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Desorption of large organic molecules induced by keV projectiles

A. Delcorte *, B.J. Garrison

[a] *Department of Chemistry, The Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, USA*

Abstract

In order to understand the emission of organic molecules in sputtering, classical molecular dynamics (MD) is used to model the 5 keV Ar atom bombardment of polystyrene oligomers adsorbed on Ag{1 1 1}. The analysis of the results shows that a significant fraction of the trajectories generates high action events in the sample. These events are characterized by the simultaneous motion of several hundreds of substrate atoms and, oftentimes, by high emission yields of substrate atoms, clusters and polystyrene molecules. Collision trees representing the energetic part of the cascades confirm that high sputtering yields of molecules occur when a large portion of the primary particle energy is quickly dissipated in the upper layers of the silver substrate. This class of events where high action occurs in the surface region might explain the ejection of organic species with a mass of several kilodaltons such as biomolecules and synthetic polymers. In the simulation, these events are capable of desorbing polystyrene molecules of ~2 kDa. © 2001 Published by Elsevier Science B.V.

1. Introduction

The ejection of large intact molecules constitutes a challenging issue in organic secondary ion mass spectrometry (SIMS) [1]. Currently, the upper mass limit for organic molecules to be efficiently sputtered and detected in experimental analysis is in the range 10–12 kDa. From the viewpoint of the sputtering process, the mechanisms by which these molecules are desorbed intact are not well known yet, nor are the reasons of the upper mass limit mentioned above. The aim of our current investigations is to understand these mechanisms of particular relevance for analytical applications.

Previous studies reveal the sensible parameters for molecule ejection and provide grounds for more ambitious investigations in this field [2–5]. First, the nature and properties of the more efficient desorption mechanisms are crucially related to the *size* of the organic molecule. In previous and ongoing works, molecules with a wide range of masses have been investigated, including benzene [3], biphenyl [4] and polystyrene oligomers [5]. The ejection may be caused either by primarily a single substrate atom or by the collective upward motion of several substrate atoms. The character of the ejection by each of these mechanisms is dependent upon the size of the molecule being ejected. The mechanism of a single substrate atom striking a benzene molecule gives rise to the intact molecules

* Corresponding author. Tel.: +32-10-473582; fax: +32-10-473452.

E-mail address: delcorte@pcpm.ucl.ac.be (A. Delcorte).

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with the highest kinetic energy. Conversely, for polystyrene tetramers, one-atom collisions primarily induce vibrational excitation in the molecules and comparatively low center-of-mass kinetic energies. In comparison, cooperative uplifting of polystyrene tetramers gives rise to fast molecules with a low internal excitation.

The *energy* of the impinging particles is another important factor. The comparison between sub-keV and keV atom bombardment shows that the volume of atoms set in motion in the sample by the primary particle increases with increasing particle energy. Above 1 keV, some of the impinging particles deposit a considerable amount of energy in a small volume near the surface [5]. The high-energy density region is characterized by the collective motion of hundreds of metal atoms, sometimes leading to the formation of craters and protrusions at the sample surface. We believe that the existence of high action events, dependent on the kinetic energy of the primary particle, are crucial for the ejection of large organic species such as biomolecules.

In this article, we focus on the description and explanation of high action and high yield events occurring upon 5 keV Ar atom bombardment of polystyrene overlayers on silver. First, we introduce the concepts of high action and high emission yield via the description of a typical trajectory provided by the molecular dynamics (MD) simulation. Second, we investigate the origin of high action trajectories in comparison with other scenarios of action and ejection.

