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# DIRECTIONAL CORRELATIONS BETWEEN INCIDENT PARTICLE AND SECONDARY IONS IN ELECTRONIC SPUTTERING OF LARGE ORGANIC MOLECULES

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Fission fragments from a  $^{252}\text{Cf}$ -source and 72 MeV  $^{127}\text{I}$ -ions from the Uppsala EN-tandem accelerator have been used to sputter secondary ions electronically from samples of biomolecules like bovine insulin (5734 u). It is found that molecular ions of insulin leave the surface preferentially at a nonzero angle to the target normal. The ejection angle is related to the direction of the incident ion. This would indicate that the intact molecular ions are ejected by the expanding material in the ion track similar to a mechanical pressure wave.

Furthermore a molecular dynamics model of electronic sputtering of large organic molecules is presented and some aspects of the measurements described are simulated.

**Key words:** organic molecules, electronic sputtering, fission products, angular dependence, ion track, pressure wave, molecular dynamics.

## INTRODUCTION

The interest in electronic sputtering of large organic molecules emanates from applications of this process to mass spectroscopy of large organic molecules, in particular biomolecules.<sup>1,2</sup> Molecular ions as large as small proteins can be ejected intact due to the impact of a fission fragment on a solid sample surface.<sup>3</sup> Further, the total electronic sputtering yield for whole neutral molecules from organic solids is large. Salehpour *et al.*<sup>4</sup> have reported that for a 90 MeV  $^{127}\text{I}$  ion incident on a multilayer sample of the amino acid leucine ( $M=131$  u) the yield of intact neutral molecules is  $1200 \pm 200$ . Hedin *et al.*<sup>5</sup> showed that this yield varied with the third power of the electronic stopping power,  $(dE/dx)_e$ , of the incident ion. Such large yields constitute a considerable volume ejected per particle impact and indeed strong evidences for crater formation have been found in electronic sputtering of molecular ions from Langmuir-Blodgett films of fatty acids.<sup>6,7</sup>

Very little is known about the velocity distributions of ejecta from organic solids in this process. For neutral ejecta there are no measurements at all to our knowledge and for large organic molecules two sets of data on axial velocity distributions of molecular ions have been published, by Widdiyasekera *et al.*<sup>8</sup> and Jacobs *et al.*<sup>9</sup> These data both involve bovine insulin ( $M=5734$  u) and primary ions which were fission fragments from a Cf-252 source. The centroids of the measured distributions correspond to an "axial" energy of 3.4–5.9 eV. Here the measured radial velocity distributions for molecular ions of bovine insulin are reported. Furthermore, a molecular dynamics model of electronic sputtering of large organic molecules is presented and some aspects of the measurements described are simulated.

## EXPERIMENTAL STUDY OF EJECTION ANGLES OF SECONDARY IONS FROM SAMPLES OF LARGE ORGANIC MOLECULES

In a linear time-of-flight mass spectrometer two sets of deflection plates were introduced (see insets in Figures 1 and 2) in the field-free region, just behind the acceleration gap. The plates were orientated so that when voltages were applied the electric fields were at right angle. In the first experiment the fission fragments bombard the sample from the back at normal incidence. The geometry and other details of the experimental arrangements have been described in Ref. 10. In Figure 1 the relative yields of positive molecular ions of bovine insulin and a small fragment ion,  $(\text{CH}_3)^+$ , as a function of voltage on one set of the deflection plates are shown. The data show that the molecular ions of insulin are ejected preferentially at an angle off the normal to the surface. This is in contrast to the fragment ions for which the integrated absolute yield is much larger. All small fragment ions have similar distributions. If one assumes that all the molecular ions of insulin ejected have an average "axial" energy as measured by Widdiyasekera *et al.*,<sup>8</sup> namely 3.4 eV, the deflection voltages on the  $x$ -axis in Figure 1 can be converted to an ejection angle scale using the radial energies given in parenthesis.

