series of Self-Assembled Monolayers of Methyl 1-(3-Mercaptopropyl)oligo(ethylene oxide)s" 77th ACS Colloid and Surface Science Meeting, Atlanta, GA, June 16, 2003.
4. "*Novel Applications of Cavity Ring-Down Spectroscopy*", December 2, 2003, Eindhoven University of Technology, Eindhoven, The Netherlands.
5. "*Novel Chemical Detection Strategies for Trichloroethylene and Perchloroethylene*", Environmental Management Science Program (EMSP) Symposium, September 10, 2003, ACS National Meeting, New York City.
6. "Oligo(ethylene oxide) Self-Assembled Monolayers: Protein Resistance and Thin-film Metrology Tools", 2003 Gordon Research Conference on Organic Thin Films, Barga, Italy, May 18-23. Poster.
7. "*Evanescent wave cavity ring-down spectroscopy*", Symposium on Next Generation Environmental Sensors, March 22, 2002, Pittsburgh Conference, New Orleans, LA.
8. "*Evanescent wave cavity ring-down spectroscopy*", March 12, 2002, Department of Chemistry, Georgetown University, Washington, DC.
9. "*Evanescent wave cavity ring-down spectroscopy*", February 20, 2002 Meeting of the Spectroscopy Society of Pittsburgh (SSP), Duquesne University, Pittsburgh, PA.
10. "Helical, Disordered, and What that Means: Structural Characterization of a New Series of Methyl 1-Thiaoligo(ethylene Oxide) Self-Assembled Monolayers", Spring Material Research Society Meeting 2002, San Francisco, CA., April 3, 2002.
11. "*Ultra-high-Q mini-cavity sensors*", January 24, 2002, Symposium on Laser resonators and Beam Control V, LASE 2002, SPIE Photonics West, San Jose, CA. "Self-Assembled Monolayers of HS(CH₂)_{0 or 1}(CH₂CH₂O)_{5 or 6}CH₃. 76th ACS Colloid & Surface Science Symposium, Univ. of Michigan, Ann Arbor, MI., June 24, 2002.
12. "*Evanescent wave cavity ring-down spectroscopy: A future technology for Process Sensing*", January 23, 2001, International Forum on Process Analytical Chemistry (IFPAC), Amelia Island, Florida.
13. "Methyl 1-Thiahexa(ethylene oxide) Monolayers for the Inhibition of Protein Adsorption", American Physical Society Meeting, Seattle, WA, March 13, 2001.
14. "*Evanescent wave cavity ring-down spectroscopy*", March 2001, DOW Chemical Co., Freeport, Texas.
15. "*Novel miniature spectrometer for remote chemical detection*", June 19, 2000, Environmental Management Science Program (EMSP) Sensors Workshop, Idaho Falls, Idaho.
16. "*Novel miniature spectrometer for remote chemical detection*", April 2000, Environmental Management Science Program (EMSP) National Meeting, Atlanta, Ga.
17. "*Extending cavity ring-down spectroscopy to surfaces, films, and liquids*", April 16, 1999, Northwestern University Chemistry Colloquium, Outstanding Graduate Thesis (1995) Award Presentation, Evanston, Illinois.

18. "Novel miniature spectrometer for remote chemical detection", Sept. 22, 1999, Environmental Management Science Program (EMSP) Symposium, Oak Ridge, TN.
19. "Evanescent wave cavity ring-down spectroscopy with a total-internal reflection minicavity", Oct. 27, 1998, NIST/CSTL Technical Achievement Award Seminar, Gaithersburg, Maryland.

9. Patents

1. A. C. R. Pipino, "Optical Probes for Chemical and Biochemical Detection in Liquids", US Provisional Application Serial No. 60/540,419, filed 2/04.
2. *Sensitive and selective chemical sensor with nanostructured surfaces*, A. C. R. Pipino, U. S. Patent # 6,515,749, issued Feb. 4, 2003.
3. *Intra-cavity total reflection for high sensitivity measurement of optical properties*, A. C. R. Pipino, U.S. Patent No. 5,986,768, issued Nov. 16, 1999.
4. *Intra-cavity total reflection for high sensitivity measurement of optical properties*, A. C. R. Pipino et al. U. S. Patent No. 5,943,136, issued Aug. 24, 1999.
5. *Broadband intra-cavity total reflection chemical sensor*, A. C. R. Pipino, U. S. Patent No. 5,835,231, issued Nov. 10, 1998.

10. Future Work

The development of EW-CRDS is in its infancy. More fundamental studies are needed. However, application of EW-CRDS to TCE detection using a monolithic folded resonator has the greatest potential for near-term field trials. The resonator could be coating with a polysiloxane polymer to yield a sensitive, selective, and robust sensor for both remediation and long-term monitoring applications, where the polymer protects the sensing surface and enriches the TCE concentration in the evanescent wave region. While chemically selective films employing molecular recognition do not yet appear to be sufficiently robust for field applications, polysiloxane polymers, which provide an enrichment mechanism based on simple partitioning, are currently used in many rugged environments. Furthermore, polysiloxane polymers have been applied previously for near-IR TCE detection with a waveguide sensing platform.

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