

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

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Research Objective

To address DOE's chemical sensing needs, a new class of chemical sensors is being developed to enable 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 achieve highly selective chemical detection in a complex matrix of interferants by combining EW-CRDS with molecular recognition (MR) chemistry and by exploiting the polarization-dependence of EW-CRDS to enhance optical selectivity.

Research Progress and Implications

This report summarizes work conducted during the first 0.75 years of a 3-year project. First year activities have focussed on 1) adding or upgrading laboratory capabilities, 2) studies of sensing with nanostructured surfaces, and 3) the synthesis and characterization of a MR film for PCE. Two publications and one patent have been submitted during this time. Our licensing agreement for the EW-CRDS technology with Informed Diagnostics Inc. (IDI) remains active, although the company focus has shifted to the medical marketplace. However, the DOW Chemical Company has expressed considerable interest in EW-CRDS. We are expecting a guest researcher from DOW to arrive on 9/1/01 to work on applications of EW-CRDS, including detection of TCE. DOW is interested in supporting the commercialization of EW-CRDS through a commercial partner, Analytical Specialties Inc. (ASI) of Houston, Tx. ASI has expressed significant interest in the TCE marketplace.

In preparation for planned experiments, we have added or upgraded our laboratory capabilities. A new laser system (a pulsed Optical Parametric Oscillator (OPO)) has been purchased (165K) through the NIST capital equipment fund and is expected to arrive August 15, 2001. The OPO system will provide tunability over a very broad range of wavelengths from 445 nm to 1750 nm with additional wavelength extension to nearly 4000 nm by frequency mixing (hardware included). The broad wavelength tuning range of the OPO is important to the project since it provides maximum flexibility to probe many different species of interest to DOE as well as the presence of contaminants and possibly surface reaction by-products. Also, the selected OPO system has been successfully applied elsewhere to nonlinear optical experiments which demand a well-controlled beam profile. Therefore, we anticipate that this system will permit near-single-mode cavity ring-down measurements, providing the highest EW-CRDS sensitivity. We have upgraded our data acquisition system and software from an 8-bit digital oscilloscope to two 12-bit, PC-based data acquisition boards. We have also completed construction of a molecular-drag-pumped chamber with pressure diagnostics that accommodates multiple monolithic, folded resonators (MFRs) for EW-CRDS and mirror mounts for gas-phase CRDS. A double-Brewster-plate resonator cell for rapid testing of MR films, has also been constructed. In both of these sampling chambers, gas-phase dosing with a selected analyte at a selected concentration is accomplished using a flow system incorporating a mass flow controller and permeation tubes. Design of MFRs for liquid phase EW-CRDS is complete. The MFRs will be fabricated from undoped YAG, which showed acceptable transmission in linear cavity CRDS measurements. A fused-silica MFR has been coated for TCE detection at 1650 nm, which will employ the new OPO system.

Studies of sensing with nanostructured surfaces have employed the double-Brewster-plate resonator. This configuration permits rapid testing of MR films deposited on optical flats, although the response is superimposed on the gas phase absorption spectrum, if present. We first coated optical flats with gold nanospheres (commercially available, 20 nm diameter, in citrate solution), since these small metal particles have a distinct surface plasmon resonance (SPR) at ~ 520 nm, which is responsive to adsorbates. A spectrum was obtained by CRDS which peaked at ~ 530 nm. Atomic force microscopy (AFM) also confirmed the presence of gold nanospheres on the surface at low density. We used NO₂ in dry nitrogen as the analyte for these initial studies, since NO₂ has shown a strong, selective response in SPR experiments on thick vapor deposited gold films. We observed a response when the nanoparticles were exposed to the analyte that could be attributed to gas-phase background only, suggesting that the citrate layer known to cover the particles deposited from solution was dominating the SP response. Several unsuccessful attempts were made to remove the citrate layer through exchange equilibria. To generate Au nanoparticles without an intermediate solution phase step, we utilized the natural granular structure which exists for ultrathin vapor deposited Au films. AFM and spectroscopic ellipsometry of the ultrathin (~ 1-3 nm) Au films confirmed the granular structure and the presence of a distinct SPR, respectively. The ellipsometry showed a peak at ~ 600 nm that shifted to ~ 550 nm with annealing, suggesting a transition

from needle-like particles to a more spherically shaped particle. However, these films showed too large an attenuation for CRDS measurements. We expect that if a mask is used to create a patterned deposition of Au nanoparticles, this attenuation can be adjusted to an optimum level. We plan to use a mask that has been generated by micromachining techniques. A strategy to create nanoparticle-covered surfaces by vapor deposition with masking could be commercially viable.