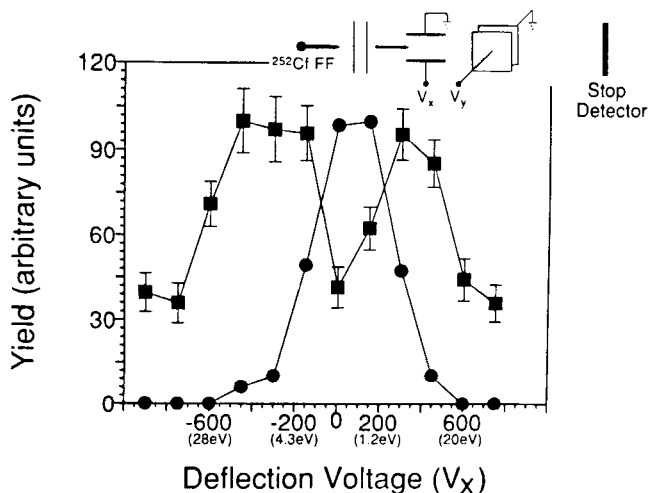


FIGURE 1 Relative yields of positive molecular ions of bovine insulin (squares) and  $\text{CH}_3^+$  ions (circles) as a function of deflection voltage. Primary ions: Fission fragments. The numbers in parenthesis on the horizontal scale are the energies corresponding to the radial velocities which can be associated with the different deflection voltages.

In a second experiment 72 MeV  $^{127}\text{I}$  ions from the Uppsala EN-tandem accelerator were used to bombard the sample from the front at 45 degrees angle of incidence (see inset in Figure 2). The deflection experiment was performed with the  $x$ -plates oriented for deflection of secondary ions in the plane of the incident ion and the axis of the TOF-spectrometer. The  $y$ -plates deflect the secondary ions in a direction perpendicular to the mentioned plane. In Figure 2 the results of the second deflection experiment are shown. The molecular ions of insulin are seen to be preferentially ejected at an angle which is off the normal to the surface. The light fragments are also ejected in a direction non-normal to the surface but slightly along the back direction of the track. This latter conclusion was checked by repeating the two experiments above in the same spectrometer on the same sample and comparing the centroids of the two  $(\text{CH}_3)^+$  distributions. Indeed they are found to be shifted with respect to each other confirming non-normal ejection back along the track for the light fragment ions. All the experimental results given above have been reproduced with mono- and multilayer samples. These experiments strongly suggest that the large, intact molecular ions are pushed out from the solid by the expanding track core (see inset of Figure 2). This requires a direct momentum transfer to the molecules (non-diffusive) unlike in a thermal process. On the other hand, the major part of the ion ejecta, i.e. small fragment ions, exit in a direction nearly along the track as in a gas-jet expansion.

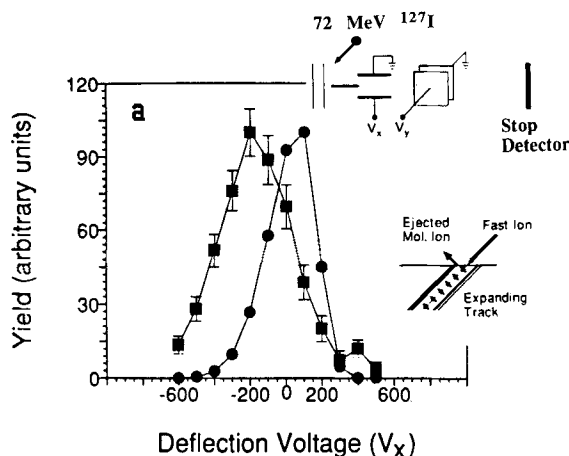


FIGURE 2 Similar data as in Figure 1 but for 72 MeV  $^{127}\text{I}$  incident from the front at 45 degrees angle of incidence. Deflection in the plane of the incident beam and the target normal.

The results for large molecules could possibly be caused by evaporation from the evolving curved surface of the crater formed. However, as the angular shifts are the same for multi- and monolayer samples this does not seem likely. Another possible cause of the deflection would be the Coulomb field of the track core. However, the results of Ref. 8 strongly suggested that the neutralization time of the track core is much shorter than the ejection time of a molecular ion of insulin. Therefore such an effect is not expected to appreciably deflect the slow heavy ion. This leaves the interesting result that large molecular ions can give us a measure of the pressure wave produced in an organic solid by a fast heavy ion track.