2. Method

The Ar bombardment of *sec*-butyl terminated polystyrene oligomers adsorbed on an Ag(1 1 1) surface is modeled using MD computer simulation. The details of the simulation have been described elsewhere [5,6]. Briefly, the first sample consists of 13 PS *tetramers* (4 styrene repeat units) placed on the Ag{1 1 1} surface (12 layers of 528 atoms each). The second sample consists of one central PS tetramer surrounded by 2 PS *hexadecamers* (16 styrene repeat units) placed on the same Ag crystal. Figs. 1(a) and 1(d) show top views of the two simulation cells. For computer efficiency, tritium isotopes (3 Da) were used instead of regular hydrogen atoms (1 Da) in the model. Therefore, the masses of tetramers and hexadecamers are, respectively, 559 and 2001 Da. The systems are quenched to a minimum energy configuration prior to Ar atom impact. A total of 500 trajectories directed along the surface normal were calculated with the first sample. Trajectories of interest characterized by high action and high yield were recalculated with the second sample. The simulation consists of integrating Hamilton's equations of motion over some time interval to determine the position and velocity of each particle as a function of time. The energy and forces in the system are described by many-body interaction potentials, in particular, the C–C, C–H and H–H interactions are described by the Brenner potential function [7,8]. One important feature of this potential is that it allows for chemical reaction and accompanying changes in atomic hybridization during the course of a reaction. The criterion for terminating the trajectory is that the total energy of any atom is too low to induce ejection. The termination times range from 0.5 to 6 ps, depending on the manner in which the energy distributes in the solid. Experimentally observable properties, such as total yield, mass spectrum, kinetic energy, and angular distributions are calculated from the final positions, velocities, and masses of all the ejected species. Mechanistic information is obtained by monitoring the time evolution of relevant collisional events.

3. Results and discussion

The theme of this article is the elucidation of the most efficient mechanisms for the sputtering of large organic molecules adsorbed on metal surfaces. In Section 3.1, we illustrate this theme with snapshots of a typical trajectory inducing the massive sputtering of material from a polystyrene tetramer overlayer on silver and demonstrate that the same event is also capable of desorbing a much larger PS molecule ($\sim$2 kDa). In Section 3.2, we proceed to the systematic analysis of a representative set of 150 trajectories. After a preliminary classification of the different sputtering scenarios, we trace the genesis of

