

**Negative Ion Detachment Cross Sections
Interim Progress Report**

R. L. Champion and L. D. Doverspike
Physics Department
College of William and Mary
Williamsburg, VA 23187

DE-FG05-88ER13874, October, 1992

During the past year we have measured absolute cross sections for electron detachment and charge exchange for collisions of O^- and S^- with atomic hydrogen, have investigated the sputtering and photodesorption of negative ions from gas covered surfaces, and have begun an investigation of photon-induced field emission of electrons from exotic structures. Brief descriptions of these activities as well as future plans for these projects are given below.

Electron detachment and charge exchange for O^- and S^-+H

Low energy collisions of O^- and H can produce free electrons via associative detachment,



or collisional detachment,



Only the former occurs for low collision energies, viz., for those relative collision energies below 1.46 eV, the electron affinity of O^- . In order to clarify the role of reaction (1) at very low collision energies, our previous cross section measurements for this channel have been extended to lower collision energies. Absolute cross sections for the production of free electrons in collisions of O^- and (isoelectronic) S^- with atomic hydrogen have been determined for relative collision energies extending down to approximately 30 meV. The total cross section for charge exchange has also been determined in the region which overlaps the threshold energy for ground state reactants.

The results for the detachment of O^- are seen in Fig. 1. Several conclusions may be drawn from these data: At collision energies below 1.4 eV, electron detachment clearly

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

originates from reaction (1). At the lowest collision energy investigated the cross section is still rising, indicating that associative detachment can not be neglected at thermal energies. Hence, any realistic model of OH production, e.g. in flames or interstellar clouds, should include (1). This low energy behavior is compatible with the intermolecular potential calculations by Huron and Tran Minh [1] in which the $^3\Pi$ and $^1\Pi$ states are attractive and cross the ground state of OH in the vicinity of 1.25 Å. A simple model curve crossing model which uses their potentials, as well as a Langevin orbiting model give results which are in satisfactory agreement with the observations.

In the case of $S^- + H$, the cross sections for electron production, $\sigma_e(H_2)$ in collisions of S^- with H_2 were measured for collision energies below those previously reported by Hug et al. [2], since the analysis of the data for $S^- + H$ required knowledge of $\sigma_e(H_2)$ in that energy range. An unexpected bonus came out of these measurements, in that the present results appear to resolve an apparent discrepancy between two previous measurements. For some time it had not been readily apparent that the measurements of $\sigma_e(H_2)$ reported in Ref.

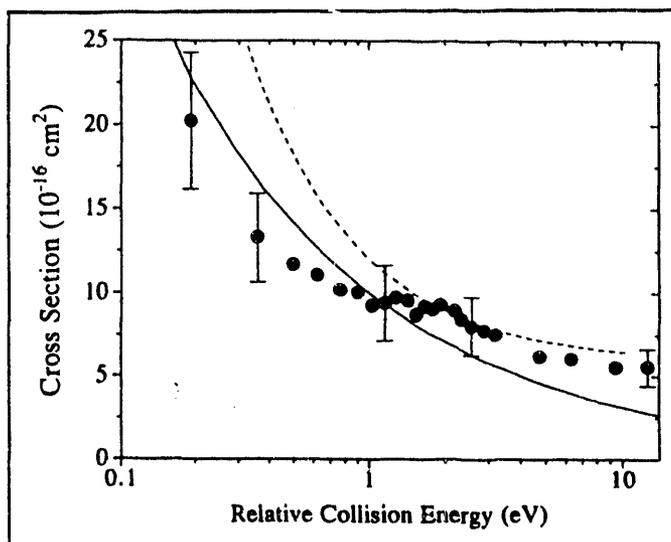


Figure 1. Cross section for $O + H$. The lines are the results of model calculations and the points are the present experimental results.

