Charge-State Dependence of Desorption of Biomolecules Induced by Fast Heavy Ions

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Fast heavy ions in definite charge states have been used to desorb molecular ions. Samples of ergosterol, glycylglycine, and cesium iodide were exposed to 20-MeV oxygen ions in charge states 2^+ to 8^+. For the first time it has been shown that the yields depend strongly on the charge state of the primary ion. Existing models for "sputtering" fail to reproduce the measured yield distributions. The results illustrate that future desorption experiments should be carried out with primary ions in well defined charge states.

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Sputtering or desorption associated with electronic stopping has been reported by several authors in the last few years.[1-5] As pointed out by Sundqvist *et al.*,[6] the so-called plasma desorption of biomolecules caused by fission fragments from a ^{252}Cf source[7,8] and later studied with accelerator beams[6,9,10] probably involves the same process. The mechanism is interesting to study in itself but also because of its applications in astrophysics[2] and bioscience.[7] The common characteristic features of the experimental results in Refs. 1–10 are the following: The primary ion velocities involved are such that ion-electron collisions dominate the interaction between the fast ion and the solid. The process is effective only in insulators.

The models suggested so far for the process are essentially thermal models.[3-7] Sigmund and Claussen[11] have given a theoretical framework for the thermal spike model. One important parameter is the amount of energy transferred into atomic motion per unit track length. It is related to the energy loss of the fast ion and assumed to be connected with the electronic stopping power in this process. The distinguishing feature of the thermal model of Seiberling *et al.*[4] is the assumption that Coulomb repulsion in the positive-ion-track core in an insulator will create a high local temperature. Brown *et al.*[2] have suggested that in the positive-track core an axial electric field is formed which causes ejection of ions from the surface. Krueger[12] has proposed a model in which the molecular ion is polar bound to the surface and the fast heavy ion induces polarization of the electron plasma which causes desorption of the molecular ion. The models are able to account for different subsets of the experimental results. New experimental data are needed to get a better understanding of the process. So far experiments involving biomolecules have been performed with primary ion beams having a distribution of charge states.

Tombrello *et al.*[4] have reported a possible charge-state dependence in the yield of uranium sputtered from a sample of UF_4 by 19-MeV fluorine ions in different charge states. Besenbacher *et al.*[3] found similar indications of a charge-state dependence for the erosion of frozen argon with He beams. However, the error bars in the experimental data presented so far do not allow definite conclusions.

In order to investigate the influence of the charge state of the primary ion on desorption yields, samples of cesium iodide [CsI; $M(\mathrm{Cs}) = 132.9$], glycylglycine ($C_4H_8O_3N_2$; $M = 132.1$) and ergosterol ($C_{28}H_{44}O$; $M = 396.7$) have been exposed to 20-MeV oxygen in charge states ranging from 2^+ to 8^+. The numbers of Cs^+, $(\mathrm{M+H})^+$, and M^+ ions (M = molecule) per incoming fast ion were measured with a time-of-flight spectrometer. The experimental setup was earlier used to study the influence of primary-ion velocity[6,13] and angle of incidence[6,14] on molecular-ion desorption from the samples mentioned. The CsI sample was prepared by evaporating a layer of CsI (~ 1000 Å) on an aluminum backing. The glycylglycine and ergosterol samples were electrosprayed[15] on aluminum backings and the layers were approximately 1000 Å thick. In Fig. 1 a typical time-of-flight spectrum of positive ions of ergosterol is shown.

The beam energy (20 MeV) was kept constant in this study and the charge state was varied. The results for the run on glycylglycine are shown in Fig. 2. The error bars shown are the statistical errors. For comparison and as a test of reproducibility the yield of secondary ions was also measured by letting the beam pass through a 100-μg/cm^2 gold foil before hitting the sample, for each charge state. The average charge state at 20 MeV for oxygen is ~ 6.5.[16] A very pronounced charge-state dependence is demonstrated. Also for Cs^+ ions from cesium iodide and M^+ ions

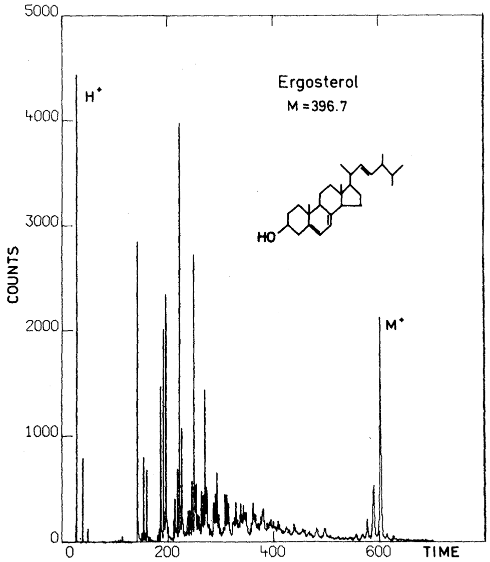

FIG. 1. Time-of-flight spectrum of positive ions from a sample of ergosterol. 1000 channels correspond to a time of flight of 20 μs.