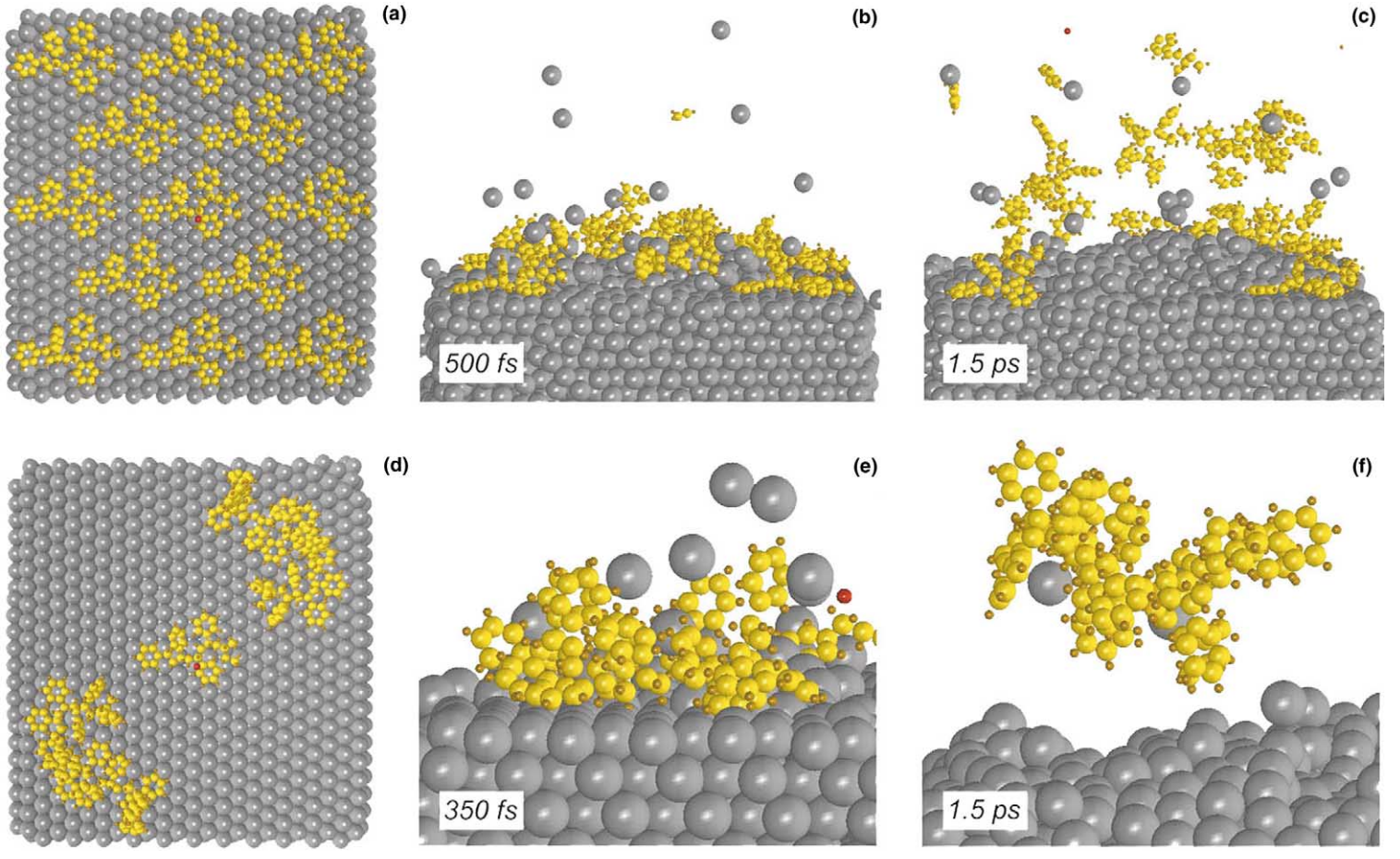

Fig. 1. Time-evolution of a 5 keV trajectory inducing high emission yield of polystyrene tetramers. Top view of the sample at 0 fs (a); side views at 500 fs (b) and 1500 fs (c). Emission of two PS hexadecamers (2001 Da) by a trajectory with the same aiming point as shown in (a)–(c). Top view of the sample at 0 fs (d); side views at 350 fs (e) and 1500 fs (f).

a few characteristic events using collision trees of the most energetic part of the cascade computed over the first 100 fs of the interaction.

3.1. Ejection of polystyrene oligomers from Ag surfaces

A typical high action event inducing the ejection of several intact polystyrene tetramers, hydrocarbon fragments, silver atoms and silver clusters is shown in Figs. 1(a)–(c). The top view of the sample (Fig. 1(a)) shows the initial configuration of the PS tetramers on the silver surface. The mass of tritiated tetramers is 559 Da and their binding energy to the surface is 2.3 eV. In the first femtoseconds of action (not shown), the impinging argon atom collides with the central PS molecule, inducing its fragmentation and the formation of a series of characteristic polystyrene fragments such as C_2H_3, C_6H_5, C_8H_8 and C_8H_9. Then, the argon atom penetrates the silver crystal surface and starts a sequence of collisions with buried silver atoms. The details of the collision cascade evolution are investigated in Section 3.2. By 500 fs, the action initially started inside the crystal has reached the sample surface (Fig. 1(b)). Many single silver atoms are ejected from the entire sample surface along with fragments of the central PS molecule. The silver surface becomes rough and disordered, with silver atoms and clusters protruding in several places. Polystyrene molecules are pushed towards the vacuum by the upward moving silver atoms. After 1.5 ps, the sample surface is still ruffled and the remaining molecules strongly distorted. Nineteen silver atoms, two silver clusters, five PS molecules and various hydrocarbon fragments are ejected. In particular, the silver tetramer in the middle of Fig. 1(c) is formed from a protuberance $\sim$1 ps after the beginning of the action. It is constituted by three first layer atoms and one second layer atom which were not direct neighbors prior to bombardment. Among the five ejected molecules, four are stable according to the internal energy threshold for fragmentation (28 eV) calculated in a previous article [5] using the RRK theory. Similar trajectories, inducing the emission of five parent-like species (intact molecules, molecules minus one H atom and molecule–metal adducts) or more occur in $\sim$8% of the trajectories and represent $\sim$25% of the total yield of these species.

