

**First-Year (1996-1997) Progress Report for EMSP Award # DE-FG07-96ER62304**

**NOVEL ANALYTICAL TECHNIQUES BASED ON AN ENHANCED ELECTRON  
ATTACHMENT PROCESS**

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## **Research Objective**

The objective of this research program is to develop new analytical techniques based on the large cross sections associated with dissociative electron attachment to highly-excited molecular states. Such highly-excited states can be populated via laser irradiation or in glow discharges via excitation transfer from high-lying, metastable states of rare gases. In one part of the research program, the analyte molecules are populated via laser excitation, and the resulting negative ions are mass analyzed using a time-of-flight mass spectrometer. In the other research project, a gas-discharge-based novel plasma mixing scheme is used to excite the molecules. In the early studies, basic studies on these two schemes will be conducted in order to clarify the electron attachment mechanisms involved.

## **Progress for the first year**

### **A. LASER-BASED STUDIES**

#### 1. Measurements Using a Gas Jet

During the past year we have conducted extensive measurements using this scheme. In these experiments, a gas jet is intercepted by a laser beam that ionizes and excites the gas to produce attaching electrons and the excited molecules for attachment. Both positive and negative ion measurements were conducted in order to clarify the electron attachment mechanisms involved in molecules laser-excited to energies above their ionization potentials (IPs). In these experiments, a molecular gas jet is intercepted by an excimer laser pulse, which excites the molecules to energies above their IPs. This leads to the ionization of some, but not all molecules. Contrary to the generally-accepted notion that the ionization is the only possible outcome, our studies have shown that highly-excited neutral states (superexcited states) are also produced, and that such states can live for long times of the order of microseconds. In a long-lived superexcited molecule, the excited electron is in a high-Rydberg orbital, and the "excess energy" is stored in the vibrational/rotational modes of the positively-charged core. A paper describing these results has been accepted for publication in *Chemical Physical letters*.

The longevity of neutral states lying above the IP depends on the particular molecule. The above mentioned microsecond lifetimes were observed for the superexcited states of benzene and triethylamine molecules; in these comparatively large molecules, the additional energy can be stored in vibrational/rotational modes of the core without dissociating the core, and this is the key to the stability. On the other hand, for a smaller molecule like methyl iodide, the core of a superexcited Rydberg state is unstable. We have shown that when a superexcited Rydberg state of a methyl iodide molecule dissociates, the Rydberg electron just acts as a distant observer to the core dissociation process; after the core dissociates, the methyl radical leaves and the Rydberg electron remains attached to the iodine atom. A paper describing this observation has been submitted for publication in the *Journal of Chemical Physics*.

## 2. Measurements Using the Gas Cell

In the TOF apparatus, the pulsed valve used in the above described experiments can be replaced with a static gas cell. The negative (and positive) ions produced in the gas cell are pushed into the TOF tube by a pulsed voltage. The mass spectra for benzene and toluene obtained using the two methods show that analytically-useful negative ions can be produced by electron attachment to highly-excited states. Negative-ion formation in benzene in conventional apparatus (where negative ions are formed by electron attachment to ground states) yield mainly the  $C_2H_2^-$  ion and other low-mass ions with  $m/z < 30$ . However, we have observed larger negative ions including the  $C_6H_5^-$  ion for benzene using the present technique. Therefore, it appears that analytically-useful negative ions could be produced by this new technique. These findings are to be submitted for publication.

### B. GAS-DISCHARGE-BASED STUDIES

A new experimental apparatus was constructed to conduct these studies. The basic idea behind the technique is the following: long-lived metastable states of rare gases are produced in a hollow cathode discharge, and these species are transferred into an adjoining "target" area by the gas flow created by a mechanical pump. The analyte gas is introduced into the target region, where they are excited to highly-excited states via excitation transfer from the rare gas metastable states. The flowing plasma carries not only the rare gas metastable states, but also electrons from the source region to the target region. Therefore, the highly-excited states undergo electron attachment in the target region thus producing characteristic negative ions.

In preliminary studies, we have monitored the reduction of electron density in the target region with the introduction of the analyte gas, using Langmuir probes. Different rare gas/analyte gas combinations were used in these experiments. We showed that when the ionization potential of the analyte gas is higher than the energy of the metastable state of the rare gas highly-excited states of the analyte molecules are produced which in turn attach electrons to produce negative ions. On the other hand, when the ionization potential of the analyte gas is lower than the energy of the metastable state of the rare gas, the analyte molecules are ionized via Penning ionization. These initial findings have been submitted for publication in Applied Physics Letters.

## Summary of Accomplishments

### Laser- Based Studies

- Positive and negative ion spectra of benzene and a few other molecules were obtained using a Time-of-Flight (TOF) mass spectrometer equipped with a pulsed gas valve. We observed microsecond lifetimes for molecules excited to energies above their ionization thresholds using this apparatus. This observation is important for establishing the mechanisms involved in electron attachment to molecules excited to energies above their ionization thresholds.
- Using the above apparatus we also observed fragment Rydberg formation via core dissociation of superexcited Rydberg states of methyl iodide. Even though this observation is not directly relevant to the project, it is an important serendipitous observation.
- Negative and positive ion spectra of benzene were also obtained with a static gas cell connected to the TOF. It turns out that analytically-useful negative ions can be produced via this method.

### Gas-Discharge-Based Studies

- A plasma mixing apparatus was constructed to conduct basic studies on electron attachment to highly-excited molecules produced via excitation transfer from metastable states of rare gases.
- Using the above apparatus we conducted preliminary studies to illustrate the proof-of-principle.

## Publications and Presentations

1. L. A. Pinnaduwege and Y. Zhu, "Long-Time Stability of Superexcited High Rydberg Molecular States", Chem. Phys. Lett. (in press, 1997).
2. L. A. Pinnaduwege and Y. Zhu, "High-Rydberg Fragment Formation via Core Dissociation of Superexcited Rydberg Molecules", J. Chem. Phys. (Submitted, 1997).
3. L. A. Pinnaduwege, Y. Zhu, M. V. Buchanan, and G. B. Hurst, "A Novel Analytical Technique Based on Electron Attachment to Highly-Excited Molecules" Anal. Chem. (Manuscript in preparation).
4. Y. Zhu and L. A. Pinnaduwege, "Long-Time Stability of Superexcited High Rydberg Molecular States", Paper presented at the 50<sup>th</sup> Annual Gaseous Electronics Conference, Madison, Wisconsin, October 6-9, 1997.
5. L. A. Pinnaduwege, W. Ding, and D. L. McCorkle, "Enhanced Electron Attachment to Highly-Excited Molecules Using a Plasma Mixing Scheme", Applied Physics Letters (submitted, 1997).