Ion-Induced Desorption by High-Energy (600 keV) Hydrogen Clusters

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Desorption has been induced from CsI by hydrogen clusters of mass ranging from 5 to 23. A cluster effect has been observed in comparison of the Cs^+ desorption yields as obtained from intact and preexploded clusters. The variation of the yield with the sum of the electronic stopping powers of the cluster components (additive stopping) shows a fourth-power dependence. The contribution of collective effects in the interaction may play a crucial role in the nonlinearity of the process.

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High-velocity-particle–induced desorption, first observed by Mac Farlane and Torgerson,[1] has received increasing attention in recent years as evidenced by numerous fundamental and applied studies. Although not yet fully elucidated, the mechanism by which the electronic excitation from the interaction is coupled to atomic motion has been described with several models. Basically they involve two concepts: the ion explosion[2] and the thermal-ionization spike,[3] which can be somewhat combined as in the thermalized ion-explosion model of Sieberling, Griffith, and Tombrello.[4] Nonlinear variation of the desorption yield as a function of the electronic stopping power $(dE/dx)_e$ has been reported to depend on the mass and energy of the incident particle, although, especially for heavy ions, Meins *et al.*[5] state that the primary ionization rate, dJ/dx, should be used as a main input for energy conversion. Following Seiberling's conclusions, a $(dJ/dx)^4$ variation would be expected if a local thermal equilibrium is reached from the initial ion explosion. However, as far as light particles are concerned, particularly in the energy region above the maximum of the electronic stopping power, but also below the maximum, there is ample experimental evidence for an approximately $(dE/dx)_e^2$ dependence. This is found in the sputtering of frozen gases,[6–8] the desorption of biomolecules,[9,10] and, to a lesser extent, the sputtering of alkali halides.[9,11] For incident ions of higher mass and energy, the yield tends to vary even more strongly with stopping power.

The yields might be further increased by use of polyatomic ions in the electronic stopping power region. In this respect no desorption studies have been reported so far. In sputtering (desorption) studies of H_2O with incident H^+, H_2^+, and H_3^+ ions in the 1-MeV range, the sputtering yield was found to vary as the square of the proton number (at a fixed velocity), thus implying a $(dE/dx)_e^2$ dependence of the sputtering process if the electronic stopping power of the molecular ions is assumed to be the sum of the stopping powers of the protons contained in the molecule. However, for sputtering with molecular ions in the collisional energy regime, even more spectacular increases in yield have been reported.[13] The objective of the present study was to evaluate the stimulation of desorption by heavier H clusters. Such clusters should indeed be of interest since, at a minimum, they might be expected to cause a linear increase in the desorption yield. One of the open questions was if an additional synergistic effect might occur. An investigation of cluster yield is thus of fundamental importance and has further practical implications, particularly for applications in microprobe analysis.[14]

Hydrogen clusters were produced by the open-air cascade accelerator of the Institut de Physique Nucléaire de Lyon.[15] The characteristics of this machine are an accelerator tube, 1.2 m long, with a gap width of 10 cm, where up to 800 keV can be ap-

plied, and a cluster source, part of a liquid He cryostat placed on top of the accelerator tube, and extending deeply into the reentrant anode. The cluster beam was produced by expansion of hydrogen gas from a stagnation reservoir when pulsed by means of an electromagnetic valve. Ionization of these clusters was realized by electron impact through a specially designed ionizer.[15] Beam analysis was achieved by the coupling of an electrostatic deflector with a magnet: Singly ionized clusters H_n^+ with $n=1,3,5,\ldots,23$ were successively energy analyzed at the target site located 2 m from the exit of this cross-field analyzer. With a mass resolution better than 0.5-amu FWHM at mass 21, the peaks are virtually interference free with the slit adjustment of the setup.[16] Optimal peak intensities during pulses typically 100 ms long were in the nanoampere range, although our experiments only required several thousand ions per pulse.