To illustrate the relevance of high action events for the ejection of larger molecules, the same trajectory has been recalculated with a second sample (Fig. 1(d)) where twelve of the thirteen PS tetramers have been replaced by two larger oligomers. These oligomers are constituted of 16 styrene repeat units (hexadecamers) and their mass is 2001 Da. Their binding energy to the sample surface is 7.2 eV. To make sure that the first stages of the collision cascade would remain unchanged with respect to the trajectory described above, the central PS tetramer is conserved in the new sample. In the first few hundred femtoseconds of the trajectory, the same high action scenario unfolds with the second sample. The close-up view of Fig. 2(e) shows the state of the bottom left PS hexadecamer of Fig. 2(d) after 350 fs. At that time, the collective motion of silver atoms reaches the PS molecule and starts to lift it up softly. After 1.5 ps, the molecule is freed from the influence of the surface. This example demonstrates that high action trajectories are capable of inducing the desorption of molecules that are much heavier and more strongly bound to the surface than PS tetramers.

3.2. Genesis of action in the surface

The reason why some trajectories barely affect the sample, without inducing any molecule emission, while other trajectories cause a dramatic perturbation accompanied by the ejection of many atoms, molecules and clusters, must still be elucidated. Indeed, snapshots of the MD simulation provide little or no information concerning the quantitative aspects of the successive energy transfers occurring inside the silver crystal in the first stages of the cascade development. Therefore, to show these details, a graphic representation of the energetic backbone of the collision cascade is more appropriate. Examples of such collision trees are described in the following discussion.

First, it is useful to classify systematically the action and ejection events based on macroscopic parameters. Such a 'mapping' of the events is shown in the inset of Fig. 2 for a subset of 150 trajectories. The values on the X-axis are estimates of the

