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 range of application of EW-CRDS. Selectivity is achieved spectroscopically by using vibrational overtones in the near infrared and chemically by using modified surfaces to encourage selective adsorption of analyte while preventing non-selective adsorption. The range of application is expanded by extending EW-CRDS to liquids and by combining EW-CRDS with the unique optical properties of nanoparticles.

Research Progress and Implications

This report summarizes work conducted during the fourth year of a 3-year project under a no-cost extension. Fourth year activities have produced successful results in four key areas: 1) A novel optical resonator has been successfully fabricated and tested for applications of EW-CRDS in liquids. 2) New results on the use of molecular cavitands, which have been reported to show molecular recognition for PCE, have been obtained, proving a selective host-guest interaction for ethyl acetate. Further, in an effort to create surfaces that resist contamination or other non-specific adsorption, the role of chemical structure and surface order for oligo(ethylene oxide) [OEO] covered surfaces, which are known to show resistance to non-selective adsorption, has been investigated, yielding new sights which will enable contamination resistant surfaces to be optimally designed for a given application. 3) Concerning the use of nanoparticle optical properties with CRDS, very sensitive detection ($>10^{-10}$ mol/L) of nitro-containing compounds has been achieved by combining CRDS detection with the surface plasmon resonance (SPR) response of gold nanoparticles. In particular, detection of 2,4-dinitrotolune (DNT), which is often present in TNT-based explosives, has been demonstrated with very high sensitivity. 4) Using a new monolithic folded optical resonator, which is fabricated from low-OH content fused silica, we have demonstrated sub-monolayer detection of O-H and C-H containing compounds using *second-order* overtones and combination bands by EW-CRDS, an ability that arises from a newly obtained $3x10^{-8}$ minimum detectable absorption (~x10 improvement over previous). Finally, our previously pending manuscripts in the 2003 report have been published.

As described in our recent patent application, a new class of optical resonators for EW-CRDS of liquids has been conceived based on ultra-low-loss optical contacting. Novel resonator designs are achieved by contacting multiple components to form integral sensing elements with low-loss, mechanically strong bonds between components that enable practical EW-CRDS probes with high chemical detection sensitivity to be realized for immersion applications. A specific resonator design was selected from this general class of designs for fabrication and testing. The new design provides a minimum detectable absorption for both TE and TM polarizations of $\sim 2x10^{-7}$ based on a base loss of $220x10^{-6}$ and a decay time measurement precision of 0.1% for a 25 laser shot average. The useful (high sensitivity) bandwidth of the resonator is ~100 nm. Five total internal reflection surfaces are available for probing the ambient immersion medium, providing an additional enhancement in sensitivity. As input and output beams are counterpropagating and closely spaced, the new design can be readily integrated into a practical immersion probe design. Furthermore, a thick polymer or other coating could be used with the new design to enhance the local concentration of analyte in the evanescent wave while protecting the ultra-smooth resonator surfaces, thereby forming a sensitive, selective, and robust chemical sensor.

Concerning enhancement of selectivity by chemical means, we have confirmed host-guest complex formation of resorcin[4]arene cavitand, with ethyl acetate. Proton (^{1}H) nuclear magnetic resonance (NMR) of recrystallized cavitand from 30% ethyl acetate/hexanes, indicated an exact ratio of ethyl acetate to resorcin[4]arene of 1/1. The NMR showed no evidence of hexane and suggested a host-guest ethyl acetate-cavitand association. X-ray crystallographic analysis of the crystals (twinned), confirmed that the ethyl acetate was associated in the cavitand "cup". These results suggest that resorcin[4]arenes of this type may be useful in small molecule metrology and chemical sensors, while the literature shows considerable controversy over this point since a non-specific hydrophobic interaction has been invoked to explain many observations. Concerning the creation of contamination resistant surfaces, we have identified the effects of a short polymethylene (C_3) chain on the surface ordering of a series of ω-methyl oligo(ethylene oxide) SAMs {$HSCH_2CH_2CH_2O$-$(CH_2CH_2O)_xCH3$, designated C_3EO_x], where x = 3 to 9. The conformational order changes over this range of x from highly ordered SAMs for C_3EO_{5-7} to more disorder for $C_3EO_{3,4,8\&9}$ providing the potential to control the efficacy of contamination resistance, which is influenced by surface order. Contamination resistance of surfaces coated with $HS(CH_2)_3O(CH_2CH_2O)_5CH_3$, as measured by (conventional) SPR response to protein adsorption, exhibited minimal non-specific adsorption at ~ 60% OEO coverage. The common onset range (~60% to ~ 80% OEO surface coverage) of minimal protein adsorption indicates that high resistance to adsorption is optimized with loosely packed, uniformly distributed OEO oligomers. Reflection-adsorption IR data shows that wide spread order is not present at ~ 60% coverage indicating that the bound oligomers are conformationally mobile. The surface at ~60% coverage apparently exhibits resistance to further adsorption of any unbound species including additional $C_3(EO)_5$ as well as the larger proteins.

Concerning the use of nanoparticle optical properties with CRDS, sensitive detection of TCE and PCE was demonstrated in previous years by probing the SPR response of Au nanoparticles with CRDS as described in Ref 6 below. We have extended these studies to NO_2-containing compounds, since many explosives contain this functional group. Further, Au surfaces have shown a unique propensity to bind NO_2 in a bidentate chelate bonding configuration, while previous conventional Au film SPR measurements showed a uniquely strong and selective response to NO_2. These observations in the literature suggested that detection of NO_2-containing compounds by probing the SPR response of Au nanoparticles with CRDS would be worthwhile. Indeed CRDS-SPR response to NO_2, nitrobenzene, and DNT yielded a very sensitive response, which appears to be NO_2 group specific. These measurements employed nanoparticle films generated under the same conditions are previous work, which yielded a mean diameter of 4.5 nm and a relative standard deviation of 24%. A manuscript describing these results is currently in preparation.

Finally, using a new monolithic folded optical resonator for EW-CRDS fabricated from ultra-low-OH content fused silica with ultra-high reflectivity coating centered at 1200 nm, we have observed O-H and C-H *second-order* overtones and combination bands. This remarkable sensitivity derives from the ultra-low loss of the resonator of $25x10^{-6}$ at the center wavelength. Further, both C-H and O-H bands are present within the coating bandwidth of the resonator.

Planned Activities

During the remainder of the FY04 no-cost extension, we will continue our experiments on chemical detection by EW-CRDS in liquid media and detection of second order overtones and combination bands.

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