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**NEGATIVE ION COLLISIONS**

Progress Report

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R. L. Champion  
Department of Physics  
College of William and Mary  
Williamsburg, Virginia 23187

(804) 221-3510

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## 1. Introduction

During the last three years, our experimental activities have concentrated on several somewhat distinct projects. First, we have measured total cross sections for electron detachment and charge transfer for collisions of various negative ions with atomic hydrogen and the molecular target, O<sub>3</sub> (ozone). The ozone was generated within a discharge, distilled at liquid nitrogen temperatures, and transported to the scattering cell. The second type of gas phase experiments investigated the collisional decomposition of the molecular ion H<sub>3</sub><sup>+</sup>. Specifically we have measured total cross sections for dissociation and proton transfer with an apparatus utilizing a static gas target cell. The targets include hydrogen, deuterium and the rare gases. We have extended these experiments to include D<sub>3</sub><sup>+</sup> in a crossed beam configuration in order to provide a more detailed understanding of the collisional dynamics for these reactants. In the area of ion-surface collisions we have measured sputtering yields for O<sup>-</sup> and electrons arising from collisions of ions with an Al/O surface. The amount of oxygen on the surface is carefully controlled and the kinetic energy distributions of the ejected anions and electrons have been determined. We have been able to develop a theoretical model which, to a large degree, can describe the process. In a slightly speculative endeavor, we have begun investigating the role of atom-catalyzed field emission, i.e., the extent to which an unoccupied negative ion state for an atom near a surface - under the influence of a strong electric field - can serve as a stepping-stone for electron field emission.

The laboratory collision energies for these experiments ranged from a few electron volts up to 500 eV. The goal of all the studies was to develop an understanding of the collisional dynamics and pathways for reactants which are both intellectually interesting and of some potential importance to various areas of applied physics.

Very brief accounts of these activities will be given in this report in section 2. Detailed discussions of the experimental results and their analyses published during the contract period may be found in the following articles which have appeared in the archival literature. Copies of these publications are appended to this report as section 4.

Published Articles:

*Electron detachment and charge transfer for collisions of  $O^-$  and  $S^-$  with H.*

J. A. Fedchak, M. A. Huels, L. D. Doverspike, and R. L. Champion,  
Phys. Rev. **A47**, 3796 (1993).

*Photon-stimulated desorption of H from a BaO surface.*

D. H. Baker, R. L. Champion, L. D. Doverspike, and Yicheng Wang,  
App. Phys Lett. **64**, 1880 (1994).

*Slow collisions of  $Na^-$  and  $K^-$  with atomic hydrogen.*

J. A. Fedchak, R. L. Champion, L. D. Doverspike, and Yicheng Wang,  
J. Phys. **B27**, 3045 (1994).

*Electron detachment in low-energy collisions of halogen anions with atomic hydrogen.*

M. A. Huels, J. A. Fedchak, R. L. Champion, L. D. Doverspike, J. P. Gauyacq and D.  
Teillet-Billy  
Phys. Rev. **A49**, 255 (1994).

*Detachment and charge transfer for collisions of negative ions with ozone.*

J. A. Fedchak, B. L. Peko, and R. L. Champion  
J. Chem Phys. **103**, 981 (1995).

*Destruction cross sections for low energy collisions of  $H_3^+$  and  $D_3^+$  with rare gas atoms.*

B. L. Peko, R. L. Champion and Yicheng Wang  
J. Chem. Phys. **104**, 6149 (1996).

*Secondary electron and negative ion emission from Al: Effect of oxygen coverage.*

J. C. Tucek, S. G. Walton, and R. L. Champion  
Phys. Rev **B53**, 14127 (1996).

*On the dynamics of secondary-electron and anion emission from an Al/O surface.*

J. C. Tucek and R. L. Champion  
Submitted to Surface Science, August, 1996.

Brief accounts of these results were also presented at various conferences:

*Electron Detachment and Charge Transfer in Low Energy Collisions of Na<sup>-</sup> with H.*

J. A. Fedchak, L. D. Doverspike and R. L. Champion

46th Gaseous Electronics Conference, Montreal, October 1993.