The ions desorbed upon cluster impact were detected with a conventional time-of-flight (TOF) system: The target was biased up to 4 kV, two grids at ground defined the drift region 11.5 cm long, and a microchannel plate assembly acted as the stop signal. Two major problems made some differences with the procedure applied to energetic (MeV/amu) monatomic ions. First, the start and stop signals must be gated by the valve aperture signal, since an important continuous leak beam was observed from direct detection by a surface-barrier detector (SBD) used as the start signal: HeH^+ for mass 5 and N^{2+} for mass 7, for example. Second, in this energy range the target must be thin enough to allow the cluster fragments to reach the SBD. We used an 85% molybdenum transmission grid coated on the back side with a 4-μg/cm^2 Formvar foil and on the front side with 40 μg/cm^2 of cesium iodide thermally evaporated. In such a way and with a SBD solid angle of 0.14 sr, even at mass 23, more than half of the transmitted particles corresponded to the maximum-energy peak (all the fragments collected). The measurements were taken with the beam line and target chamber at 10^{-6} Torr vacuum. The desorption yields are defined as the number of Cs^+ ions for 100 detected events on the SBD but are only relative values: No attempt was made to correct them for detection efficiency since we still observed noticeable variations from sample to sample. Comparisons of yield with cluster size have been obtained from a single sequence of runs on the same target.

The mass-analyzed beam is only characterized, with our setup, by the energy spectrum of the incident particles. As shown in Fig. 1(a), some in-flight fragmentation is evident as low-energy peaks corresponding to incomplete fragment collection. The maximum-energy peak is thus not a definite proof that the intact cluster impinges on the target; however, the cluster must explode very close to the target in order for all

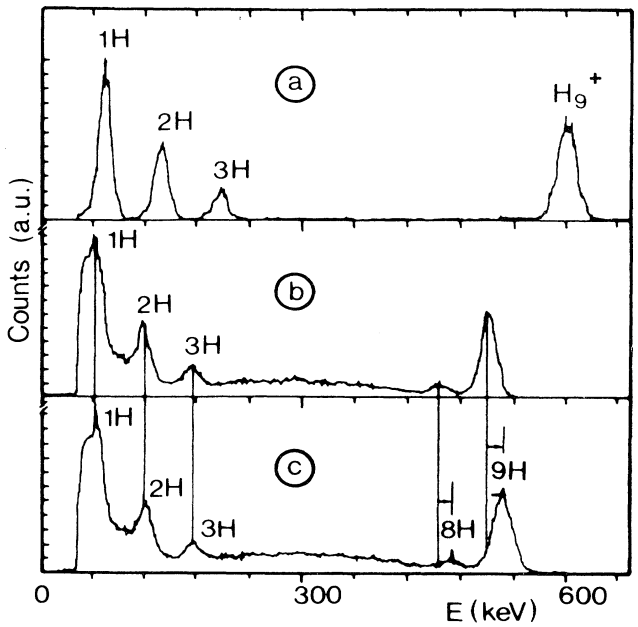

FIG. 1. SBD spectra taken with the same geometry from 600-keV H_9^+ clusters: (a) directly impinging on the SBD, (b) after passing the target at ground, and (c) after passing the target 4 kV biased. The peak labeled H_9^+ is the maximum-energy peak from the intact cluster detection. Peaks labeled 1H, 2H, . . . , 9H are for equivalent number of simultaneously detected protons.

