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Negative Ion Detachment Cross Sections
Interim Progress Report

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During the past year, we have measured cross sections for associative and collisional detachment for several negative ions in collisions with atomic hydrogen. Additional experiments have been performed in which the formation of secondary negative ions and electrons by means of low energy ion impact on surfaces has been studied. Brief descriptions of these activities along with future plans for the project follow.

<u>Associative and collisional electron detachment: $O^- + H$</u>.

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

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

or collisional detachment,

$$O^- + H \rightarrow O + H + e. \qquad (2)$$

Only the former occurs for low collision energies, viz., for those relative collision energies below 1.46 eV, the electron affinity of O^-. This anion had been considered as a participant in the negative ion chemistry of interstellar molecules but was dismissed as reaction (1) was assumed to be slow at temperatures relevant to the interstellar environment. This assumption prompted a calculation of the intermolecular potentials for the molecular ion OH^- which, in turn, led to the suggestion that associative detachment might <u>not</u> be slow.

The ground electronic state of OH^- is of $^1\Sigma$ symmetry, has a vertical electron affinity of about 1.8 eV and has been well-

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characterized. It does not cross the $^2\Pi$ state of OH and does not couple strongly to that state; hence collisions at low energies which are attributed to the $^1\Sigma$ state of OH^- are essentially non-reactive. However, in a collision the excited electronic states of the molecular anion which result from $O^-(^2P)$ interacting with $H(^2S)$ must also be considered in the dynamics for (1) and (2). In addition to the $^1\Sigma$ state there are the $^1\Pi$, $^3\Pi$ and $^3\Sigma$ states. The $^1\Pi$ and $^3\Pi$ states were determined to be attractive, intersecting the neutral $OH(^2\Pi)$ at an internuclear separation of about 2.5Å. The combined statistical weights of these two states is 2/3 and the attractive curves are somewhat similar to the induced dipole potential given by $-\alpha e^2/2R^4$ (where α is the polarizability of H); hence one might expect (1) to be <u>fast</u>, with a rate constant in the neighborhood of 2/3 of that predicted by a simple Langevin orbiting model.

Our recent results (obtained from a crossed-beam configuration) for the associative and collisional electron detachment cross sections are given in Figure 1; the two channels, (1) and (2), cannot be distinguished in this experiment. For $E < 1.46$ eV, however, only associative detachment [i.e., (1)] is energetically possible. The increase in the cross section as E is lowered below the electron affinity of oxygen implies, unambiguously, that one or more of the intermolecular potentials which describe $O^- + H$ must be attractive and must couple strongly to the $^2\Pi$ state of OH. Although the $^1\Sigma$ state of OH^- is attractive, it probably does not lead to associative detachment and, even if it did, it could not account for the observed cross section as its relative statistical weight is only 1/12. Hence we are led to conclude that other states are attractive and lead to the low energy behavior observed in Figure 1 for the detachment cross section. In fact the Langevin cross section for $\alpha = 0.7Å^3$ (the polarizability of hydrogen) is about $15Å^2$ for $E = 1$ eV; the measured cross section at 1 eV is $6Å^2$. The combined statistical weights of those two states which have been calculated to be

attractive is 2/3. Their contribution to the associative detachment cross section at E = 1 eV could then be expected to be a maximum of about 10Å². The observation that the cross section is ~60% of that given by the simple Langevin model is also observed for the reactants Cl^- + H.

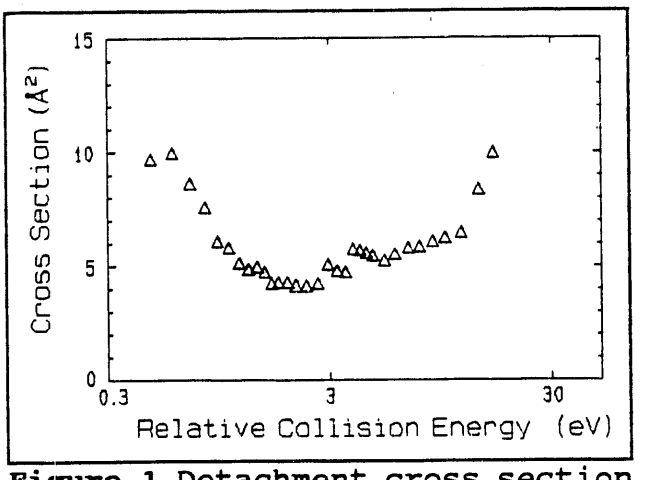

Figure 1 Detachment cross section as a function of collision energy; O^- + H

At the present the experimental measurements are being extended to collision energies below 0.5 eV. The observation that this lowest energy measurement gives a cross section which is below that at E = 0.6 eV may imply that a slight barrier to associative detachment occurs in the incoming channels. If this is true (one data point is completely inadequate information upon which to draw such a conclusion, however), the thermal rate constant for associative detachment could be small.

