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NEGATIVE ION DETACHMENT PROCESSES

Progress Report

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DISCLAIMER

I. INTRODUCTION

The principal focus of the experimental studies undertaken during the past three years was to measure cross sections at low collision energies for electron detachment, associative electron detachment and charge transfer for collisions of various negative ions with atomic hydrogen and deuterium. This project necessitated the construction of a crossed-beam apparatus in which an rf discharge was used to produce the atomic beam of hydrogen or deuterium. Cross sections for collisions of H^-, D^- and several halogen anions with H and D have been determined with this apparatus. A separate apparatus has been used to determine cross sections for other systems including SF_6^-, SF_5^-, halogen anions and O^- in collisions with a variety of atomic and molecular targets. The laboratory collision energies for these experiments ranged from a few eV up to 500 eV. The goal of all the experiments performed during this contract period was to develop an understanding of the collisional dynamics for a number of negative ion-atom systems which are both intellectually interesting and of some importance to various areas of applied physics.

Detailed accounts of the experimental results and their analyses for work during the contract period (4/88-3/91) may be found in the following articles which have appeared in the archival literature during the three-year contract period:

"Low-Energy Collisions of O^{2+} with Atoms and Molecules"
Phys. Rev. A 37, 2349 (1988).

"Reactive Scattering and Electron Detachment for Collisions of Halogen Negative Ions with HCl, DCl and HBr"
J. Chem. Phys. 88, 5475 (1988).

"Electron detachment in low-energy $H^-(D^-)$-Na collisions"
Phys. Rev. A 38, 2284 (1988).

"Negative-Ion Formation on Alkali-Metal Surfaces"
Phys. Rev. Letters 61, 1194 (1988).

"Positive ion production in halogen negative ion collisions"
J. Phys. B 21, 3375 (1988).

"Collisional electron detachment and decomposition cross sections for SF_6^-, SF_5^- and F^- on SF_6 and rare gas targets"
J. Chem. Phys. 91, 2254 (1989).

"Collisional electron detachment and decomposition rates of SF_6^-, SF_5^-, and F^- in SF_6: Implications for ion transport and electrical discharges"
J. Chem. Phys. 91, 2261 (1989).

"Charge transfer and electron detachment for collisions of H^- and D^- with H"
Phys. Rev. A41, 4809 (1990).

"Reactive Scattering and electron Detachment in O^- collisions with H_2. Nascent product energy distributions."
J. Chem. Phys. 92, 2305 (1990).

Copies of these papers are included as the appendix of this report. Brief accounts of these studies were also presented at the ICPEAC, DAMOP, GEC and Gaseous Dielectrics conferences:

"Negative Ion Formation on Alkali-coated Surfaces"
Bull. Am. Phys. Soc. 33, 933 (1988)
[DAMOP meeting, Baltimore, April 1988].

"Charge Transfer and Electron Detachment for Collisions of Negative Ions with Atomic Hydrogen"
Bull. Am. Phys. Soc. 34, 1366 (1989)
[DAMOP meeting, Windsor, Canada, May 1989].

"Charge Transfer and Detachment for Collisions of Negative Ions with Atomic Hydrogen"
XVIth Int'l. Conf. on Physics of Electronics and Atomic Collisions, July 1989, NY.

"Collisional Detachment Cross Sections for SF_6^-, SF_5^- and F^- on SF_6 and Rare Gas Targets"
Bull. Am. Phys. Soc. 34, 299 (1989)
[41st Gaseous Electronics Conference].

"Associative and Collisional Detachment for Collisions of Negative Ions with Atomic Hydrogen"
Bull. Am. Phys. Soc. 35, 1195 (1990)
[DAMOP meeting, Monterey, CA, May 1990].

"Collisional Electron Detachment in Dielectric Gases"
Sixth Int'l. Symposium on Gaseous Dielectrics, Knoxville, September 1990.

II. BRIEF REVIEWS OF WORK PERFORMED

In this section, we present synopses which focus upon the highlights of the work performed during the contract period. The review is divided into several distinct areas of inquiry. The reader is referred to the complete articles contained herein for more detailed discussions.