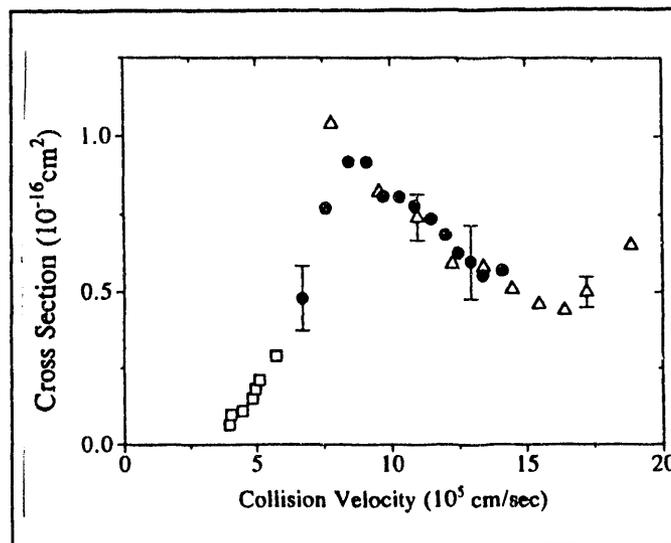


Figure 2. Cross section for $S^- + H_2$. The squares are Ref. 3; the triangles are Ref. 2 and the solid points are the present results.

[2] were consistent with the $\sigma_e(D_2)$ results of Tellinghuisen et al. [3]. But as can be seen in Fig. 2, the present results agree remarkably well with the previous high energy results and clearly extrapolate to the low energy results of [3] if (and only if) the cross sections are plotted as functions of the collision velocity. These results imply the existence of a barrier in the associative detachment channel. What remains unclear however, is why the lower energy measurements scale with collision velocity and not collision energy.

The cross sections for electron

+ H are shown in Fig. 3. The system exhibits a small exchange cross section and the electron detachment cross section resembles that for $O^- + H$, suggesting that the electronic molecular potentials may also be similar. The $OH(^2\Pi)$ state has an equilibrium separation of 0.97 Å while that of $SH(^2\Pi)$ is 1.35 Å [4], so that one would expect, if the electronic structure is similar, the cross sections for S^- to be greater than those for O^- ; this is observed to be the case.

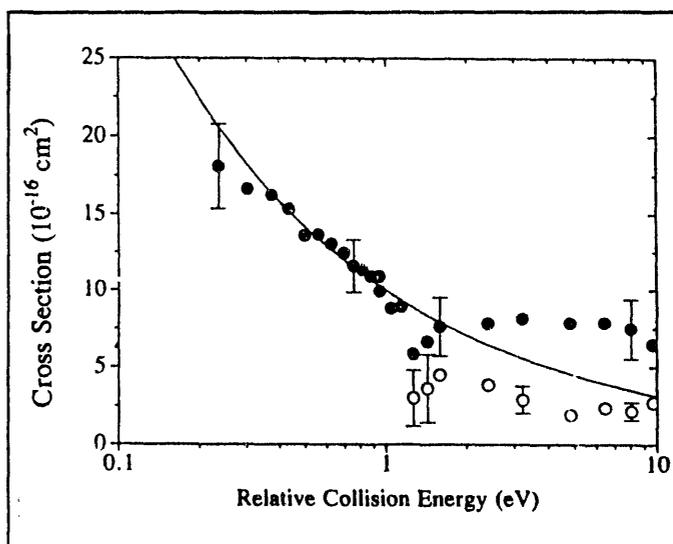


Figure 3. Cross sections for $S^- + H$. The solid (open) circles are for detachment (charge transfer). The line is the result of a model calculation for detachment.

Negative ion and electron emission from surfaces

We have completed a series of experiments in which negative ion and electron yields for collisions of positive alkali ions with a gas-covered, heterogeneous molybdenum surface have been measured for impact energies ranging up to 300 eV. These yields depend strongly upon the work function of the surface which is controlled by varying the partial coverage of the alkali metal on the surface. An example of these yields is shown in Fig. 4 for situations where the work function is low (curves b) and high (curves a). Mass analysis of the sputtered negative ions reveals that the sputtered anions are principally O_2^- , C_2^- , H^- , and O^- with O_2^- being the dominant ion for collision energies in the near-threshold region. The

branching ratios for these ions are presented in Fig. 5 as a function of the alkali ion impact energy.