*Electron detachment and charge transfer for collisions of negative ions with ozone*

J. A. Fedchak, B. L. Peko, L. K. Keyt and R. L. Champion

47th Gaseous Electronics Conference, Gaithersburg, MD, October 1994.

*Secondary electron and anion emission from surfaces at low impact energies*

J. C. Tucek, D. H. Baker, S. G. Walton and R. L. Champion

47th Gaseous Electronics Conference, Gaithersburg, MD, October 1994.

*Cross sections for destruction of H<sub>3</sub><sup>-</sup> by collisions with H<sub>2</sub> and ion kinetics in H<sub>2</sub> at high E/N.*

R.J. Van Brunt, J.K. Olthoff, Y. Wang and R. L. Champion

48th Gaseous Electronics Conference, Berkeley, CA, October, 1995.

*Secondary electron and anion emission from oxidized surfaces at low impact energies.*

J. C. Tucek, S. G. Walton and R. L. Champion

48th Gaseous Electronics Conference, Berkeley, CA, October, 1995.

*Charge transfer and decomposition cross sections for collisions of H<sub>3</sub><sup>+</sup> on H<sub>2</sub> and rare gases.*

B. L. Peko, R. L. Champion, and Yicheng Wang

48th Gaseous Electronics Conference, Berkeley, CA, October, 1995.

*Proton and electron transfer for low energy collisions of H<sub>3</sub><sup>+</sup> and D<sub>3</sub><sup>+</sup> with H<sub>2</sub> and D<sub>2</sub>.*

B. L. Peko and R. L. Champion

49th Gaseous Electronics Conference, Argonne National Laboratory, October, 1996.

*Secondary electron and negative ion emission from oxidized aluminum.*

J. C. Tucek and R. L. Champion

49th Gaseous Electronics Conference, Argonne National Laboratory, October, 1996.

*Distributions of H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, and H<sub>3</sub><sup>+</sup> ions in Townsend discharge and determinations of their collision cross sections.*

J. Bretagne, G. Gousset, T. Simko, M.V.V.S. Rao, R.J. Van Brunt, Yicheng Wang, J.K. Olthoff, B.L. Peko, and R.L. Champion

XIIIth European Sectional Conference on Atomic and Molecular Physics of Ionized Gases (Poprad, Slovakia, 1996).

## 2. Brief reviews of work performed

### A. Negative ion collisions with O<sub>3</sub>

Cross sections for electron detachment and charge transfer have been measured for collisions of O<sup>-</sup>, S<sup>-</sup> and halogen anions with O<sub>3</sub> for collision energies ranging up to a few hundred eV. The measurements are absolute and the ozone is prepared via LN<sub>2</sub> condensation in an oxygen discharge. The results for O<sup>-</sup> + O<sub>3</sub> are

given in Fig. 1 where it is seen that both cross sections are quite large over the entire energy range of these experiments. Electron detachment can occur with or without concomitant chemical reaction yielding products O + O<sub>3</sub> + e or O<sub>2</sub> + O<sub>2</sub> + e, the latter of which is exothermic by 2.6 eV. Charge transfer can lead to O<sub>3</sub><sup>-</sup> + O (exothermic by 0.6 eV) or O<sub>2</sub><sup>-</sup> + O<sub>2</sub> (exothermic by 3 eV). If one extrapolates a previously determined thermal rate constant for simple charge transfer

( $2 \times 10^{-10}$  cm<sup>3</sup>/s) to 2 eV, the equivalent cross section lies an order of magnitude below the above observation at E = 2 eV. It is clear, then, that some barrier limits the charge transfer mechanism at thermal collision energies.