A. H^- and D^- collisions with atomic hydrogen.

Cross sections for collisional detachment

$$X^- + H \rightarrow X + H + e, \qquad (1)$$

and charge transfer

$$X^- + H \rightarrow X + H^- \qquad (2)$$

have been measured for laboratory collision energies ranging from a few eV up to several hundred eV for $X^- = H^-$ and D^-. Atomic hydrogen is produced in a radio-frequency discharge source and the effusing neutral beam intersects the negative ion beam within a cylindrical electrostatic energy analyzer. The electric field between the curved plates of the analyzer is chosen such that the negative ion beam will pass resonantly through the device. This same electric field serves simultaneously to extract the slow reaction products in (1) & (2) above; the extracted ions and electrons are subsequently separated in a weak magnetic field. The dissociation fraction in the neutral H/H_2 beam (≈85%) is determined by comparing the charge transfer and detachment cross sections for H^- + H and H_2 to the total electron loss cross sections recently reported by Gealy and Van Zyl[1]. The experimental results are given in Fig. 1.

The cross section for resonant charge transfer, $\sigma_{ot}(E)$, continues to increase as the collision energy is decreased below 400 eV. Isotopic substitution reveals that $\sigma_{ct}(E)$ for H^- and D^- are approximately equal at the same collision velocities. The detachment cross section, $\sigma_e(E)$, does not exhibit a steep rise for E < 400 eV, as has been suggested previously. Rather, $\sigma_e(E)$ remains approximately constant and is very close to the geometrical cross section $(1/2)\pi(R_a^2 + R_b^2)$, where R_a and R_b are the crossing points of the $^2\Sigma_u$ and $^2\Sigma_g$ states of H^- + H with the relevant H + H states.

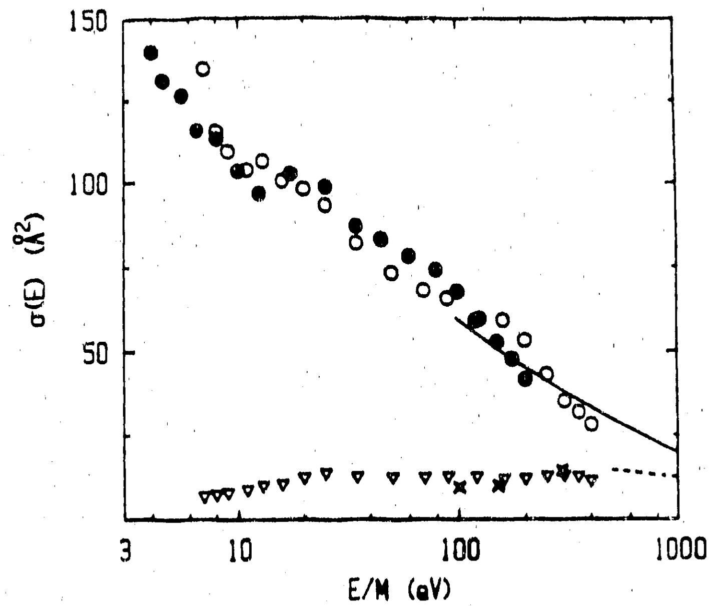

Figure 1 - Charge transfer for H^- (O) & D^- (●) + H and detachment for H^- + H. The results of references 2 (--)and 3(X) are also shown.

B. <u>Collisional decomposition of SF_6^-</u>

Interest in SF_6 stems mainly from its use as a gas dielectric in high voltage applications. Two properties of SF_6 make it attractive for such applications: it has a large attachment cross section for thermal energy electrons and it is apparently stable against collisional electron detachment for relative collision energies which exceed the electron affinity of SF_6 (≈1 eV) by as much as a factor of eight. There is further evidence which suggests that the destruction of the negative ion is dominated by collisional dissociation of SF_6^- into various ionic fragments. However, all existing experimental data concerning decomposition of SF_6^- are model dependent, being inferred from drift-tube measurements.

