

To be submitted to the Second International Workshop on MeV and keV Ion and Cluster Interactions with Surfaces and Materials, September 5-8, 1988, Orsay, France.

DESORPTION OF Cs⁺ IONS WITH FAST INCIDENT ATOMIC AND MOLECULAR IONS*

Mehran Salehpour¹, Jerry E. Hunt and L. C. Tou², Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U. S. A.

Allan Hedin and Bo Sundqvist, Department of Radiation Sciences, Ion Physics Division, Box 533, Uppsala University, Uppsala, Sweden.

CONF-8809134--2

DE89 003958

RÉSUMÉ

The submitted manuscript has been authored by a contractor of the U.S. Government under contract number W-31-109-ENG-38. Accordingly, the U.S. Government retains a certain, non-exclusive, non-transferable, irrevocable and exclusive license to publish or reproduce the published form of this contribution or allow others to do so, for U.S. Government purposes.

ABSTRACT

Preliminary results on desorption yield measurements of secondary Cs⁺ ions, desorbed as a result of the impact of C⁺, O⁺, CO⁺, O₂⁺, CO₂⁺ and C₄H₉⁺ incident ions, in the energy range of 950 keV- 3.5 MeV are presented. Molecular beams are found to give high yields of secondary Cs⁺ ions, which is of interest in the field of applications. Comparison of the yield of Cs⁺ as a result of impact of O₂⁺ compared to O⁺ incident ions, indicate no "collective" molecular effects.

* Work performed under the auspices of the Office of Basic Energy Sciences, U.S. Dept. of Energy under contract number W-31-109-ENG-38.

¹ Present address: Department of Radiation Sciences, Ion Physics Division, Box 535, Uppsala University, Uppsala, Sweden.

² Permanent Address: Dow Chemical, Midland, Michigan 48667, U. S. A.

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.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ps

Particle induced desorption of polyatomic ions from surfaces is of general theoretical interest, as well as having practical applications in the field of mass spectrometry /1/. A large body of experimental data exist on the use of fast ($v \geq v_{\text{Bohr}}=0.22 \text{ cm/ns}$) atomic incident ions in desorption studies /1/. However, few reports exist on the use of fast molecular ions as the primary ions in desorption experiments. Brown et al. /2/ and Thomas et al. /3,4/, have used hydrogen cluster ions to measure yields of H_2O molecules and Cs^+ ions, respectively (yield is defined as the number of atoms or molecules detected per incident ions). We recently reported on some results using heavy incident molecular ions such as C_2^+ , C_3^+ , O_2^+ , CO^+ , CO_2^+ , CH^+ , CH_3^+ , C_3H_3^+ , CF^+ , CF_3^+ , C_3F_5^+ , and C_4F_7^+ in the energy range 600 keV - 3.7 MeV on organic samples /5,6,7,8/.

One of the general characteristics of fast ion induced desorption, reported by us /7,8/ and the Uppsala, Orsay and Darmstadt group /1/ is that the secondary ion yields, depending on the velocity range/primary ion/target combination, generally vary nonlinearly with respect to the electronic stopping power (energy deposited per unit path length, $\frac{dE}{dx}$) of the incident ion in the medium. In previous experiments we measured the secondary negative ion yields of the amino acid valine (MW=117) as a function of atomic and molecular primary ion velocity /5,6,7,8/. Two types of nonlinearities were observed; one associated with the atomic ions as mentioned above, and the other associated with the "molecularity" of the incident projectile. By "molecularity" we refer not to the molecular bonding but rather to the spatial and temporal correlation of the fast moving charges in the solid. For example, the yield of valine negative molecular ions with incident C^+ , $Y(\text{C})$, was found to follow a near square dependence on $\frac{dE}{dx}$ /7,8/, i.e., $Y(\text{C}) \propto (\frac{dE}{dx}(\text{C}))^2$. However, the secondary ion yields with C_2^+ incident ions, $Y(\text{C}_2)$, and C_3^+ incident ions, $Y(\text{C}_3)$, was found to be approximately, 8 and 16 times that of incident C^+ ions, respectively, in the velocity range of 0.2-0.5 cm/ns. This is significantly more than that expected from a square dependence on $\frac{dE}{dx}$ (factors of 4 and 9 for C_2^+ and C_3^+). Similar results have been observed with other incident ions /8/. Thus, there is another effect which also contributes to the nonlinearity with respect to $\frac{dE}{dx}$ observed in the molecular primary ion desorption data.

It has been shown experimentally that the electronic stopping power of an atom in a fast moving cluster in solids, is higher in magnitude than that of the individual atom in the same medium. The enhancement in $\frac{dE}{dx}$ per atom for X_n clusters was parameterized by Brandt et. al /9/ by the energy loss factor, $R = \frac{\frac{dE}{dx}(X_n)}{\sum \frac{dE}{dx}(X_i)}$. Brandt et. al /9/ reported R values in the range 1-1.5, for H_2^+ and H_3^+ incident ions in thin carbon targets. Tape et. al /10/ obtained similar results with H_2^+ and H_3^+ as well as O_2^- incident ions in the same velocity range as this experiment. The question of interest is whether such enhancements in $\frac{dE}{dx}$ would be expected to effect desorption yields.