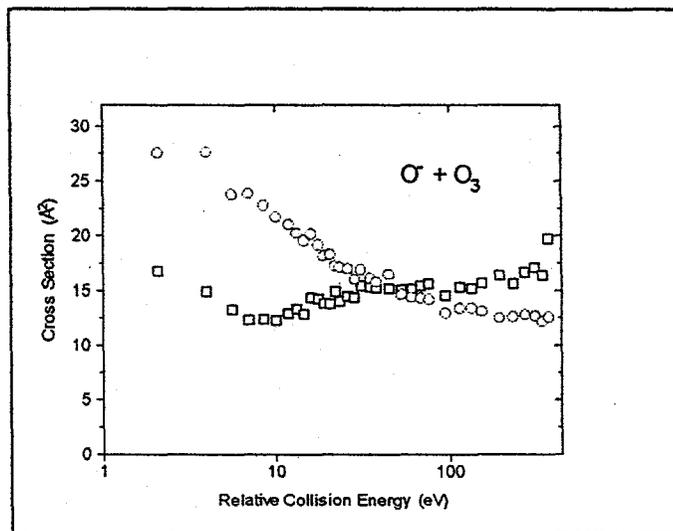


Figure 1 Detachment (squares) and charge transfer cross sections (circles) for O<sup>-</sup> + ozone.

### B. Secondary negative ion and electron emission from surfaces

Figure 2 illustrates the salient features of the experimental measurements related to the sputtering yields for electrons and oxygen negative ions. Those yields are shown in the top panel of figure 2 as a function of the amount of oxygen on the surface for two different collision energies, 150 and 350 eV. The important thing to note is that both the electron and ion yields are small (essentially zero) with no oxygen coverage and there is a large increase in the yields as the

oxygen coverage increases. Note also that the anions generally are dominant at 150 eV whereas the converse is true for 350 eV. In the bottom panel of figure 2, the electron and anion yields are shown as a function of the collision energy of the  $\text{Na}^+$  ion for a *fixed* oxygen coverage of about 1/3 monolayer. The energetic thresholds for each process are in the vicinity of 50 eV. The kinetic energy spectra of the electrons and the sputtered  $\text{O}^-$  ions are shown in figure 3 (see page 7) for an impact energy of 450 eV and an oxygen coverage of about 2/3 monolayer. In the top panel of figure 3, the ion measurements are shown along with the results of a calculation based on widths and levels calculated for the  $\text{O}^-$  state in the proximity of an aluminum surface. In the bottom panel an electron kinetic energy spectrum is given along with the results which have been reported for the collisional detachment of  $\text{O}^-$  by Ar at 500 eV.

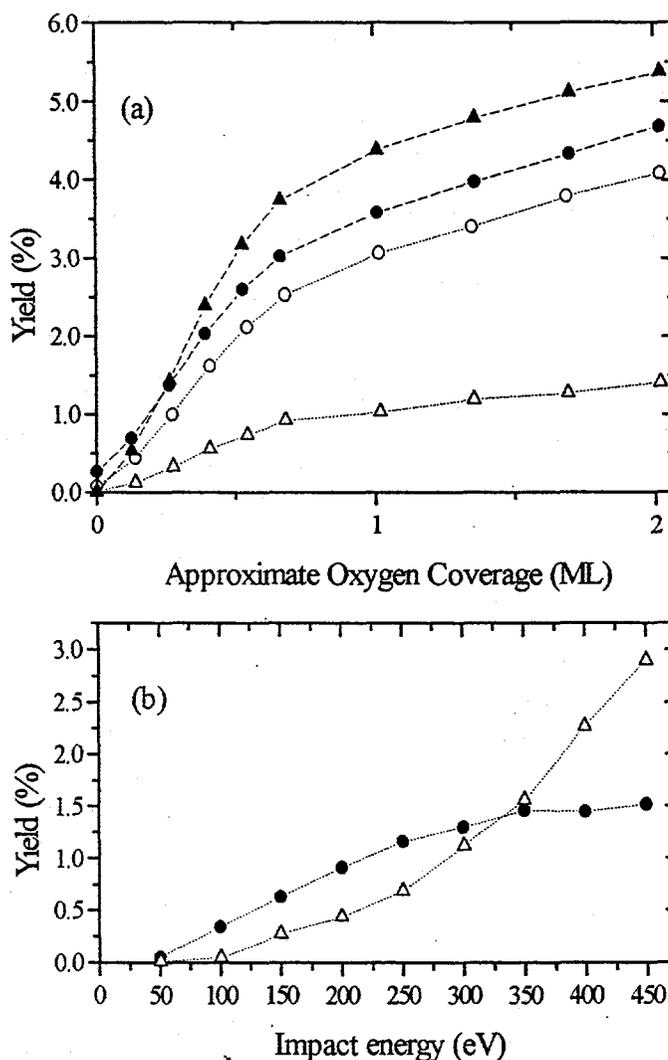


Figure 2 (a) Sputtering yields for  $\text{O}^-$  [circles] and  $e^-$  for impact energies of 150 and 350 [solid symbols] eV. (b) The yields are given as a function of impact energy for an oxygen coverage of about 1/3 ML.