Secondary Negative Ion Emission from Surfaces

Studies are currently being completed in which the dynamics of secondary negative ion emission from surfaces is being investigated. Negative ions and electrons are ejected from surfaces which are bombarded by positive alkali ions, in an environment similar to that found in negative ion sources in which alkali metal has been added to improve the source performance. The yields of both negative ions and electrons have been measured as a function of the alkali ion's impact energy, the alkali coverage on the surface (and hence its work function) and various gas treatments. The results for the yields vs. impact energy are shown in Fig. 2. The onsets for electron and negative ion emission occur at the same threshold energy,

suggesting a collision mechanism common to both. The surface is molybdenum and the various negative ions probably arise from surface oxides and adsorbed water.

The question concerning the mechanism for producing secondary electrons is very interesting. At the low collision energies involved in these experiments, the traditional mechanism of producing secondaries at high (> 1 keV) energies, viz., kinetic emission, is completely inoperative. Auger processes are likewise impossible owing to the low recombination energy (i.e., ionization potential) of the impacting alkali ion. We propose that the secondary electrons observed in Fig. 2 result from the sputtering of negative ions which are unstable with respect to autodetachment. An example of this mechanism is for the case of sputtering $O_2^-(v)$: If $v > 3$, then the molecular anion will autodetach yielding a free secondary electron. This mechanism, if correct, will shed light on a longstanding question of secondary electron emission by low energy projectiles.

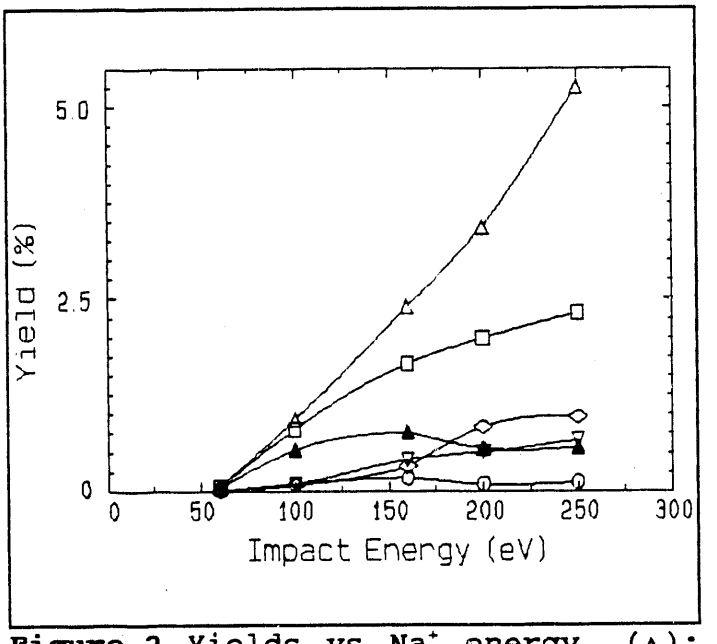

Figure 2 Yields vs Na^+ energy. (△): totals for negative ions + electrons. (▲): O_2^-; (▽): H^-; (◇): O^-; (○): C_2^-; (□): total yield for all anions.

Future Plans

Measurements on the O^- + H system are currently being extended to energies below 0.6 eV and an investigation of the isoelectronic system S^- + H will follow. These results should clarify the questions raised about the low energy behavior of the associative detachment process. A detailed study of the collisional dynamics of hydrogen atoms and alkali negative ions

is also planned to follow these measurements. An alkali ion source has been designed, built and tested. Cross sections for charge exchange, direct and associative electron detachment will be measured. An ozone source will subsequently be installed in the crossed beam apparatus to enable cross sections, similar to those determined for the hydrogen target, to be measured for a variety of systems involving collisions of atomic negative ions with O_3. In the area of secondary electron and negative ion desorption from surfaces, we will examine the role of photons and strong (eV/angstrom) electric fields in this desorption process. We will continue to try to understand the mechanism(s) responsible for these processes.

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