

Environmental Management Science Program

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Novel Analytical Techniques Based on an Enhanced Electron Attachment Process

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Research Objective

Sensitive and selective detection of dense non-aqueous liquids (DNAPL), volatile organic compounds (VOC), and other organics, such as polychlorinated biphenyls (PCB), is an area of importance.

Current analytical methods for the detection of these compounds rely on their propensity to form negative ions. However, for compounds with smaller electron capture cross sections, including PCBs with few chlorine atoms and non-chlorinated VOCs, these methods are considerably less sensitive.

The objective of our research program is to develop novel analytical techniques that can be expected to be applicable for a wide variety of molecules with high sensitivity. These are based on the recently discovered enhanced negative ion formation process involving electron attachment to highly-excited states of molecules. We are using two approaches to produce the precursor highly-excited states; one is laser excitation, and the other is discharge based.

Research Progress and Implications

Within the past year and a half we have achieved the following:

1. Laser-Based Approach

The basic physics involved in the dissociative electron attachment to laser-excited molecules was investigated:

- L. A. Pinnaduwege and Y. Zhu, "Long-time stability of superexcited high-Rydberg molecular states", *Chem. Phys. Lett.* 277, 147 (1997).
- L. A. Pinnaduwege and Y. Zhu, "High-Rydberg fragment formation via core dissociation of superexcited Rydberg molecules", *J. Chem. Phys.* 108, 6633 (1998).
- L. A. Pinnaduwege and K. Nagesha, *Phys. Rev. Lett.* (A comment, submitted 1998).
- Y. Zhu and L. A. Pinnaduwege, "Long-Time Stability of Superexcited High Rydberg Molecular States", 50th Annual Gaseous Electronics Conference, Madison, Wisconsin, October 6-9, 1997.

It was illustrated the analytically useful negative ions can be produced by this method in benzene and toluene, which is not possible using conventional negative ion technique.

- L. A. Pinnaduwege, K. Nagesha, Y. Zhu, M. V. Buchanan, and G. B. Hurst, *Anal. Chem.* (Submitted, 1998).

2. Discharge-Based Approach

It was illustrated that molecules can be efficiently excited via excitation transfer from metastable states of rare gases produced in a glow discharge, and that electron attachment to those highly-excited molecules leads to abundant negative ion formation:

- L. A. Pinnaduwege, D. L. McCorkle, and W. Ding, "Enhanced electron attachment to highly excited molecules using a plasma mixing scheme", *Appl. Phys. Lett.* 71, 3634 (1997).
- W. Ding, D. L. McCorkle, and L. A. Pinnaduwege, "Enhanced formation of negative ions by electron attachment to highly-excited molecules in a flowing afterglow plasma", *J. Appl. Phys.* (Submitted, 1998)

This is a novel method for producing characteristic negative ions. In these pioneering experiments, we have produced H⁻ and O⁻ ions from CH₄ and O₂ to illustrate the concept.

Planned Activities

1. Our studies on negative ion formation in laser-irradiated molecules have shown that it is indeed an extremely efficient process. However, the negative ion formation in those experiments is limited by the limited number of electrons produced by laser photoionization. We plan to provide additional electrons by using an external electron gun. The electron gun needed for these studies is being designed. (Anticipated time period: 1998-1999).
2. Using the new electron gun, mass spectrometric studies will be conducted on a variety of volatile organics of relevance to the DOE's environmental restoration program to characterize ion fragment formation. (Anticipated time period: 1999-2002).
3. We will evaluate the analytical capabilities of this novel method, such as the sensitivity (detection limits) and the selectivity (effects of interferences) (Anticipated time period: 2000-).
4. A novel pulsed discharge technique will be tested for the enhanced production of characteristic negative ions.(Anticipated time period: 1998-1999). If successful, this could be developed to a novel electron capture detector. (Anticipated time period: 1999-2000).
5. A mass spectrometer can be incorporated to the plasma apparatus to conduct mass spectrometric studies of negative ions, and then to study characteristic anion formation. (Anticipated time period: 1999-2002).