the fragment to be simultaneously detected. Further information on the intact state of impinging clusters was obtained from the energy shift of the transmission peak between biased and unbiased target [Figs. 1(b) and 1(c)] at 4 kV. The shift of the H_9 and H_8 peaks in the spectrum indicate that the incident particles were dominant charge-1 clusters and not a shower of time-correlated protons as would be expected if fragmentation had occurred before the target.[17] Finally, the best demonstration for intact clusters is to deliberately break them up prior to impact. This was done by the interposing of a 4-μg/cm^2 Formvar film on the beam trajectory about 1 m from the target. The mass 7, chosen for this experiment, is a compromise between the difficulty of detecting all the individual hydrogen atoms from larger clusters and the lower desorption yield induced by smaller clusters. It can be seen in Fig. 2(b) that all the masses are detected including the maximum one but with an important reduction in yield. This can be compared with Fig. 1(a) where in-flight fragmentation does not show masses higher than 3. When we interpose the film before the target, the spectrum has no structure between 3 and 8 but a broad distribution [Fig. 1(c)]. Figures 2(c) and 2(d) show the TOF spectra resulting from dissociated and intact H_7 clusters. The Cs^+ peak is, in the last case, larger

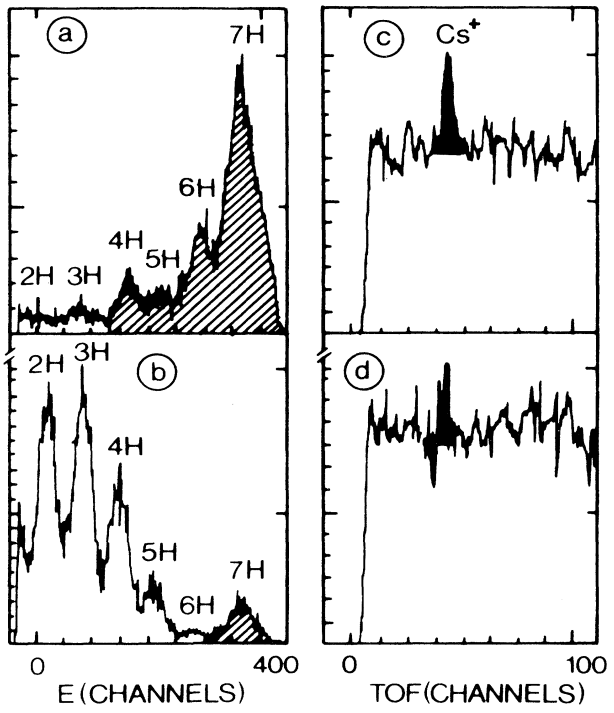

FIG. 2. Comparison of SBD and TOF spectra of intact and exploded 600-keV H_7^+ clusters: (a),(c) SBD and TOF spectra from intact clusters passing the target foil; (b),(d) SBD and TOF spectra from cluster fragments passing the target foil.

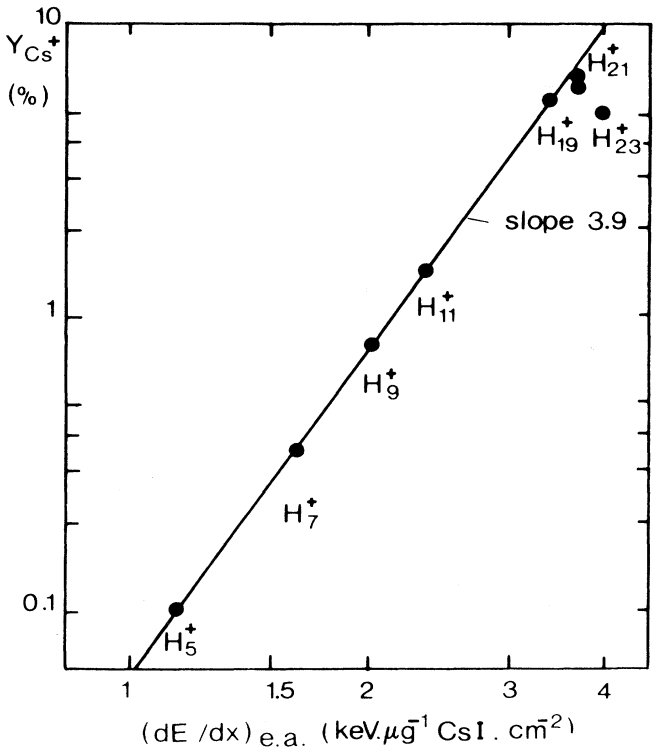

FIG. 3. Desorption yield of Cs^+ as a function of the additive electronic stopping per individual cluster. Related cluster masses are indicated.

and better defined than the small, poor signal-to-noise peak induced by the fragments. The corresponding yield (taken from the ratio of the corresponding shaded and black areas) can only be stated as 0.08% (close to the detection limit), while 0.17% was obtained from the intact cluster.