At this point, we feel that we understand the dynamics associated with ion emission fairly well, but the same is not true for the electron emission. Secondary electrons do not arise from excited autoionizing or autodetaching states, nor are they emitted in coincidence with  $\text{O}^-$ . We can only suggest that, following the neutralization of the incoming  $\text{Na}^+$ , it collides (perhaps after

interacting with the metallic substrate) with an  $O^-$  residing on the surface,  $Na + O^- \rightarrow Na + O + e$ , such that the detached electron has sufficient kinetic energy to escape the surface. Most of the electrons liberated in this manner would, in fact, not find their way into the vacuum but would return to the surface. Those that would escape would lose kinetic energy in so doing and the distribution observed in figure 3(b) may simply represent that of the surviving electrons.

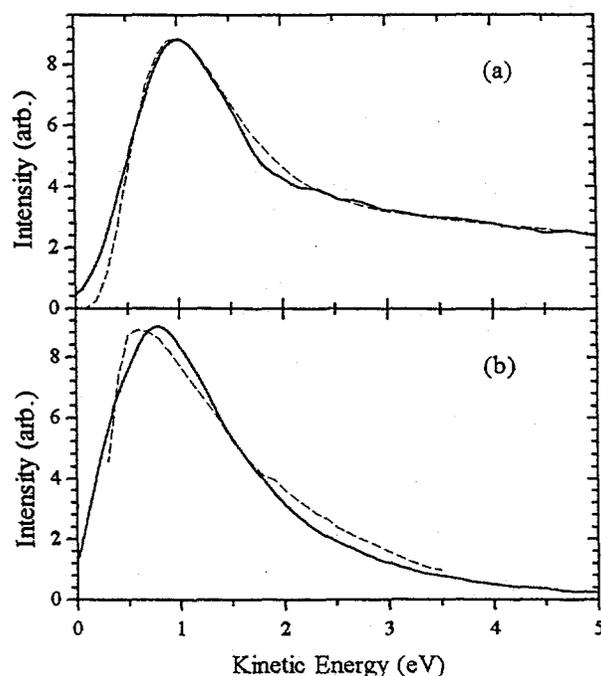
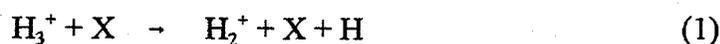


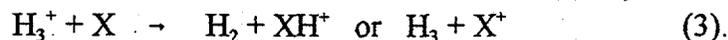
Figure 3 (a) The kinetic energy distribution for  $O^-$  along with the results of a model calculation [dashed line]. (b) The kinetic energy distribution of secondary electrons and those from  $O^- + Ar$  [dashed line].

### C. Collisional decomposition of $H_3^+$ and $D_3^+$ : total cross sections

By using a simple electrostatic retardation/trapping scheme we have measured cross sections for decomposition:



and for proton or electron transfer:



In the above reactions, the products can be separated and trapped with essentially 100% collection efficiency as their kinetic energies are, roughly, 2/3, 1/3 and 0/3 that of the original  $H_3^+$

projectile. Some results for  $H_3^+ + H_2$  are shown in Fig. 4. The proton transfer mechanism is undoubtedly responsible for the abrupt rise in the cross section seen in Fig. 4(a) as the collision energy drops below about 40 eV. These results differ markedly from cross section estimates used in the past to model hydrogen discharges. These experiments are far from elegant but, at the same time, so straight-forward that substantial errors are highly improbable. The  $H_3^+$  projectiles are formed in a high pressure discharge ( $\approx 100 - 200$  microns) and should be vibrationally cool.