As fast molecular ions enter a solid medium, within a few atomic layers, the bonding electrons are stripped off the molecule. The resulting repulsive coulombic force between the constituent atoms causes the molecule to undergo a "Coulomb explosion", increasing the internuclear distance, r_0 , in the molecule as it traverses the solid. When r_0 becomes larger than the dynamic screening length, a , the molecular constituent atoms act as separate charges. Based on Brandt et. al's formulation /9/, we have shown /8/ that over the desorption depth ($\approx 100-250 \text{ \AA}$, /11,12/), $r_0 < a$. Thus we concluded that any enhancements in $\frac{dE}{dx}$ might be expected to be reflected in desorption yields using polyatomic incident ions. The R values that were used to fit the valine data were in good general agreement with the values reported in the literature for incident ions for a comparable velocity range and atomic number /10/.

Preliminary results for the negative molecular ion yields from another compound with very different chemical properties, chlorophyll a (MW=893), showed similar results /13/. Due to the experimental arrangement, where secondary electrons were used as the start signal for the time-of-flight measurement, all our data so far have concerned negative ion yield measurements.

Hedin et al. /14/ recently reported on desorption measurements for valine and cesium iodide targets, using 0.5 cm/ns, C^+ and C_2^+ incident ions. They prepared very thin targets (about 3000 \AA), and studied both positive and negative secondary ions. The results for valine negative secondary ions were in qualitative agreements with ours /8/, i.e., $R > 1$, although they obtained a

somewhat smaller R value. However, for positive valine secondary ions and Cs^+ ions they found no molecular effects, i.e., $R=1$.

In a collaboration with the Uppsala group, we have measured the yield of Cs^+ ions from thin targets as a function of the velocity of C^+ , O^+ , CO^+ , O_2^+ , CO_2^+ and C_4H_9^+ incident ions, shown in figure 1. The 4.5-MV Dynamitron accelerator at Argonne was used to accelerate ion produced in a low energy electron impact ion source. A time-of-flight mass spectrometer was used to measure the yield of secondary ions. From a mass spectrometry point-of-view, the enhancements in the yield for the larger incident molecular ion is of practical interest. From a fundamental stand point, the O^+ and O_2^+ data can be used to extract an R value to see if collective effects are reflected in the desorption yields.

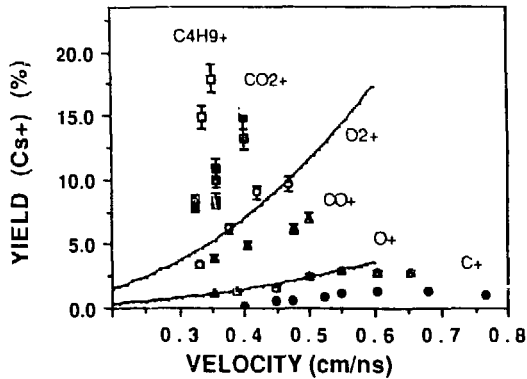


Figure 1. The secondary yield of Cs^+ ions as a function of the velocity of incident C^+ , O^+ , CO^+ , O_2^+ , CO_2^+ and C_4H_9^+ . The fit to the O^+ and O_2^+ are based on $Y = \text{constant} \cdot \left(\frac{dE}{dx}\right)^{2.2}$, and $R=1.0$ for O_2^+ data. $\frac{dE}{dx}$ values are calculated using the Linhard formulation.

In this velocity range few measurements exist on absolute $\frac{dE}{dx}$ values. The tables of Northcliff and Schilling /15/ are known to be rather questionable in this velocity range and the Ziegler tables for heavy ions /16/ do not cover the velocity range of our experiment. Thus, we have used the Linhard formulation /17/ which is only valid in the velocity region, well below the electronic stopping power maximum, i.e., $v \ll v_{\text{Bohr}} \cdot Z^{2/3}$. In

addition, we have used the effective charge, Z_{eff} , concept /18/ to extrapolate the stopping power of protons to oxygen ions. For the oxygen data, a least squares fit to $Y = K \cdot (\frac{dE}{dx})^n$, using the Linhard and Z_{eff} scaling formulation for $\frac{dE}{dx}$, gave n values which were quite close, i.e., n - values of 2.2 and 2.26). Shown in figure 1 is the least square fit to the O^+ data using the Linhard stopping; as expected the fit worsens as the peak of the stopping power is reached. The empirical fit was then applied to the O_2^+ data, as discussed in reference /5/ and it was found that $R=1$ (see figure), in agreement with the Uppsala result /14/.

