

Project Title: Miniature Chemical Sensor combining Molecular Recognition
with Evanescent Wave Cavity Ring-Down Spectroscopy

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Research Objective

To address the chemical sensing needs of DOE, a new class of chemical sensors is being developed that enables qualitative and quantitative, remote, real-time, optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases by employing evanescent wave cavity ring-down spectroscopy (EW-CRDS). The feasibility and sensitivity of EW-CRDS was demonstrated previously under Project #60231. The objective of this project is to enhance the selectivity and domain of application of EW-CRDS. Selectivity is enhanced by using molecular recognition (MR) chemistry and polarized “fingerprint” near-IR spectroscopy, while the domain of application is expanded by combining EW-CRDS with the unique optical properties of nanoparticles and by extending the technique to liquids.

Research Progress and Implications

This report summarizes work conducted during the third year of a 3-year project. Third year activities have produced successful results in three key areas: 1) very sensitive detection ($\sim 10^{-8}$ mol/L) of perchloroethylene (PCE) and trichloroethylene (TCE) has been achieved at a visible wavelength by combining CRDS with the surface plasmon resonance (SPR) response of gold nanoparticles, 2) selective detection with determination of absolute surface coverage of cis-dichloroethylene (c-DCE), trans-DCE, and TCE by EW-CRDS has been achieved, and 3) new class of resonators to permit EW-CRDS in liquids as described in detail in the proprietary information section has been conceived, modeled, and a selected design is in fabrication.

CRDS was used to probe the absolute optical response of the SPR of a gold nanoparticle distribution to adsorption of trichloroethylene (TCE) and perchloroethylene (PCE) from the gas phase. An approximately Gaussian distribution of nanospheres with a mean diameter of 4.5 nm and a standard deviation of 1.1 nm, as determined by atomic force microscopy, was provided by the intrinsic granularity of an ultra-thin, gold film, having a nominal thickness of ~ 0.18 nm. Based on a relative decay time precision of 0.1 % for ensembles averages of 25 laser shots from a pulsed optical parametric oscillator (OPO), the minimum detectable concentrations of PCE and TCE were found to be 2×10^{-8} mol/L and 7×10^{-8} mol/L, respectively, based on a 30 s integration time. The measurements employed a linear resonator with an intra-cavity flow cell, which was formed by a pair of ultra-smooth, fused-silica optical flats at Brewster's angle, where the Au film was present on a single flat. Extended Mie theory for a coated sphere with a particle-size-dependent dielectric function was used to elucidate size-dispersion effects, the size-dependence of the SPR sensitivity to adsorption, and the kinetics of adsorption. A manuscript describing these results in detail is currently in review. A NIST internal report (NISTIR #6957) will soon be available describing the preliminary results of this work.

The absolute number densities of cis-dichloroethylene (c-DCE), trans-dichloroethylene (t-DCE), and trichloroethylene (TCE) adsorbed on a silica monolithic folded resonator were determined using the first C-H stretching overtones. Gas-phase CRDS measurements of known concentrations provided absolute absorption cross sections for these species, while EW-CRDS measurements provide absolute adsorbed-phase spectra. The absolute surface number densities were then found by invoking conservation of the integrated line strength with adsorption. The requisite measure of molecular orientation of the adsorbed species was provided by the polarization anisotropy of the surface spectra. The C-H overtone spectra of the three haloethylenes was probed around 6050 cm^{-1} using the idler of the pulsed OPO. The EW-CRDS measurements employ a fused-silica monolithic folded resonator with a peak finesse of $\sim 28,500$ around 1650 nm. An independent determination of absolute surface coverage for TCE on an SiO_2

surface was provided by mass-spectrometer-based uptake measurements through a collaboration with researchers at the University of Maryland (UMD-CP). The sensitivity of EW-CRDS for TCE detection using the first C-H overtone with an unclad resonator surface was found to be comparable to that obtained for a long-effective-path-length waveguide with a TCE-enriching polysiloxane coating (parts-per-thousand level; enrichment $\sim \times 300$). Therefore, by combining the EW-CRDS technique with the TCE-enriching polysiloxane coating, part-per-million level detection should be feasible. The polysiloxane coating would also serve to protect the resonator surface and prevent interferants (e.g., particles) from entering the evanescent wave region without significantly increasing the response time. Furthermore, the distinctive C-H overtone spectra for each compound, together with the corresponding spectral polarization anisotropies, provide a high degree of selectivity.

EW-CRDS measurements have also been performed in the 940 nm region using an existing monolithic TIR-ring resonator to evaluate the transmission properties of very low OH content fused silica and to assess the potential for using EW-CRDS as a humidity sensor. The low OH (estimated at 50 ppb bulk content) material was found to provide a very low bulk loss of < 10 ppm loss/cm @ 925 nm. Additional measurements are planned in FY2003 to examine the polarization anisotropy of the small OH loss signals at 940 nm and 1380 nm, which will then allow an initial assessment of the humidity sensing capability of EW-CRDS.

Concerning molecular recognition, IR-ATR was used to examine the adsorption of PCE to multilayers of molecular cavitand, indicating that upon adsorption to the cavitand, the 920 cm^{-1} band of gas-phase PCE shifts to 910 cm^{-1} . Transmission infrared was used to observe the adsorption of PCE and TCE to disordered monolayers of cavitand from CHCl_3 and ordered cavitand (ordering induced by 60°C annealing overnight in a 7/3 mixture of CHCl_3 and ethanol) as well as control surfaces of BaF_2 and an octadecanethiol monolayer. These measurements indicated that PCE and TCE prefer to adsorb to ordered cavitand rather than disordered cavitand. Further, PCE shows greater partitioning into the cavitand surface than does TCE, although the signal-to-noise ratio of these measurements preclude an analysis of the orientation distribution of PCE or TCE bound to the cavitand to identify the existence of specific molecular recognition for vapor binding. Our previous SPR kinetic uptake data in water indicated that the adsorption of PCE and TCE to the cavitand layers is not selective. The preparation of a novel resorcin[4]arene, which possesses only a single γ -mercaptopolymethylene segment for surface binding compared to four dialkylsulfides in the cavitand used to this point in the work, is in progress. This new molecule will also be tested for selective binding of PCE and TCE.

Finally, an array of γ -CH₃-terminated oligoethylene oxide (OEO) surfaces with variable composition were prepared and evaluated to determine the molecular structural requirements for the design of an inert matrix to prevent binding of interferants to an EW-CRDS sensing surface. SPR data with TCE, PCE, and proteins (bovine serum albumin, fibrinogen, and lysozyme) show that relatively high but less than complete packing densities for the OEO surface layer appear to be optimal. Hence, slightly disordered surfaces appear to resist non-selective adsorption of large and small interferants.

Planned Activities

We have applied for a 1 year no-cost extension. During the remainder of FY03 and into FY2004 if the no-cost extension is granted, we will continue our molecular recognition studies, combine the nanoparticle sensing with EW-CRDS, and test the new resonator design for liquids (proprietary information section). Depending on the outcome of these studies, we will explore the use of both direct spectroscopic detection and nanoparticle-based detection in an aqueous media.

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