A systematic investigation of the yield as a function of the cluster mass has been carried out at 600 keV. The start signal was taken from the maximum-energy peak (from the area of which the number of incident clusters is obtained). However, a larger energy window did not significantly change the yield value; i.e., lower-mass peaks were also due to intact incident clusters. The ion current does not vary by more than a factor of 2 for the various masses, but this parameter has no effect on the Cs^+ yield as long as pileup is avoided. As was done for megaelectronvolt molecular ions,[12] variation of the Cs^+ yield has been plotted as a function of the additive stopping power $(dE/dx)_{EA}$, which is defined as n times the electronic stopping power of the proton at the velocity of the H_n^+ cluster. From the log-log plot of Fig. 3 it can be seen that there is a definitive trend for a $(dE/dx)_{EA}^4$ variation up to mass 21. The data are for a cluster series from mass 5 to 23 on a single CsI target. This variation does not depend on the cluster mass sequence (from the lightest to the heaviest or conversely): If any evolution of the surface composition is suspected under irradiation, it does not appear systematic. From six independent runs, the power exponent has been determined between the extreme values of 3.5 and 4.3.

One of the main difficulties in relating these results to the existing theories lies in our lack of knowledge about the interactions of cluster ions with matter. For example, the effective charge carried by the cluster is an open question. On the one hand, taking $(dE/dx)_{EA}$ as the input for the yield variation suggests an individual behavior of the protons as they penetrate the target from the incident cluster. However, the overlapping of their contributions may lead to time-expanding spherical "hot spots" forming a hot cylinder, as proposed by Brown *et al.*[18] In this respect, at some threshold mass, such an overlapping of energy deposition zones at the surface may allow a local thermal equilibrium to be reached. Then the surprisingly good scaling with a fourth power dependence would favor the Seiberling model.[4] On the other hand, if we take into account the coherence in the position of the pro-

tons, a cluster stopping power can be inferred from the extreme hypothesis of an effective charge N, expressed as $N^2(dE/dx)_{EP}$ from the stopping power of the proton at the same velocity. The log-log plot of such a yield variation leads to a power exponent 1.5, which is somewhat inconclusive. Nevertheless, the hypothesis of a cluster stopping higher than the additive stopping because of collective effects cannot be rejected, since it has been experimentally observed by Matthew *et al.*[19] for larger clusters $(H_2O)_nH^+$ with n between 50 and 150 in the nuclear stopping regime. Then, even if a cluster effect has been clearly shown in our case, it is too early at this stage of experiment to favor one model.

In summary, we have shown that very large desorption yields are obtained when 600-keV hydrogen clusters interact with CsI. The cluster effect is certainly related to the coherence of the particles impinging on the target. However, it is not clear yet if collective effects can be introduced as an intrinsic property of the particle or if it is the result of the overlapping of individual contributions. The magnitude of such effects has considerable implications in biosciences and astrophysics where desorption induced by monatomic fast heavy ions has been used thus far. It should also be of interest in the characterization of surfaces. Moreover, cluster beams appear well suited for microprobe analysis. Given their high yield, the simple use of microcollimators is sufficient to define a microbeam for which edge scattering is no longer a problem, as the dissociated fragments will have a negligible contribution to the total yield. Cluster microbeams could thus complement the present techniques which are deficient in lateral resolution.

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