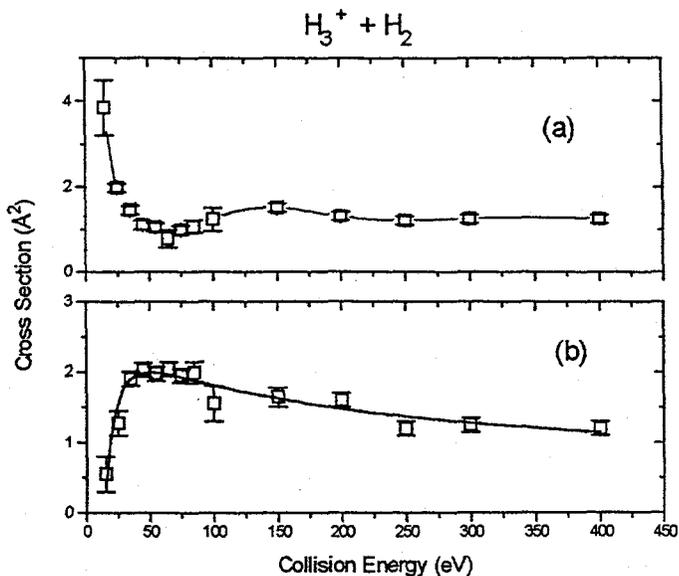


Figure 4 Cross sections for (a) electron or proton transfer and (b) collisional decomposition into  $H^+$

D. Collisional decomposition of  $H_3^+$  and  $D_3^+$ : isotope effects

The above measurements have been used in a collaborative effort with personnel at NIST and a group at the Université Paris-Sud (Orsay) to determine and model energy and species distributions in a DC hydrogen discharge. The experiments described in [C] above were performed with a geometry utilizing a static gas target cell and proton transfer from the  $H_3^+$  ion to the target could not be

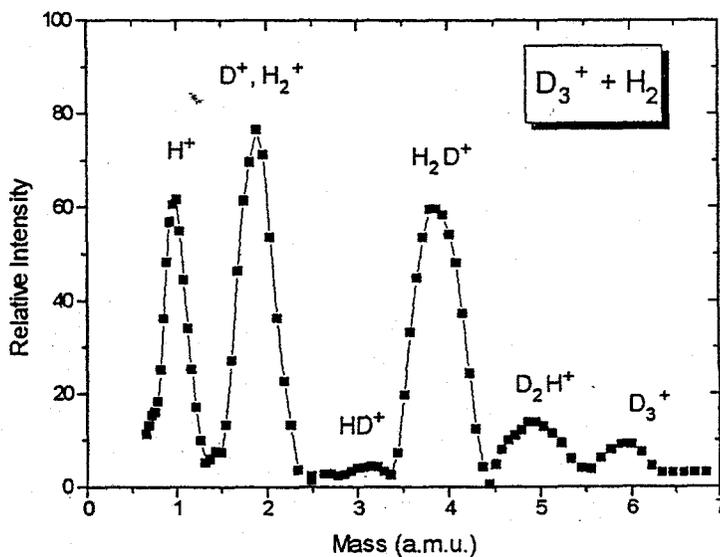


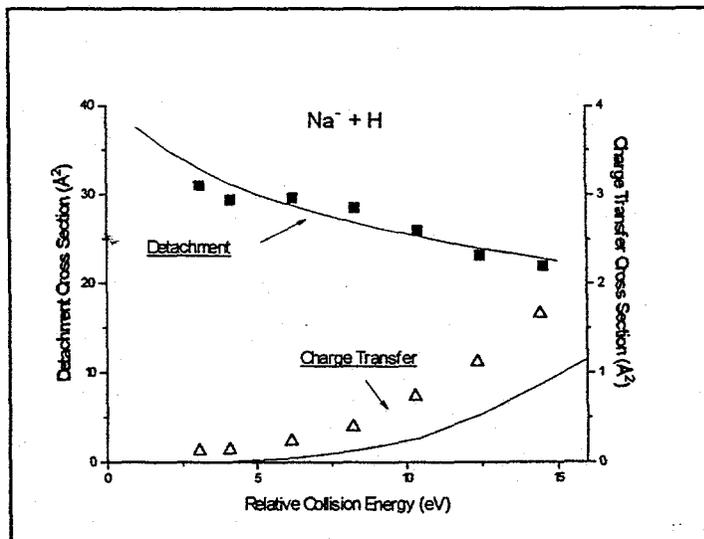
Figure 5 The relative intensities of various slow product ions which are produced in collisions of  $D_3^+$  with  $H_2$  for  $E_{lab} = 20$  eV is shown.

distinguished from electron transfer from the target. In a discharge it is crucial to distinguish between the two and to determine each cross section independently. Consequently we have performed a crossed beam study of the processes indicated in (1) - (3) above, with a special focus on isotopic substitution. An example of the complexity which occurs in collisions of  $D_3^+$  with  $H_2$  at a laboratory collision energy of 20 eV is shown in Figure 5. The relative intensities observed in the crossed beam studies provide branching ratios for the various inclusive measurements described in (C).