In particular, very little information is available on how SF_6^- decomposes in binary collisions with gaseous targets. The purpose of this project was to measure various absolute cross sections for collisions of SF_6^-, SF_5^- and F^- with the rare gases and SF_6. Results for the SF_6 target are shown below.

The cross sections for electron detachment of SF_6^- are observed to be surprisingly small for relative collision energies below several tens of electron volts. The cross sections for collision induced dissociation into either F^- or SF_5^- dominate at low collision energies. These observations are clearly important in developing an understanding of electrical breakdown when using SF_6 as the dielectric. In fact, these cross sections were used to calculate detachment and ion-conversion coefficients as functions of E/N (ratio of electric field to gas density) for ion drift in SF_6. This analysis indicated that prompt electron detachment from SF_6^- and SF_5^- in SF_6 are insignificant processes in such ion drift experiments. Calculated rates for ion conversion processes indicate the necessity to: (i) reexamine rates in previous SF_6 drift tube experiments, and (ii) use ion kinetic energy distributions with larger high energy tails than previously assumed in earlier calculations. These same rate coefficients are

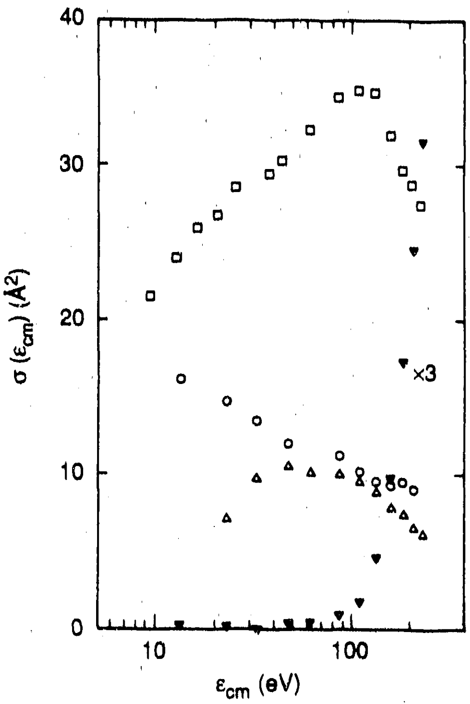

Figure 2 - Cross sections for detachment(▼), F^-(□), SF_5^-(O) production, and charge transfer(Δ). Note that the detachment data are multiplied by three.

also used in a model in which detachment of long-lived, energetically unstable states of SF_6^- was invoked to explain the pressure dependence of detachment coefficients and high detachment thresholds extracted from electrical breakdown data for SF_6. The model indicates that at high pressure, detachment coefficients depend primarily upon rates for ion conversion and prompt collisional detachment from F^-. Further details of this work are contained in one of our attached publications.

C. Two-electron loss processes in negative ion collisions

In an ongoing collaboration with a French group, we have studied positive ion production in collisions of halogen anions with atomic and molecular targets. There are several interesting observations: First, the cross section for double ionization at moderate collision energies is found to range from surprisingly large (e.g., F^-+Ne) to quite small (e.g., Cl^-+Ar). Secondly, by measuring the kinetic energy spectra of the ejected electrons, it is found that the "second" electron which is ejected in the doubly-ionizing collision originates primarily from an autoionizing state of the neutral, viz., $F^* \rightarrow F^+ + e$ in the above example.

