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Project Title: **Novel Analytical Techniques Based on an Enhanced Electron Attachment Process**

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NOVEL ANALYTICAL TECHNIQUES BASED ON AN ENHANCED ELECTRON ATTACHMENT PROCESS

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 to the DOE's environmental restoration program.

Current negative-ion based analytical methods for the detection of these compounds rely on their propensity to form negative ions (in their ground electronic states). 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-Rydberg 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 two and a half years we have achieved the following:

1. Laser-Based Approach

● The basic physics involved in the dissociative electron attachment to laser-excited molecules was investigated (publications 1,3,5,9,10).

● 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 (publication 8).

● Experiments were conducted to show that the negative ion formation can be further enhanced by applying small electric and/or magnetic fields; this was shown to be due to the lengthening of the lifetimes of the Rydberg states by these external fields (publication 9).

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 (publications 2, 4).

● Enhanced electron attachment to Rydberg states in plasmas was investigated; this study showed that electron attachment to Rydberg states could have major implications for a variety of discharge plasmas (publication 6).

● It was experimentally verified that enhanced negative ion formation can be achieved in a pulsed glow discharge. It was shown that the high-Rydberg states produced during the discharge survive into the afterglow and efficiently attach electrons due to the rapid cooling of the electrons in the afterglow (publication 7).

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 has been built. (Anticipated time period: 1999-2000).

2. Using the new electron gun, laser-based 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: 1999-2001).

3.We will evaluate the analytical capabilities of this laser-based method, such as the sensitivity (detection limits) and the selectivity (effects of interferences) (Anticipated time period: 2000-2002).

4. The pulsed discharge technique will be utilized to develop a novel electron capture detector. (Anticipated time period: 1999-2001).

5. A mass spectrometer can be incorporated to the glow discharge apparatus to conduct mass spectrometric studies of negative ions, and then to study characteristic anion formation. (Anticipated time period: 2000-2002).

Publications (*peer-reviewed publications)*:

1. L. A. Pinnaduwage and Y. Zhu, “Long-time stability of superexcited high-Rydberg molecular states”, *Chem. Phys. Lett*. **277**, 147 (1997).
2. L. A. Pinnaduwage, D. L. McCorkle, and W. Ding, “Enhanced electron attachment to highly excited molecules using a plasma mixing scheme”, *Appl. Phys. Lett.* **71**, 3634 (1997).
3. L. A. Pinnaduwage and Y. Zhu, “High-Rydberg fragment formation via core dissociation of superexcited Rydberg molecules”, *J. Chem. Phys*. **108**, 6633 (1998).
4. W. Ding, D. L. McCorkle, and L. A. Pinnaduwage, “Enhanced formation of negative ions by electron attachment to highly-excited molecules in a flowing afterglow plasma”, *J. Appl. Phys*. **84**, 3051 (1998).
5. K. Nagesha and L. A. Pinnaduwage, “O^- Formation from O_2 via Rydberg-Rydberg Electron Transfer”, *J. Chem. Phys*. **109**, 7124 (1998).
6. L. A. Pinnaduwage, W. Ding, D. L. McCorkle, S. H. Lin, A. M. Mebel, and A. Garscadden, “Enhanced Electron Attachment to Rydberg States in Molecular Hydrogen Volume Discharges”,

J. Appl. Phys., **85**, 7064 (1999).

7. W. Ding, L. A. Pinnaduwage, C. Tav, and D. L. McCorkle, "The Role of High Rydberg States in Enhanced O^- Formation in a Pulsed O_2 Discharge", *Plasma Sources Sci. Technol.*. **8**, 384 (in press, 1999).
8. L. A. Pinnaduwage, K. Nagesha, Y. Zhu, M. V. Buchanan, and G. B. Hurst, "Laser-Enhanced Negative Ion Mass Spectroscopy for Weakly-Electron-Attaching Species", *Int. J. Mass Spectrom. Ion Processes* (submitted, 1999).
9. K. Nagesha and L. A. Pinnaduwage, "Magnetic and Electric Field Induced Enhancements in Laser Induced Anion Formation", *Chemical Physics Letters* (submitted, 1999).
10. C. Tav and L. A. Pinnaduwage, "Enhanced Dissociative Electron Attachment to Laser-Excited Benzene", to be submitted to *J. Chem. Phys.* (1999).

Conference Proceedings

1. L. A. Pinnaduwage, "Implications of Electron Attachment to Highly-Excited States in Pulsed Power Discharges",11th IEEE Pulsed Power Conference, Baltimore, Maryland, June 29-July 2, 1997; a full paper has been published in the conference proceedings.
2. Y. Zhu and L. A. Pinnaduwage, "Long-Time Stability of Superexcited High Rydberg Molecular States", 50th Annual Gaseous Electronics Conference, Madison, Wisconsin, October 6-9, 1997.
3. L. A, Pinnaduwage, W. X. Ding, and D. L. McCorkle,"Enhanced Electron Attachment to Superexcited Rydberg States of Molecular Hydrogen Using a Plasma Mixing Scheme", presented at the 1998 International Congress on Plasma Physics, Prague, Czech Republic, June 27- July 3, 1998; a full paper is to be published in the conference proceedings.
4. L. A. Pinnaduwage, M. V. Buchanan, and G. B. Hurst, "Novel Analytical Techniques Based on an Enhanced Electron Attachment Process", presented at the Environmental Management Science Program Workshop, Chicago, IL, July 27-30, 1998.
5. C. Tav and L. A. Pinnaduwage, "Dissociative Electron Attachment to Laser-Excited Benzene", 52nd Annual Gaseous Electronics Conference, Norfolk, Virginia, October 5-8, 1999.
6. K. Nagesha and L. A. Pinnaduwage, "Magnetic and Electric Field Induced Enhancements in Laser Induced Anion Formation", 52nd Annual Gaseous Electronics Conference, Norfolk, Virginia, October 5-8, 1999.
7. L. A. Pinnaduwage, W. Ding, and D. L. McCorkle,"Negative Ion Formation in Pulsed Plasmas", 52nd Annual Gaseous Electronics Conference, Norfolk, Virginia, October 5-8, 1999.

Patent

The following patent has been issued:

L. A. Pinnaduwage, "Plasma Mixing Glow Discharge Device for Analytical Applications", US patent #5,896,196 issued on April 20, 1999.