Comparing the atomic O^+ data to that of Håkansson et. al /18/ we found good agreement for $v < 0.5$ cm/ns, whereas at higher velocities disagreements existed. This is due to the fact that the O^+ ions used in this experiment were not charge equilibrated. As discussed in /9/, for incident ions in this velocity region, the L-shell electron loss cross section decreases rapidly with velocity, so for the faster ions, charge equilibration distance becomes comparable or longer than the desorption length, thus a charge state dependence of the yield is expected. Hedin et. al /19/ showed that at 0.5 cm/ns no noticeable yield dependence on charge state existed for O^+ , O^{+3} , O^{+4} ions.

We have attempted similar experiments with valine positive molecular ions, however, due to sample preparation problems the experiment could not be performed and will be repeated in the near future. However, comparing valine negative molecular ion results and Cs^+ data it is apparent that the effects are different. Having reproduced the Uppsala Cs^+ data, it appears likely that the valine positive secondary results with C_2^+ incident ion, i.e., $R=1$, should be valid. Thus, it suggests that negative and positive secondary ion may be desorbed through different mechanism. Differences in desorption yields of positive and negative secondary ions with respect to different beam parameters have been reported before /20,21,22/ and discussed in these proceedings /23/.

REFERENCES

- /1/ For a review, see, B. U. R. Sundqvist and R. D. Macfarlane, *Rev. Mass Spectrom.* **4** (1985) 421.
- /2/ W. L. Brown, W. M. Augustyniak, E. Simmons, K. J. Marcantonio, L. J. Lanzerotti, R. E. Johnson, J. W. Boring, C. T. Reiman, G. Foti and V. Pirronello, *Nucl. Instr. Meth.* **198** (1982) 1.
- /3/ J. P. Thomas, P. E. Filpus-Luyckx, M. Fallavier and E. A. Schweikert, *Phys. Rev. Lett.* **55** (1985) 103.
- /4/ J P Thomas, M Fallavier and P. E. Filpus-Luyckx, *Rad Eff* **99** (1986) 213.
- /5/ M. Salehpour, D. L. Fishel and J. E. Hunt, *J. Appl. Phys.* **64** (1988) 831.
- /6/ M. Salehpour, D. L. Fishel and J. E. Hunt, *Int. J. Mass Spectrom. Ion Proc.* **84** (1988) R7.
- /7/ M. Salehpour, D. L. Fishel and J. E. Hunt, *Rap. Comm. Mass Spectrom.* **2** (1988) 59.
- /8/ M. Salehpour, D. L. Fishel and J. E. Hunt, To appear in *Phys. Rev. B.*, 1988.
- /9/ W. Brandt, A. Ratkowski and R. H. Ritchie, *Phys. Rev. Lett.* **33** (1974) 1325.
- /10/ J.W. Tape, W. M. Gibson, J. Remillieux, R. Laubert and H. E. Wegner, *Nucl. Instr. Meth.* **132** (1976) 75.
- /11/ G. Säwe, P. Håkansson, B. U. R. Sundqvist and U. Jönsson, *Nucl. Instr. Meth.* **B26** (1987) 579.
- /12/ G. Säwe, P. Håkansson, B. U. R. Sundqvist, R. E. Johnson, E. Söderström and S. E. Lindquist, *App. Phys. Lett.* **51** (1987) 1379.
- /13/ J. E. Hunt, M. Salehpour, D. Fishel, E. Kanter, B. Zabransky, A. Ruthenburg, and R. Amrein, the proceedings of the 11th International Mass Spectrometry Conference, Bordeaux, France, August 29-September 2, 1988.
- /14/ A. Hedin, P. Håkansson and B. U. R. Sundqvist, these proceedings.
- /15/ L. C. Northcliffe and R. F. Schilling, *Nucl. Data Tables* **7** (1970) 233.
- /16/ Handbook of stopping cross-sections of energetic ion in all elements, (The Stopping and Ranges of Ions in Matter, Vol. 5), J. F. Ziegler, ed., Pergamon Press, New York, U.S.A., 1980.
- /17/ J. Linhard and M. Scharff, *Phys. Rev.* **124** (1961) 128.
- /18/ W. Brandt, in *Atomic Collisions in Solids*, Vol. 1 (Eds. S. Datz, B. R. Appleton and C.D. Moak; Plenum Press, New York, 1975) p. 261.
- /19/ A. Hedin, private communication, 1988.
- /20/ A. Hedin, P. Håkansson, M. Salehpour and B. Sundqvist, *Phys. Rev. B* **35** (1987) 7377
- /21/ O. Becker, S. Della-Negra, Y. LeBeyec and K. Wien, *Nucl. Instr. Meth.* **B16** (1986) 321.
- /22/ B. Nees, E. Nieschler, N. Bischof, H. Frölich, K. Riemer, W. Tiereth and H. Voit, *Surf. Sci.* **145** (1984) 197.
- /23/ J. E. Hunt, M. Salehpour, D. L. Fishel and J. C. Tou, see these proceedings.