The preparation of the "bowl-shaped" resorcin[4]arene molecule, $-[1,3\text{-bis}(\text{XO})\text{C}_6\text{H}_2\text{-4-CHR}]_4-$, where $\text{X} = \text{H}$ and $\text{R} = (\text{CH}_2)_8\text{S}(\text{CH}_2)_9\text{CH}_3$, which shows high selectivity for PCE and self-assembles into densely packed monolayer films, has been successfully completed. The synthesis was accomplished in three steps. First, resorcinol was condensed with undecylenyl aldehyde under acidic conditions to give ($\text{X} = \text{H}$, $\text{R} = (\text{CH}_2)_8\text{CH}=\text{CH}_2$). In contrast to literature reports, we obtained nearly quantitative organic yield and although this material was far from pure, we did not observe the presence of intensely red impurities. The synthesis was continued without further purification of this material. Next, condensation of this octahydroxy compound with bromochloromethane under alkaline conditions and yielded the "capped" compound ($\text{X}, \text{X} = \text{CH}_2$, $\text{R} = (\text{CH}_2)_8\text{CH}=\text{CH}_2$). Attempts to purify this material by literature methods were unsuccessful but alternative purification protocols (chromatography and recrystallization) were successful (purity > 95%). Finally, the target compound [$\text{X}, \text{X} = \text{CH}_2$, $\text{R} = (\text{CH}_2)_8\text{S}(\text{CH}_2)_9\text{CH}_3$] was prepared by the anti-Markovnikov addition of 1-decanethiol to the double bonds using 9-borabicyclononane (9-BBN) as catalyst. All compounds were characterized by proton (^1H)- and ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. The ^1H - and/or ^{13}C -NMR spectra of the last two compounds exactly matched those previously reported. The ^1H NMR spectrum of $-[1,3\text{-bis}(\text{XO})\text{C}_6\text{H}_2\text{-4-CHR}]_4-$, where $\text{X} = \text{H}$ and $\text{R} = (\text{CH}_2)_8\text{S}(\text{CH}_2)_9\text{CH}_3$, indicate small amounts of impurities. Final purification is in progress.

Planned Activities

During the remainder of FY01 and during FY02 detection of TCE and water will be studied by EW-CRDS using MFR's, the OPO laser system, the molecular-drag-pumped sample chamber, and the flow system. We add H_2O to our list of analytes for several reasons: 1. DOE is interested in water detection in arid environments (NV-18, NV-01), 2) our new commercial partner is interested in trace water detection, and 3) the nascent -OH present on fused silica may serve as a natural molecular recognition layer. Also, DOE is interested in tritium detection and water serves as a surrogate for tritium oxide. Detection limits, adsorption isotherms, response times, and polarization dependence will be studied for TCE and water. A model will be developed to interpret the polarization-dependent response of EW-CRDS, which will facilitate a general understanding of the effect of refractive index change, film thickness, mass distribution, molecular orientation, and surface anisotropy in general on EW-CRDS measurements.

We will continue experiments with the Brewster plate resonator on ultrathin Au films generated by vapor deposition by using a micromachined mask as mentioned. However, we will also use conventional SPR measurements to characterize our MR films. Our SPR laboratory is fully equipped for this purpose and substantial in-house expertise is available. In particular, we will use SPR to characterize the response of monolayer films of molecular cavitands to PCE. We will also explore modification of the cavitands to increase selectivity to TCE by altering the symmetry of the cavitand bowl structure. EW-CRDS experiments will be carried out using films that successfully demonstrate the desired selective response.

In addition, undoped-YAG MFRs for liquid phase EW-CRDS will be fabricated, along with a cell for liquid phase studies.

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