Two observations suggest that the secondary electrons and the sputtered negative ions originate from a common dynamical mechanism. First, the threshold energies are identical for the electrons and the dominant negative ions species, O_2^- . Secondly, both the electron and negative ion yields at a given impact energy increase in a

very similar manner with increased alkali coverage. One possible explanation for these observations is that the incoming positive ion sputters particles, some of which are electronegative and may form both stable and unstable negative ions when leaving the surface. In such a scenario, the unstable negative ions autodesorb giving rise to the secondary electrons observed in the process. For example, $O_2^-(v)$ is unstable if the vibrational quantum number, v , is greater than three. In the near-threshold region, it may well be that the average vibrational quantum number, \bar{v} , for $O_2^-(\bar{v})$ is small (below 3) and as the impact energy increases, \bar{v} increases accordingly. Hence at low energy, it would be more likely to observe

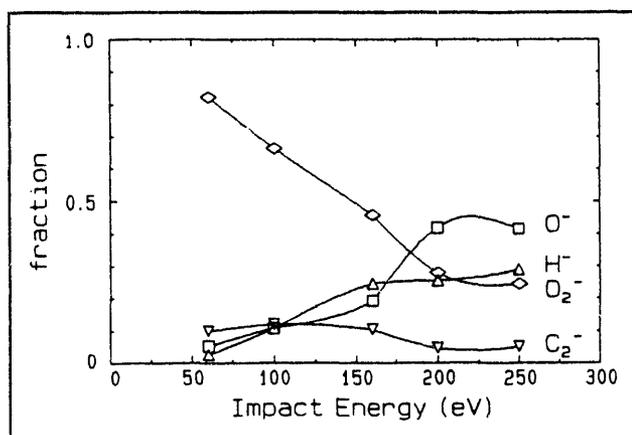


Figure 5. Fractional composition of negative ions desorbed from surface as a function of impact energy.

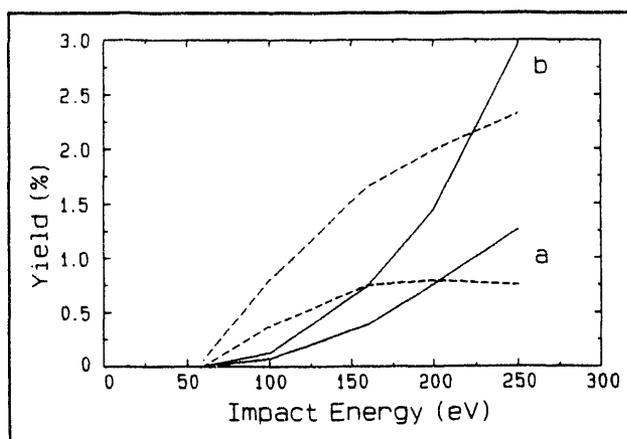


Figure 4. Electron (solid lines) and negative ion (dashed lines) yields for high(a) and low-(b) work functions

the stable molecular negative ion, which at higher energies the secondary electron signal would exceed that for O_2^- as is observed in the present experiment. Thus the suggestion is that secondary electron emission for these low energy collisions is **not** an independent process but rather follows from sputtering an unstable negative ion which autodesorbs after the anion is a few angstroms from the surface.

The mechanism responsible for secondary electron emission owing to collisions

of low energy ions (or neutrals) with surfaces has long been a mystery; the present measurements provide considerable insight into the nature of that process.

Photodesorption of H⁻

We have examined the process of photodesorption of H⁻ from barium (containing interstitial hydrogen) over the range of wavelengths extending down to 250 nm. The light source for the present experiments consists of a mercury arc lamp and a 1/4 meter monochromator. The relative yield of the hydrogen negative ions is observed to increase almost exponentially with increasing photon energy for energies above a threshold of about 3 eV. This observed threshold of 3 eV is compatible with the relevant binding energies for (BaH)_{surface} [-1.2 eV], the work function for Barium [-2.5 eV] and the electron affinity of hydrogen [0.75 eV]. The relative yield of H⁻ (i.e., the number of ions per incident photon) as a function of photon energy is seen in figure 6. Our goal is to determine the absolute yield and to extend these measurements to shorter wavelengths. It may well be that far UV photons are an important source of hydrogen anions in so-called "convertor" ion sources which use the barium (because of its low work function and its ability to store hydrogen) to increase the output of the ion source.

Photon-assisted field emission

A cathode with micron-sized TaSi₂ structures [5] is being examined for use as a high brightness, pulsed electron source. An electric field is applied to the structure such that field emission just onsets. When an additional field due to a polarized pulsed laser is applied to the cathode, the field emission is greatly enhanced. The laser utilized in these initial experiments is a NdYag (@1064 nm) with only moderate pulsed power; the experiments are being reconfigured to allow for transport to other light sources.

