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Directional correlation between the primary particle and ejected molecular ions in electronic sputtering of large organic molecules

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Fission fragments from a ^{252}Cf source and 72-MeV ^{127}I ions from an EN-tandem accelerator have been used to sputter secondary ions electronically from samples of biomolecules such as bovine insulin (5733 u). It is found that intact molecular ions of insulin are ejected from the surface at an angle which correlates with the incident ion direction. This study shows that from the ionized cylindrical region produced by the passage of a fast ion there is a direct radial momentum transfer, i.e., a nondiffusive process, which ejects large molecular ions.

When a fast ion, i.e., an ion with a velocity larger than the Bohr velocity, interacts with a solid, the dominating primary interaction is that of ion-electron collisions. The fast ion causes direct ionization within the so-called infratrack,[1] the radius of which is determined by the Bohr adiabatic radius. The high-energy recoiling electrons cause secondary ionizations outside the infratrack and the radius of this region, the ultratrack, is determined by the projected range of the so-called δ electrons.[1] Fast ions, like fission fragments, have long been known to create etchable tracks in certain insulators.[2] Based on these observations, Haff[3] predicted that track-forming materials, unlike metals, would erode under fast-ion bombardment. Such an effect was later observed in several types of insulator solids: alkali halides,[4] condensed noble gases,[5] ices,[6] and organic solids.[7,8] Already in 1974, Torgerson and Macfarlane[9] observed that fission fragments from a ^{252}Cf source could desorb and ionize thermally labile molecules such as some of the amino acids from a thin film of these molecules. The secondary ions were mass analyzed with a time-of-flight technique and they proposed the name plasma desorption mass spectrometry (PDMS) for the technique. About 1980 it was demonstrated that larger organic molecules could be studied by PDMS than with other mass spectrometric methods available at the time.[10,11] The PDMS method has recently been reviewed by Sundqvist and Macfarlane.[12] Samples are commonly prepared by the electrospray technique[13] in which a thick (multilayer) deposit is formed on a conductive backing. Recently, much higher yields and better quality spectra for peptides and proteins have been obtained when monolayers of sample are adsorbed to a polymer backing such as nitrocellulose.[14] Molecular ions ejected from nitrocellulose have less internal energy and, therefore, are more stable. With this technique, the largest intact molecular ion studied with PDMS so far is porcine pepsin (34684 u).[15]

In this Rapid Communication we describe experiments which demonstrate for the first time that large organic ions, electronically sputtered by a fast heavy ion, leave the surface with a direction correlated to that of the incident fast ion. This is of central importance as the mechanisms involved in electronic sputtering of large organic molecules are poorly known at present. (See, for example, a recent review by Johnson.[16]) The demonstrated effect has also practical implications for the analysis of biomolecules with the PDMS method.

Even the basic processes involved in the conversion of electronic energy to atomic and molecular motion are not well established. The energy deposited by the fast ion in a solid may couple directly to atoms via a Coulomb "explosion" due to the short-lived charge separation following the passage of the ion.[17] Such an explosion can lead to the formation of a thermal spike[18] or shock waves.[19] In addition, secondary electrons recombine and, thereby, transfer energy to atoms and molecules via repulsive decays[20] and low-energy secondary electrons excite low-lying vibrational levels in a large number of molecules in the ultra track.[21] These processes can, in principle, all lead to an expansion of the volume excited. Such an expanding cylinder, if it forms, should give rise to a preferred direction of ejecta related to the volume expansion of the track. In the absence of such a correlated process, the deposited energy can partially equilibrate and molecules may be ejected from a thermally activated surface.[22,23] In such thermal models, the memory of the incident ion direction is lost so one would expect molecules to leave the surface with an angular distribution peaked at zero degrees.

Samples of proteins and peptides were prepared by the electrospray technique[13] (multilayer) and by adsorption to nitrocellulose[14] (monolayer). Mass spectra were obtained with two linear time-of-flight spectrometers which are described in detail in Refs. 24 and 25. Both instruments were equipped with electrostatic deflection plates in two perpendicular orientations. The deflecting plates were placed in the field-free region immediately after the acceleration grid. In the "off-line" experiment,[24] sample molecules were desorbed and ionized by ^{252}Cf fission fragments incident from behind the sample foil with an angle of incidence of 0° to the normal. The flight distance in this off-line spectrometer was 75 cm, the deflection plates were placed 15 cm from the target. The plates were 3.0 cm along the axis and separated by 1.7 cm. In the "on-line" experiment, 72-MeV $^{127}I^{18+}$ primary ions from the Uppsala EN-tandem accelerator were used to bombard the samples from the front at 45° angle of incidence. Here the flight distance used was 100 cm and the deflection plates were situated 11.6 cm from the target.

The plates were 3.0 cm along the axis and separated by 1.4 cm.

By measuring the secondary-ion yield as a function of deflection voltage, detailed radial velocity distributions were determined for samples of the peptide luteinizing hormone releasing hormone (LHRH) (1182 u) and bovine insuline (5734 u). The radial velocity is the component of the velocity perpendicular to the instrument axis, i.e., parallel to the target surface. Angular distributions were then deduced from earlier measurements of axial velocity distributions made in the same instrument and for the same sample.