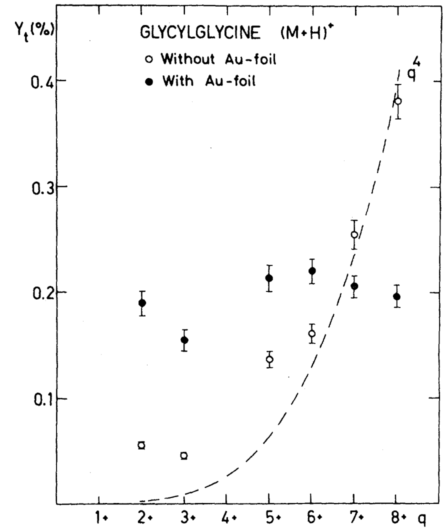

FIG. 2. Yields of $(M+H)^+$ ions from glycylglycine bombarded with 20-MeV oxygen ions in different charge states (open circles). Yields measured with a beam of 20-MeV oxygen with an equilibrium charge-state distribution ($\bar{q} \sim 6.5$) after the passage of 100 $\mu g/cm^2$ Au (closed circles).

from ergosterol the same effect was found (Fig. 3). It is interesting to note how identical the yield versus charge-state distributions are for the three different secondary ions. The fragmentation patterns in the spectra from glycylglycine and ergosterol are not changed when different charge states are used. In Refs. 13 and 14 it is shown that when other primary-ion parameters like velocity and angle of incidence are varied the fragmentation patterns in spectra from these samples also remain the same.

In most models suggested so far the electronic stopping power, $(dE/dx)_e$, is supposed to be an important parameter. The models predict a dependence on $(dE/dx)_e$ either to the second[2,3] or to the fourth power.[4] Experimental data[13] on ergosterol show that the yields of M^+ ions roughly scale as $(dE/dx)_e^2$. The data cover many different primary ions and velocities. The stopping power for a heavy ion in a particular charge state is not a well defined quantity as two modes of energy loss, electron capture and electron loss, change the charge state of the ion. If only ion-electron collisions are considered the energy loss would be proportional to the charge state squared. The ion-explosion model of Brown *et al.*[2] leads one to expect that the energy loss in the surface is the most important quantity. The data in this study are not in conflict with the yield dependence expected from that model: $(dE/dx)_e^2$ or q^4 at least for the highest charge states.

In measurements on almost fully stripped 40-MeV oxygen ions in carbon foils, Sofield *et al.*[17] found that charge equilibrium is reached 500–600 Å below the surface. This would imply that the

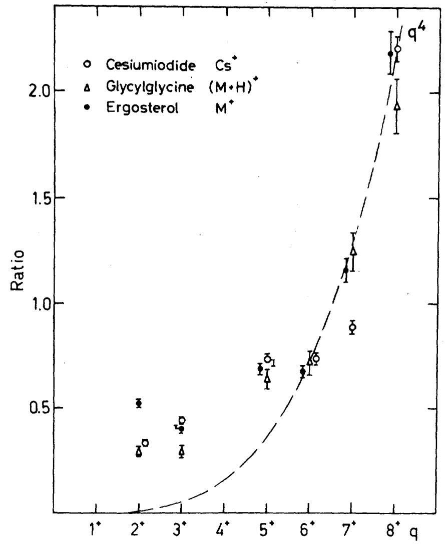

FIG. 3. Relative yields for Cs^+, glycylglycine $(M+H)^+$, and ergosterol M^+ ions with 20-MeV oxygen ions in different charge states. The yields were normalized to the yield for 20-MeV oxygen ions with an equilibrium charge-state distribution ($\bar{q} \sim 6.5$).

oxygen ions are likely to be very close to their original charge state in the first few monolayers of the samples. It seems that also in the thermal models the yields should be quite sensitive to the energy loss in the surface region although to a lesser extent than in the model of Brown *et al.* The relatively large yields for the lower charge states may indicate that energy deposited by a more stripped fast ion further into the sample influences the desorption yield. At present it is, therefore, difficult to draw any definite conclusions about the validity of the different models.

This study has demonstrated that the interactions of the primary ion during the time it takes until charge-state equilibrium is reached to a large extent determine the yields. The present experiment illustrates the importance of using beams of fixed charge states in these kind of studies. Further experiments on the primary-ion velocity and angle of incidence dependences of desorption yields using ions in fixed charge states are probably needed to understand the details of the mechanism. Particularly clean experimental conditions will involve fully stripped primary ions.

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