# MOLECULAR DYNAMICS (MD) SIMULATION OF ELECTRONIC SPUTTERING OF LARGE ORGANIC MOLECULES

When a fast ion interacts with a solid the dominant part of the energy deposited is in the production of secondary electrons. A basic problem in the field of electronic sputtering is to understand what the mechanisms are for converting this electronic energy into atomic and molecular motion.<sup>11,12</sup> Three possible modes of energy conversion are Coulomb explosion of the infra-track,<sup>13</sup> repulsive decays of electronically excited molecules,<sup>14,15</sup> and excitation of a large number of low-lying vibrational levels by low energy electrons in the track, leading to molecular expansion.<sup>16</sup> All these modes lead to expansion of the volume in which the energy is deposited. The third mode may be of particular importance for large molecule

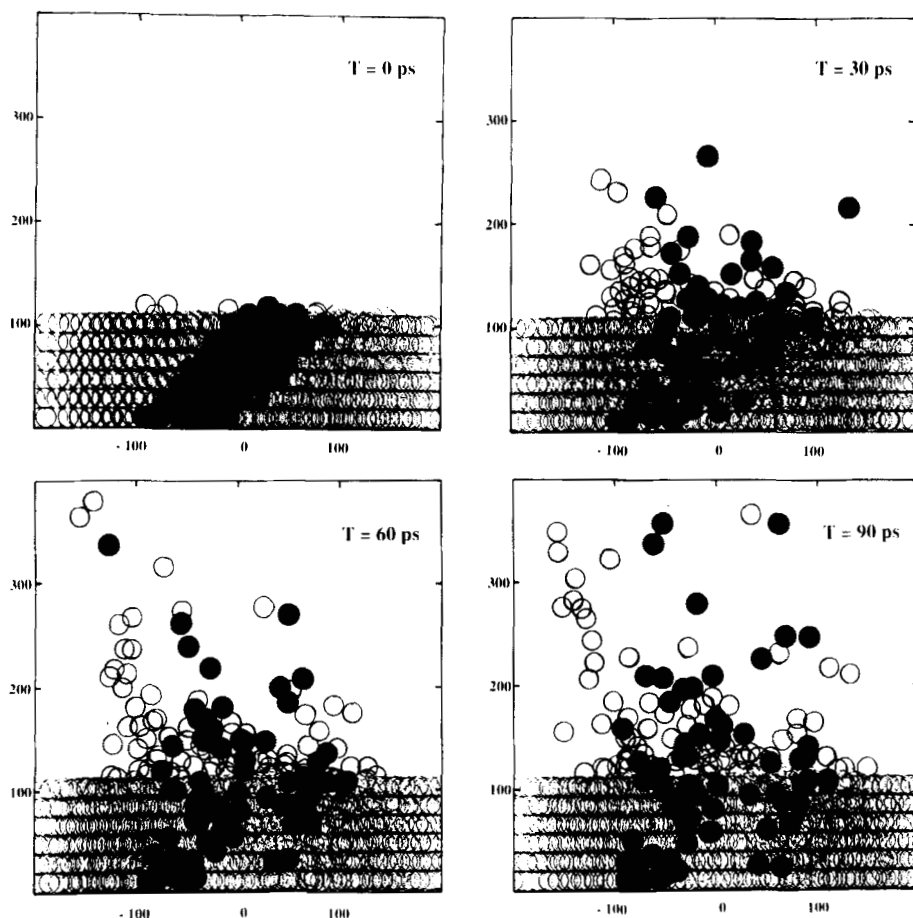


FIGURE 3 The sample at 0, 30, 60 and 90 ps after the expansion of a cylindrical track. Expanded and non expanded molecules are shown as filled and unfilled circles, respectively. A side projection of the cylindrical matrix is shown. The angle of incidence of the fast ion is 45 degrees.

ejection as expansion in this mode is probably favoured over fragmentation on the time scale of the ejection process. In order to test if large molecular ejection can be explained by a sudden expansion of the ion track region, a molecular dynamics model simulation has been developed. For this we have chosen to use an expansion driven by the third mode listed above. A detailed description of this model is given in Ref. 17.