Figure 1 shows results from experiments with the off-line spectrometer. The intensity of low-mass secondary ions show a single-peaked symmetric distribution around a deflection voltage close to zero in both directions. (Some asymmetry is expected because one plate is held at ground potential.) For molecular ions of bovine insulin, the distributions always show a local minimum in the "zero-voltage" direction. In Fig. 2, the results are shown from the corresponding experiment in which fast primary ions from the accelerator are incident from the front. For deflection in the horizontal plane (containing the incident beam direction and the target normal), the distribution for low-mass secondary ions and the molecular ion of insulin both show a single peak but are shifted with respect to one another. Radial velocity distributions in the perpendicular direction, where the deflection voltage is changed in the vertical plane, are approximately symmetric with respect to the same voltage for all the secondary ions. The data suggest that the molecular ions of insulin leave the surface with a considerable velocity componenet perpendicular to the direction of the incident primary ions.

The radial velocity v_r from an ion striking the center of the detector can be calculated for each value of the deflection voltage. The corresponding "radial energy," $mv_r^2/2$ is also shown in Fig. 1. In the calculation we have taken account of the fringing fields of the plates[26] and we assume that the centroid of the distribution for light fragment ions corresponds to zero radial velocity. The small deflection voltage at this centroid is assumed to compensate for a small instrumental misalignment. Accurate measurements of the alignment are in progress. The average axial velocity distribution of insulin sputtered under the same conditions have been measured previously in the same spectrometers as in the present experiment.[27] The average axial velocity was found to be $v_a = 3.4 \times 10^2$ m/s corresponding to an "axial energy" of 3.4 eV. Combining this average axial velocity with the radial velocity corresponding to the maximum yield (see Figs. 1 and 2) gives angles of ejection of $50 \pm 10°$ for both experiments. These numbers are subject to some uncertainty because the separation of the deflection plates is quite large compared to their length[26] and the instrument alignment is not accurately known. In the off-line experiment (Fig. 1) where the fission fragments are incident normal to the surface, the assumption that light ions are symmetric with respect to zero radial velocity is reasonable. Similarly, in the on-line experiment one expects radial velocities in the

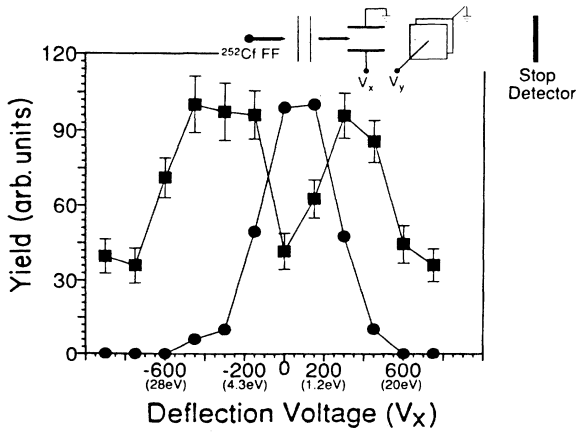

FIG. 1. Relative yield of positive molecular ions of bovine insulin (squares) and CH_3^+ ions (circles) emitted when a sample of bovine insulin was bombarded with fission fragments from a ^{252}Cf source from behind the target foil at normal incidence as a function of deflection voltage in a direction perpendicular to the direction of the secondary ions. (See inset.) The numbers in parenthesis on the x axis give $\frac{1}{2} mv_r^2$ where v_r is the radial velocity of ions which strike the center of the detector with the corresponding deflection voltage.

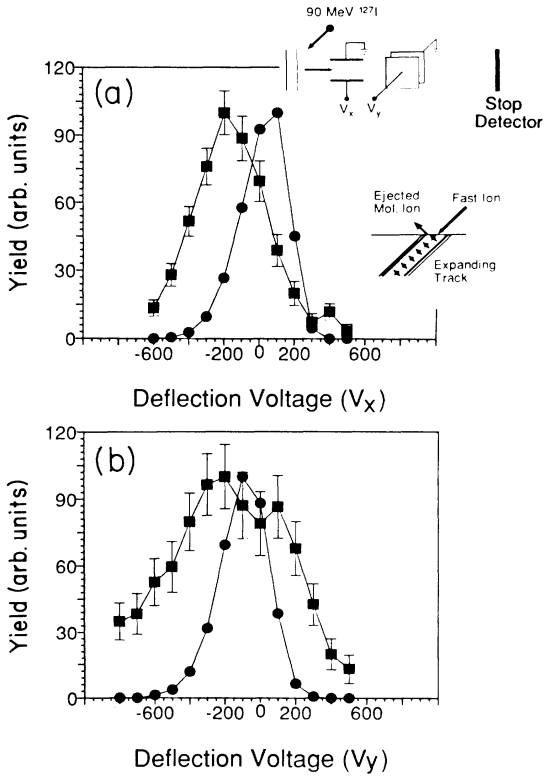

FIG. 2. Relative yield of molecular ions of bovine insulin (squares) and CH_3^+ ions (circles) for a sample of bovine insulin as a function of deflection voltage for 72-MeV ^{127}I incident at 45° from the front. (a) Deflection in the plane of the incident beam and the target normal and (b) deflection in a direction perpendicular to the plane of the incident beam and the target normal. The inset illustrates the expansion of the ion-track region.

