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Project Title: **Novel Miniature Spectrometer for Remote Chemical Detection**

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RESEARCH OBJECTIVE:

A entirely new class of chemical sensors is being developed that will enable qualitative and quantitative remote, real-time, optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases through a completely novel implementation of cavity ring-down spectroscopy. The sensor design uses a tiny, solid block (< $1cm^3$) of ultra-high purity optical material that is fabricated into a regular, planar polygon with a single convex facet to form a total-internal-reflection (TIR) ring minicavity. The lifetime of a light pulse that is injected into the cavity is extremely sensitive to chemical species in contact with the cavity. By using optical fiber to remotely locate the light source and detector, this new technology will permit high-sensitivity, remote chemical sensing with a rugged, cost-effective device.

RESEARCH PROGRESS AND IMPLICATIONS:

This report summarizes work conducted after the second year of a 3-year project. In brief, the performance of the technology is reaching or exceeding expectations. A commercial partner has been found and, based on contact with personnel at the Savannah River Site, deployment of the technology in a cone penetrometer may be possible. A Cooperative Research and Development Agreement (CRADA) is being negotiated with Informed Diagnostics Inc., (IDI), to develop and build prototype, portable, miniature spectrometers, which will be fiber-optic-coupled to inexpensive diode laser sources. Based on improvements in cavity ring-down detection, the availability of ultra-high transmission optical materials, and reduction in fabrication costs, the technology may exceed initial expectations of performance. However, the new level of sensitivity permitted by the technology may give rise to new fundamental measurement-science questions.

Using a square, fused-silica, TIR-ring minicavity, detection of an extremely small fraction ($6x10^{-5}$) of an adsorbed monolayer of iodine can now be routinely achieved, which shows a significant improvement over initial efforts. This sensitivity level was achieved using an excimer-pumped, pulsed dye laser and a commercial 8-bit, 1-Ghz digital oscilloscope to acquire the ring-down decays. By employing a diode laser source and a 12 bit digitizer, an additional improvement of 10-100 over this sensitivity should be obtained. The evanescent optical field at the cavity facets, where chemical detection occurs, has a well-defined, easily calculated direction and magnitude for the in-plane and out-of-plane polarization directions, which allows molecular orientation to be probed. Since the orientation of an adsorbed molecule can significantly affect an optical absorption measurement, this effect was addressed. Adsorbed iodine, which has an optical transition moment that is parallel to the molecular axis, showed a much stronger out-of-plane polarized (S-state) absorption than in-plane absorption (P-state), indicating that the adsorbed form of iodine is oriented parallel to the cavity surface.

Similar results for detection of adsorbed iodine were obtained using a new non-ring resonator design, which combines high-reflectivity coatings with TIR to form a stable optical cavity (disclosed last year in the proprietary information section). Although the non-ring design has a narrow spectral bandwidth due to the use of high-reflectivity coatings, this single element cavity can be excited directly by an incident laser. Direct excitation of the cavity through a coated surface facilitates interfacing the cavity to experiments and will speed application testing. Experiments on reactions of NO_x compounds are currently being explored. The TIR-ring cavity design is superior in sensitivity and spectral bandwidth in comparison to the non-ring design, but is excited by a photon tunneling mechanism which requires the use of coupling prisms. These small coupling prisms must be mounted on the cavity with a precise and stable separation between the cavity and the coupling optic. Strategies to achieve this goal have been devised that will be carried out in collaboration with IDI through a CRADA. The goal of the CRADA is to engineer prototype miniature spectrometers that will have mounted coupling optics, mode-matching optics (for single-mode excitation which improves measurement precision), polarization-selective optics (for orientational information), and fiber-optic connectors (for remote detection and general convenience of use).

Finally, a hexagonal TIR-ring cavity has been designed and successfully fabricated from sapphire. The high index of refraction of sapphire permits dense liquids to be probed by immersion of the hexagonal cavity design in the medium of interest. A miniature spectrometer based on the hexagonal sapphire cavity should be field deployable in the cone penetrometer, for example, since sapphire is a durable material. Simple cleaning procedures, which can be easily field implemented, have been developed to recover the baseline response after chemical exposure.

PLANNED ACTIVITIES:

Fused-silica, square and sapphire, hexagonal TIR-ring cavities will be incorporated in prototype miniature spectrometers during the next year. The square and hexagonal designs are appropriate for vapor and liquid sensing applications, respectively, in the visible and near-IR. Diode lasers will be employed in addition to a dye laser. Vapor and liquid sensing applications will be explored when miniature spectrometers have been successfully engineered. For the mid-IR, cavities may be fabricated from un-doped YAG, CaF, or fluoride glass, depending on laser source availability (an OPO may be available but will not be purchased; mid-IR quantum cascade lasers (QCL) may also be available).

Contact will continue with potential DOE end users of the technology.

INFORMATION ACCESS:

1. *Broadband intra-cavity total reflection chemical sensor*, A. C. R. Pipino, U. S. Patent No. 5,835,231, Nov. 10, 1998.
2. *Intra-cavity total reflection for high sensitivity measurement of optical properties*, A. C. R. Pipino et al. U. S. Patent Application Serial No. 08/962,170 (Notice of Allowance has issued).
3. *Intra-cavity total reflection for high sensitivity measurement of optical properties*, A. C. R. Pipino, U. S. Patent Application Serial No. 09/188,415, pending.
4. *Evanescent wave cavity ring-down spectroscopy for ultra-sensitive chemical detection*, SPIE Vol. 3535, p 57, Boston, Mass. Nov. 1998.
5. *Ultra-sensitive surface spectroscopy with a miniature optical resonator*, A. C. R. Pipino, in preparation.
6. *Monolithic resonator for evanescent wave cavity ring-down spectroscopy*, A. C. R. Pipino, in preparation.
7. *Evanescent wave cavity ring-down spectroscopy as a probe of surface processes*, A.C.R. Pipino, et al., Chem. Phys. Lett. 280, 104 (1997).
8. *Evanescent wave cavity ring-down spectroscopy with a total-internal-reflection minicavity*, A. C. R. Pipino, et al., Rev. Sci. Instrum. 68, 2978 (1997).