

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 sensitivity of EW-CRDS was demonstrated previously under Project #60231. The objective of this project is to enhance the range of application and selectivity of the technique by combining EW-CRDS with refractive-index-sensitive nanoparticle optics, molecular recognition (MR) chemistry, and by utilizing the polarization-dependence of EW-CRDS.

Research Progress and Implications

This report summarizes work conducted during the second year of a 3-year project. Second year activities have produced successful results in key areas: 1) detection of non-absorbing perchloroethylene (PCE) by combining cavity ring-down spectroscopy (CRDS) with the surface plasmon resonance response of gold nanoparticles, and 2) detection of trichloroethylene by polarization-dependent EW-CRDS. Additional studies of molecular recognition-enhanced selectivity and high sensitivity water detection have also been pursued, although a decisive outcome in these areas is still pending. Using NIST capital equipment funds, a pulsed optical parametric oscillator/amplifier was purchased and installed, providing a wavelength tuning range of 440 nm to 1830 nm to cover all of the optical diagnostic needs of the project. In addition, an exclusive-license agreement for the EW-CRDS patents, which covers environmental sensing applications, is being negotiated between NIST and Meeco/Tiger Optics of Warrington, PA. Tiger Optics is the only company so far to successfully produce a commercial product based on CRDS.

Detection of PCE has been achieved with CRDS at a visible wavelength where PCE has no appreciable absorption by exploiting the surface plasmon resonance response of gold nanoparticles. Ultra-smooth optical flats, which are tilted at Brewster's angle to form windows of a flow cell, were coated with a very low density of approximately oblate spheroidal Au nanoparticles, as revealed by atomic force microscopy. These nanoparticles are known to possess a strong visible absorption which is sensitive to adsorption at the particle's surface. To generate Au nanoparticles, we utilized the natural granular structure which exists for ultrathin vapor deposited Au films with additional control provided by a deposition mask. Identifying the optimal nanoparticle preparation conditions was a significant second year activity. Gold deposition conditions and the spatial mask configuration were varied to find conditions that provided maximum response to PCE, while providing a sufficiently long ring-down time for digitization. Optimal conditions were found in which a 0.8 nm average thickness Au film was deposited through two stacked 2000 Mesh grids with 5 x 7 micrometer holes, followed by annealing at 750 degrees C for 2 minutes in Ar. Atomic force microscopy revealed discontinuous films having surface features of 10 nm diameter and 2 nm height with a density of several hundred per square micron. These conditions provided a detection sensitivity for PCE of approximately 100 parts-per-million at atmospheric pressure. Since a significantly different response from Au nanoparticles was observed for TCE versus PCE, some selectivity may be derivable from the pure Au nanoparticles response based on refractive index or sticking coefficient differences.

We have also been modifying the nano-particles with "bowl-shaped" resorcin[4]arene molecular cavitands, which were originally demonstrated to possess enhanced selectivity for PCE, since the molecular bowl is optimally sized for PCE. However, this conclusion has been questioned in recent years, with studies suggesting instead that a simple hydrophobic interaction can account for the effect. We deposited the resorcin[4]arene tetrasulfide cavitand on the gold surfaces using the

literature procedure from 0.25 mmol solution of 7:3 vol/vol mixture of ethanol: chloroform at 60 degrees for ~16 hours. Prior to deposition, the cavitand was purified by chromatography, yielding a purity of > 99 % as confirmed by NMR analysis. Our infrared spectroscopic analysis of cavitands on thick Au films reveals that the higher temperature deposition creates a more ordered layer as reported (J. Amer. Chem. Soc., 117, 6853 (1995)), compared to room temperature conditions used for other calix[4]resorcinarene tetrathiol monolayers (Langmuir, 17, 1470, (2001)). Therefore, the higher temperature procedure was used to encourage efficient packing on the particles, since packing density may influence surface binding of PCE. However, packing of the cavitands may be quite different on Au nanoparticles than on thick Au films. So far, we have not observed enhanced selectivity with cavitands in our gas phase studies.

To improve selectivity, we are developing a surface film, which prevents non-specific binding, to fill the spaces between cavitands on the sensing surfaces. Work done in parallel (Langmuir 18, 4674, (2002)) shows that disordered monolayers of methyl 1-thiahexa (ethylene oxide) are resistant to protein adsorption. The ability of methyl 1-thiahexa (ethylene oxide) surfaces to resist contamination such as protein, supports our idea to use it as a matrix material in our sensors. To compare and contrast the properties of methyl 1-thiahexa (ethylene oxide), alkanethiol and cavitand surfaces, we also performed surface plasmon resonance (SPR) measurements of adsorption of PCE and TCE to cavitand, alkanethiol, and methyl 1-thia hexa (ethylene oxide) covered surfaces in aqueous solutions. These measurements yielded adsorption curves of PCE and TCE to cavitand and alkanethiol surfaces, while indicating no detectable binding on the ethylene oxide layer. Since the ethylene oxide covered surfaces do not absorb PCE and TCE, this effect provided a correction for the SPR response arising from the bulk refractive index change associated with the the introduction of PCE or TCE into the flow stream. The pure surface-binding response of the cavitand- and alkanethiol-covered surfaces could then be extracted. By comparing the adsorption data for PCE and TCE on cavitand and alkanethiol covered surfaces, we found that the initially adsorbed layers for these two analytes showed similar kinetics. This result suggests that the cavitands probably do not specifically recognize the PCE and TCE *in aqueous solutions*.

EW-CRDS experiments of TCE detection by direct absorption near 1640 nm have also been performed using a monolithic, folded resonator (MFR). The absorption spectrum of adsorbed TCE on the folded resonator surface was obtained, along with the polarization dependence of the absorption. With a dosing pressure near the atmospheric vapor pressure of TCE, multiple peaks are observed in the spectrum, suggesting multiple forms of adsorbed TCE on the surface. Although polarization measurements cannot decisively determine molecular orientation at the surface, these measurements suggest the existence of an isotropic component for the adsorbed layer under these dosing conditions. The sensitivity for TCE detection is currently in the range of a part-per-thousand. However, a significant improvement can be expected by shifting the high-reflectivity coating center wavelength from 1650 nm to ~1550 nm, thereby increasing the resonator throughput above 1605 nm, where the InGaAs detector sensitivity begins to fall off rapidly. EW-CRDS measurements have also been performed in the 940 nm region using an existing MFR to detect water, i.e., for humidity sensing. Initial results indicate a need for a resonator material with a lower OH content than our existing MFRs. However, we have several square total-internal-reflection ring cavities that are fabricated from extremely low OH (50 ppb) material. These measurements are in the queue for the remainder of FY2002.

Planned Activities

During the remainder of FY02, we will complete our studies of refractive index sensing with

Au nanoparticles and direct detection of TCE. We will also expect to complete our assessment of using EW-CRDS for water detection. During FY03, we will complete our studies of detection selectivity with molecular cavitands and continue to pursue EW-CRDS experiments in liquids, which have been delayed due to lack of an acceptable resonator material.

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