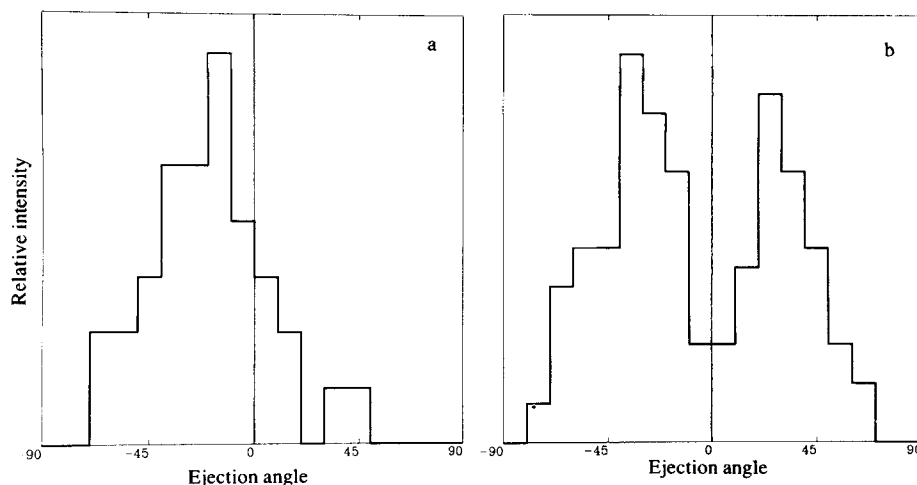


FIGURE 4 Angular distribution of non expanded molecules having a kinetic energy larger than 0.1 eV for (a) 45 degrees angle of incidence of the fast ion, (b) 0 degree angle of incidence of the fast ion (along the normal to the surface).

In the simulation 1668 molecules of mass 10,000 u are arranged in a cylindrical matrix (six layers thick) on an infinitely heavy substrate. The molecules interact via a Lennard-Jones potential. The parameters of the potential have been fixed by fitting the cohesive energy, the velocity of sound and the density of the solid. In order to achieve this a hard core had to be introduced in the potential. At time zero molecules in a cylinder around the ion track are expanded. When expanded molecules interact the two-body potential will be shifted from the attractive minimum to the repulsive part of the potential. The motion of each molecule is then followed using a time step of  $10^{-14}$  s for the integration of the equations of motion. In Figure 3 the positions of the molecules are shown at different times in the ps time scale where the filled circles are the expanded molecules and the other circles non-expanded. In this figure one can observe that fast non-expanded molecules are ejected preferentially to the left in the figure and that the opposite is the case for the fast expanded molecules. The latter are more likely to be the origin of the fragment ions. In Figure 4a the ejection angle distribution of non-expanded molecules with an energy larger than 0.1 eV is shown in the case of incidence at 45 degrees from the front and in Figure 4b the corresponding angular distribution for the case of normal impact of the primary ion is shown. These two figures qualitatively describe the experimental distributions of molecular ions in Figures 1 and 2. As a further suggestive comparison it was stated in the introduction that the

yield of neutral leucine molecules at 45 degrees angle of incident scaled roughly with the third power of the electronic stopping power.<sup>5</sup> Over the range of excitation parameters studied, the MD simulation gives that result also if one makes the reasonable assumption that the repulsive energy input is proportional to the total energy deposited per unit length in the solid.

## SUMMARY

In electronic sputtering of solids composed of large organic molecules, intact molecular ions are found to be ejected with an average angle which is not normal to the surface. This ejection angle is related to the direction of the incident ion. This would appear to indicate that the intact molecular ions are ejected by the expanding material in the ion track similar to a mechanical pressure wave.<sup>18</sup> A molecular dynamics model of this process based on the idea that the incident ion induces a fast expansion of the track qualitatively describes the experimental results presented here for the ejection of large organic molecules. This indicates that a direct momentum transfer (non-diffusive) ejection process is responsible for the rapid ejection of large thermally labile molecules which is very different from evaporation from a hot substrate, a process known to destroy these molecules. Therefore, the study of these large molecular ions can be used to quantify the rapid conversion of electronic energy into lattice motion. The experiments and simulations also indicate that there is an ejection of material, in particular small fragments from highly excited molecules, along the ion track as in a gas-jet expansion.<sup>19</sup>

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