#### E. Detachment and Charge transfer: $Na^-$ and $K^- + H$ .

Total cross sections for electron detachment and charge transfer were measured for collisions of  $Na^-$  and  $K^-$  with atomic hydrogen for relative collision energies ranging from 2 - 20 eV. The cross sections for detachment are considerably larger than those for charge transfer and the experimental results for  $Na^- + H$  are analyzed with a model which employs available potential energy curves and an average width to describe the molecular anion in its unstable region. The charge transfer cross section for  $Na^- + H$  was compared to the results of a perturbed stationary state calculation which uses the average width inferred from the detachment results and a term of the form  $H_{12} = 6 \exp(-\gamma R)$  to describe the long-range coupling between the ground and  $A^2\Sigma$  excited states of  $NaH^-$ . Our PSS calculation underestimates the observed low energy cross section for charge transfer. Both the experimental and theoretical results (solid lines) for  $Na^- + H$  are shown in Fig. 6.

The alkali hydrides are well known for their large dipole moments and ability to bind an electron, forming a stable negative ion and, in the extreme limit of the Born-Oppenheimer approximation, an infinite number of bound excited states. However, when the normal rotational motion of the molecule is considered, most of the bound excited states vanish. A detailed multi configurational calculation of the properties



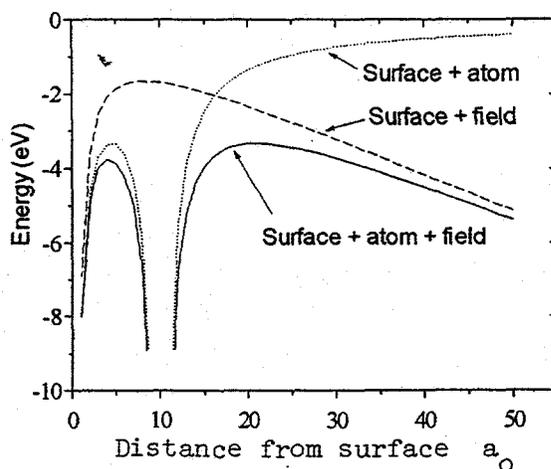
**Figure 6** Detachment and charge transfer for collisions of  $Na^-$  with atomic hydrogen. The lines are the results of semi-empirical calculations.

of the  $\text{LiH}^-$  indicates that the first excited state of that molecular anion (of  $A^2\Sigma^+$  symmetry) is bound, lying about 2.8 meV below the ground state of  $\text{LiH}$ . One would expect the same type of behavior for the  $\text{NaH}$  and  $\text{KH}$  molecular anions as they have larger dipole moments than  $\text{LiH}$ . However, the intermolecular potentials associated with these "barely-bound" excited states are probably not relevant to the collision dynamics in the present experiments: The electron wave functions simply can not adjust fast enough to the subtle configurational mixing required for stabilizing the excited  $A^2\Sigma$  molecular anion at small internuclear separations. In some sense then, *less* sophisticated calculations of the excited anion states would be expected to provide a more accurate description of the collision dynamics in the present studies. Under any circumstances, there are as yet no calculations for the  $A^2\Sigma$  state of  $\text{NaH}^-$  or  $\text{KH}^-$  which display a bound state.

#### F. Atom catalyzed field emission.

During the current contract period we have been assembling an experimental apparatus to investigate the extent to which an unoccupied negative ion state for an atom or molecule near a surface - which is also under the influence of a strong applied electric field - can serve as a stepping stone for electron field emission. There are no results to report as yet, but a discussion of the motivation behind the project is in order.