vertical plane [Fig. 2(b)] to be positive or negative with equal probability. However, in the horizontal plane we cannot be sure what deflection voltage corresponds to zero radial velocity. It is possible that the light ions also have a preferred ejection angle, and if so this direction is back along the direction of the incident ion. Still it is clear that the angle of emission for the molecular ion of insulin is considerably different from that of the light ion and that the direction is correlated to the direction of the incident primary ion. Less-detailed measurements were made in the two instruments with sample molecules larger than bovine insulin. In all the cases, the results were qualitatively similar to those obtained for bovine insulin. The sample preparation technique, namely monolayer or multilayer targets, has also been changed and was found to have no influence on the results.

The experimental results presented show that large molecular ions (M several thousands of u) are, on the average, ejected from the surface at an angle which is directed away from the direction of the incident particle. It is difficult to reconcile these results with a thermal model of desorption where molecules are evaporated one by one from a thermally activated surface. Considering the large neutral yields measured in electronic sputtering of organic molecules[28] one may imagine evaporation from a curved "instantanous" crater surface to cause the observed effect. However, as the results are the same for monolayer and multilayer targets, this can be ruled out. Rather it appears that there is collective motion of the lattice which directly, in a nondiffusive process, transfers momentum outward from the track. This would result in an ejection velocity with a considerable component along a direction at right angle with the track direction. This is schematically sketched in the inset of Fig. 2.

Recent experiments on electronic sputtering from Langmuir-Blodgett films of fatty acids[29,30] and on total sputtering yields of intact molecules of the amino acid leucine[28] strongly suggest that a crater is formed at the impact of the fast heavy ion. The picture which emerges is that the fast heavy ion excites a cylinder of the molecular solid which expands on the time scale of the velocity of sound in the solid. This expansion is radial in the bulk and of course directed out from the surface. Many of the large intact molecules will, therefore, be ejected with a velocity component related to the expanding track core. If the mechanism for the ejection of large molecular ions by electronic sputtering involves the collective motion of a large number of atoms, then the observed angular effect should be more pronounced for larger more labile molecules ejected further from the track. Since fragment ions and smaller (and more stable) molecular ions are likely to be ejected more frequently from nearer the track where other processes may dominate, the radial velocity distribution should be more symmetric. Our data seem to bear this out: Molecular ions from LHRH (1182 u) give a radial velocity distribution intermediate between those observed for light-fragment ions (< 100 u) and bovine insulin (5733 u). In the on-line experiment, the LHRH distribution shows a similar but smaller shift from "zero voltage" compared to insulin. In the off-line spectrometer, the radial velocity distribution for LHRH does not show a local minimum but it is considerably broader than the distribution for light ions. The intensity of the light-fragment ion is many times larger than for the molecular ion of insulin, i.e., in Figs. 1 and 2 the intensity maxima for the distributions have been normalized.

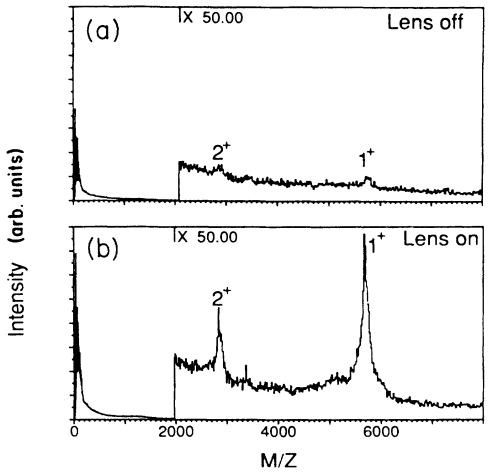

FIG. 3. Positive-ion spectra of secondary ions from a sample of bovine insulin bombarded from behind with ^{252}Cf fission fragments. The labels 1^+ and 2^+ correspond to singly and doubly charged molecular ions of bovine insulin. (a) Without secondary ion focusing; (b) with secondary ion focusing provided by an einzel lens in the field-free region immediately after the acceleration region.

A very important practical consequence of the present results is that the required acceptance angle of the detector for large molecular ions desorbed by fast ions is much larger than might be expected from measurements with low-mass secondary ions. Thus, even for modest length flight tubes, some focusing with either an electrostatic particle guide[31] or an einzel lens will normally be required. The effect of a simple lens near the target is illustrated for a 75 cm flight path, 12 kV acceleration, and a 2 cm diam detector in Fig. 3. Without the lens, the molecular ions of insulin (singly and doubly charged) are barely observable above the background. The lens increases the low-mass intensities by about 40% but has a much more dramatic effect on the insulin molecular ion peaks and the intensity increases by more than a factor 10.

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