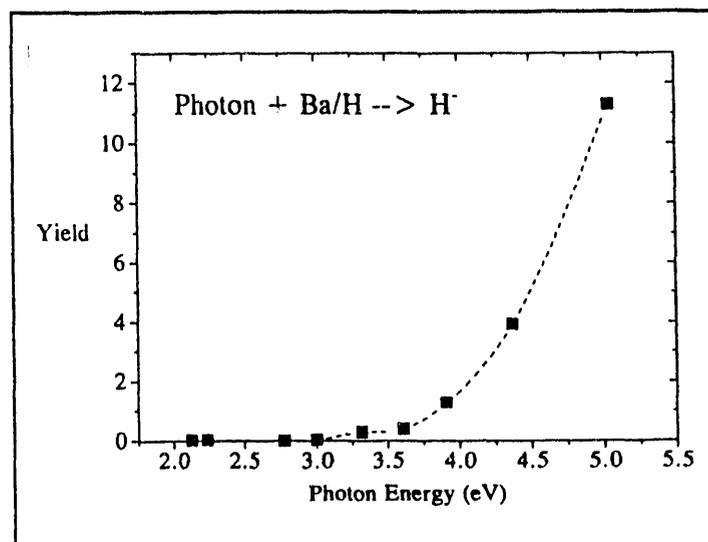


Figure 6. Relative yield of H⁻ from photon impact of hydrogen-containing barium.

Future plans

Absolute electron detachment and charge exchange cross sections will be measured for collisions between alkali anions and atomic hydrogen. These measurements will emphasize collision energies in the range 30 meV to 300 eV and be performed on the crossed beam apparatus. Following these studies, the apparatus will be modified to include a gaseous ozone target and numerous experiments involving collisions between halogen anions and ozone will be conducted. These studies will emphasize the various ozone destruction mechanisms which are possible in such collisions.

A more detailed study of secondary negative ion and electron emission from gas-covered surfaces will be extended to include Ba and Niobium surfaces. These will be accompanied by surface analysis (SIMS) in order to characterize the surface adsorbate which is the source of the emitted negative ions and electrons. The photodesorption of negative ions and the photon-assisted, field emission experiments will be further investigated with additional light sources. The effects of photon intensity and polarization upon the electron emission will be examined in an attempt to characterize the emission mechanism.

Personnel

The following persons have participated in and received some form of support from the project during the past year:

Roy Champion - (co- PI; two months summer support)

Lynn Doverspike - (co- PI; two months summer support)

Doug Baker - (graduate student; 12 months support)

Jim Fedchak - (graduate student; 12 months support)

Sandrine Lacombe - (visiting graduate student from Orsay; one month support)

William Brown - (Transylvania undergraduate student; summer, 1992)

Geoffrey Mueller - (W&M undergraduate student doing senior thesis)

Chris Surridge - (W&M undergraduate student doing senior thesis)

Messrs Mueller and Brown also received support from the NSF program, Research Experiences for Undergraduates.

Publications

"Negative ion and electron emission from surfaces at low impact energies", D. H. Baker, L. D. Doverspike and R. L. Champion, Phys. Rev. A46, 296 (1992).

"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, submitted to Phys Rev. A.

"Formation and desorption of negative ions from metal surfaces", D. H. Baker, PhD thesis.

References

1. B. Huron and F. Tran Minh, Astron. and Astrophys. 38, 165 (1975).
2. M. S. Huq, D. Scott, R. L. Champion and L. D. Doverspike, J. Chem. Phys. 82, 3118 (1985).
3. The results of J. Tellinghuisen, M. McFarland, D. L. Albritton, F. C. Fehsenfeld and W. Lindinger have been reported in F. C. Fehsenfeld, "Nato Advanced Study Institute Series, edited by Pierre Ausloos (Plenum, New York, 1974), vol. 6, p. 387.
4. G. Herzberg "Molecular Spectra and Molecular Structure," I. Spectra of Diatomic Molecules, 2nd ed. (Von Nostrand Reinhold Co., New York, 1950).
5. D. A. Kirkpatrick et al., Appl. Phys. Lett. 59, 2094 (1991).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

**DATE
FILMED**

2 / 24 / 93