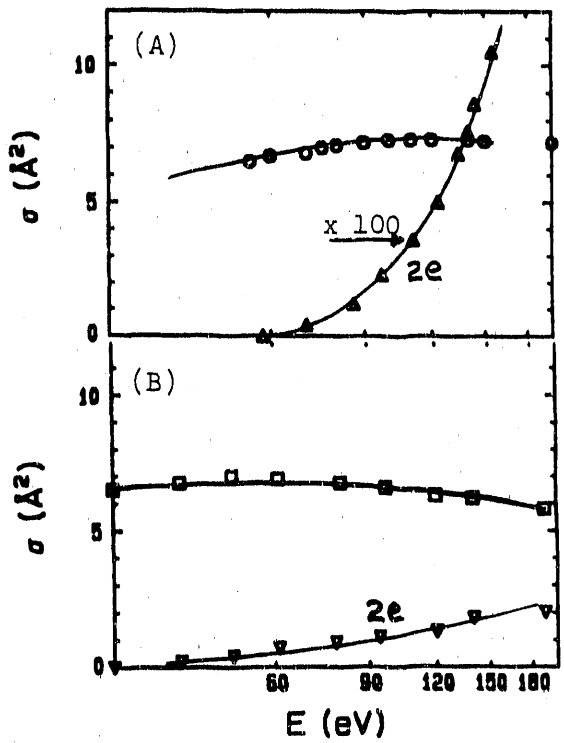

Figure 3 - Total cross sections for one- and two-electron loss mechanisms. A: Cl^-+ Ar, B: F^- + Ne.

Total cross sections for one- and two-electron loss collisions are shown in Fig. 3 for the examples of F^-+Ne and Cl^-+Ar. It is concluded from these experiments that the results relevant to ionization via autodetaching levels should be applicable as well to collisions involving the parent neutral atoms, since the process is characteristic of these systems rather than those of the negative ion-atom reactants.

D. Associative electron detachment

We are currently extending the measurements discussed in section A by determining cross sections for associative and collisional electron detachment in collisions of F^-, Cl^-, Br^- and I^- with atomic hydrogen and deuterium; the measurements will be completed by the end of the project period. Although the reactants Cl^- + H have been well characterized, the same is not true for other halogen anions. Owing to the heavy-on-light nature of these reactants relative collision energies below the electron affinity for the halogen can be sampled. Hence, the cross sections for the associative detachment process can be isolated. These systems offer us the unique opportunity to study the dynamical interaction between a negative ion molecular state and a bound neutral molecular state without interference from other final scattering states. The preliminary results for

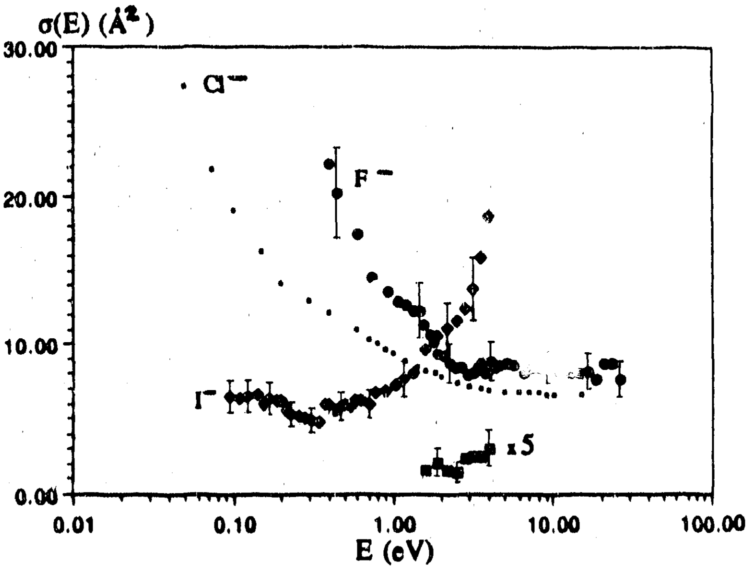

Figure 4 - Detachment cross sections for I^-, Cl^-, & F^- on H, normalized to calculations of ref. 4. Charge transfer for I^- (multiplied by five) is also shown.

several of the halogen anion - atomic hydogen systems are shown in Fig. 4. The only reactants for which a non-zero signal for charge transfer is observed is for $I^- + H$.

E. <u>Negative ion desorption from surfaces</u>

Recent experiments in this laboratory which involved collisions of H^- with alkali atoms revealed that surfaces which became coated with the alkali metal could become sources of negatively charged emissions. It was recognized that the surfaces were actually emitting negative ions, and the emission was particularly noticeable when gaseous H_2O or SF_6 was admitted into the vacuum chamber containing the alkali-coated surfaces.