As an electronegative atom or molecule approaches a metallic surface, the magnitude of its electron affinity increases, basically in response to the attractive ion/metal image potential that the extra electron on the atom will feel in the proximity of the surface. Theoretical calculations have shown that the simple image charge correction for the affinity level provides a very good approximation to results of more sophisticated calculations. What we wish to consider is the case where a neutral electronegative atom or molecule approaches



**Figure 7** Schematic diagram of potential experienced by an electron for an electronegative atom located  $10 a_0$  from a surface under the influence of a strong electric field.

a metallic surface which is also under the influence of an electric field of the polarity required to extract electrons from the metal. The schematic energy diagram given in figure 7 is designed to illustrate the potential that an electron will experience when the atom is at a given distance -  $10 a_0$  in the figure - from the surface.

In the absence of an atom, field emission can occur for strong fields (on the order of a few tenths of a volt per atomic unit of distance) when metal electrons near the fermi level tunnel through or pass over the Schottky barrier indicated by "surface + field" in the figure. By having an atom positioned near the surface the metal electron will see a lowered barrier and, in fact, an intermediate, unoccupied, quasi-bound state which separates it from the vacuum. Such a potential is shown as "surface + atom + field" in the figure. It is obvious that field emission can be enhanced by the presence of the atom. As the atom moves toward the surface its affinity level approaches the fermi level of the metal and a metal electron can transfer and fill the unoccupied state of the negative ion. This state can subsequently decay with the electron going back into the metal (which will occur with no applied electric field and a slow, adiabatic departure of the anion from the surface) or the electron can escape into the vacuum if there is an adequately strong applied electric field. The time that a thermal atom spends in the vicinity of the surface is long (e.g.,  $10^{-13}$  sec.) compared to tunneling times (e.g.,  $10^{-15}$  sec.) and a single atom colliding with and rebounding from a surface may stimulate more than one electron to tunnel from the metal into the vacuum. Hence the phrase coined above: atom-catalyzed field emission.

### III. Students and Personnel

During the contract period, the following Ph. D. graduate students have been involved in various aspects of the projects and have received support from the contract.

James A. Fedchak - graduated in the fall of 1994; currently a post-doc at Argonne National Lab working on polarized hydrogen sources.

John C. Tucek - Senior graduate student working on surface related collision studies; should complete the Ph. D. degree within the current academic year.

Scott G. Walton - fourth year graduate student; working on surface related collision studies and the field emission experiment.

Brian L. Peko - fourth year graduate student working on gas phase collision studies; experimental aspects of Ph. D. thesis should be completed within the current academic year.

Ilya Dyakov - joined A&M group during the summer of 1996, after passing the Ph. D. qualifying exam; will work on gas phase collision experiments and in particular with the microwave atomic beam source.

R. L. Champion was supported by grant funds during the summer for each summer of the contract period. We were saddened by the loss of our colleague and co-PI, L. D. Doverspike, who died in April of 1995. He had received partial summer support prior to then.

#### 4. Reprints/preprints of articles published during the contract period.

Copies of the following papers are appended:

*Electron detachment and charge transfer for collisions of O<sup>-</sup> and S<sup>-</sup> with H.*

Phys. Rev. **A47**, 3796 (1993).

*Photon-stimulated desorption of H from a BaO surface.*

App. Phys Lett. **64**, 1880 (1994).

*Slow collisions of Na<sup>-</sup> and K<sup>-</sup> with atomic hydrogen.*

J. Phys. **B27**, 3045 (1994).

*Electron detachment in low-energy collisions of halogen anions with atomic hydrogen.*

Phys. Rev. **A49**, 255 (1994).

*Detachment and charge transfer for collisions of negative ions with ozone.*

J. Chem Phys. **103**, 981 (1995).

*Destruction cross sections for low energy collisions of H<sub>3</sub><sup>+</sup> and D<sub>3</sub><sup>+</sup> with rare gas atoms.*

J. Chem. Phys. **104**, 6149 (1996).

*Secondary electron and negative ion emission from Al: Effect of oxygen coverage.*

Phys. Rev **B53**, 14127 (1996).

*On the dynamics of secondary-electron and anion emission from an Al/O surface.*

Submitted to Surface Science, August, 1996.