During the contract period a study of this surface phenomenon was completed using a simple experimental setup. The observations may be summarized as follows. Room temperature SF_6 molecules interact with an alkali surface (also at room temperature) to produce F^-, SF_i^- (i = 0-5), and other negative ions which desorb from the surface. The efficiency of this process is surprisingly large, of order 10^{-5}. It is believed that exothermic chemical reactions on the surface provide the energy necessary to overcome the energy which binds the negative ions to the surface.

An additional study was performed to see if photons could be

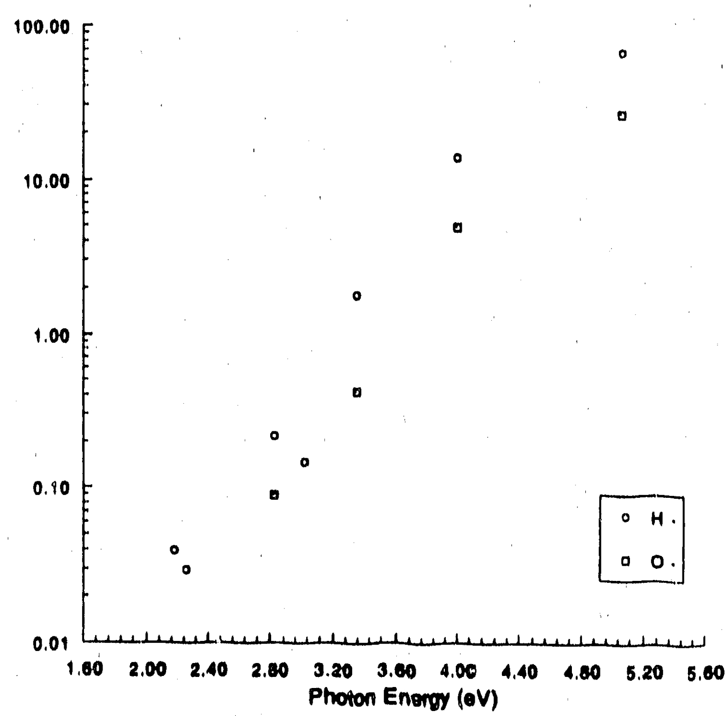

Figure 5 - Relative yields of O^- and H^- photodesorbed from a barium surface as a function of photon energy.

effective in desorbing negative ions from certain surfaces. Although the present results are definitely preliminary in nature, it appears that photodesorption of H^- and O^- from barium surfaces does occur, although the relative yields (ions per incident photon) is small. The relative yield of H^- and O^- ions from a barium surface is shown in Fig. 5 as a function of the photon energy.

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[1] M.W. Gealy and B. Van Zyl, Phys. Rev. A36, 3091 (1987)

[2] D.G. Hummer et al., Phys. Rev. 119, 668 (1960)

[3] V.A. Esaulov, J. Phys. B 13, 4039 (1980)

[4] J.P. Gauyacq, J. Phys. B 17, 4041 (1986) and private communication

III. STUDENTS AND PERSONNEL

During the project period the following graduate students have been supported in part from the contract and are involved with the various projects:

Michael Huels - will complete requirements for PhD in October, 1990.

Douglas Baker - in the middle of his research project.

Jim Fedchak - just completed first year of residency; has been designing neutral/neutral crossed beam experiment.

We have also been able to support a post-doctoral research associate for about 18 months during the 36 month contract period. He was Yicheng Wang (one of our PhD students) who has now joined Notre Dame Radiation Laboratory in a permanent position.

Another aspect of our educational program at William and Mary includes undergraduate students, for whom a senior thesis is a graduation requirement. These students don't receive financial support from the contract, but they are an integral part of the project. They were:

David Gallagher (1988 - now grad student at UVa)

Benjamin Davies (1989 - now grad student at UVa)

Thomas Collins (1989 - now grad student at MIT)

Stephen Irons (1990 - now grad student at UCal, Davis)

Lee Harrell (1990 - now senior at W&M)

John Finn (1990 - now senior at W&M)

All of these undergraduate students coincidentally received "Research Experiences for Undergraduates" fellowships from NSF during the summers bridging their third and fourth year in the undergraduate program.

The principal investigators were supported for two months during the summers for each summer of the contract year.

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