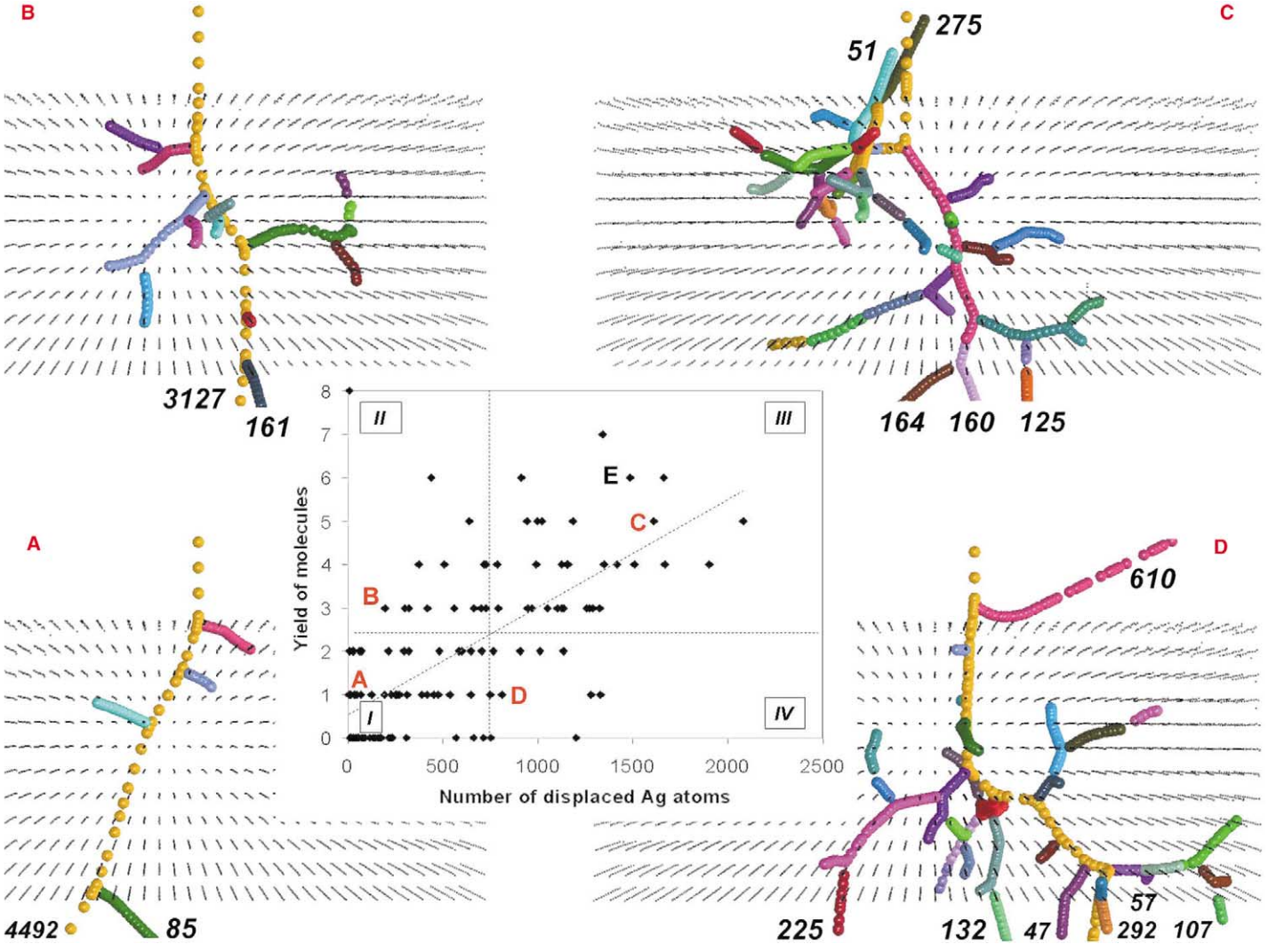

Fig. 2. Collision trees of the first 100 fs of the interaction for four trajectories representative of the different sputtering scenarios. The successive positions of the recoil atoms are indicated by colored spheres provided that they are set in motion with more than 100 eV of energy. They are 'turned off' when their energy falls below 25 eV. The numbers on the charts refer to the quantity of energy in eV leaving the crystal with the corresponding atoms. The central *inset* shows a scatter plots correlating the yield of sputtered molecules with the number of silver atoms displaced by 10 Å or more. In this graph, dehydrogenated molecules and molecule–metal aggregates are considered as yield. The trajectories illustrated in the figure are labeled with capital letters A, B, C and D.

amount of action occurring in the sample. They correspond to the number of silver atoms which move away from their initial lattice position by 10 Å or more in the course of the trajectory. The values on the Y-axis are the yields of parent-like species sputtered in the considered events. The two sets of data are correlated and the best regression through the data is shown by a dashed line. It is convenient to divide the graph in quadrants where representative trajectories can be selected for further analysis. Although the choice is somewhat arbitrary, we consider trajectories ejecting three or more polystyrene molecules as *high yield*, and trajectories in which more than 750 silver atoms are displaced as *high action*. In this manner, four groups of trajectories are defined. They represent various fractions of the total number of trajectories and of the total yield of molecules as indicated in Table 1. It is important to realize that, according to our definition, high yield events represent 35% of the trajectories and 70% of the sputtered yield of parent-like species. Similar percentages are found when silver atoms or total sputtered mass are considered instead of PS molecules.

With the classification described above, characteristic trajectories of the different scenarios of action and sputtering observed in the MD simulations can be easily identified. To illustrate these scenarios, we picked up four trajectories labeled A, B, C and D (inset of Fig. 2). The collision tree of each trajectory is shown in Fig. 2. These trees show the high-energy part of the cascade in the first hundred femtoseconds of the trajectories. In this representation, atoms at rest or with a low kinetic energy are displayed as black dots. Atoms are ''turned on'' as colored spheres when they receive more than 100 eV of kinetic energy and they are ''turned off'' when there kinetic energy drops below 25 eV. In this manner, the energetic part of the collision cascade is highlighted.

Trajectory A is typical of a low action trajectory with low sputtering yield (1 molecule). The Ar atom plunges into the sample, interacting with very few silver atoms, and leaves the bottom of the crystal with almost 4.5 keV of kinetic energy. That is, only a few hundred eV are dissipated in the sample and a small fraction of this energy is reflected to the surface, inducing the ejection of a single molecule. There is more action in trajectory B, characteristic of the low action/high yield events but, again, the primary particle leaves the crystal with a major fraction of its initial energy (more than 3 keV). In this case, however, at least two sub-cascades reflect momentum towards the surface and three molecules are ejected, along with two silver dimers and a few single silver atoms. Selected snapshots of trajectory C, which belongs to the high action/high yield category, have been shown in Figs. 1(b)–(c). In this case, the tree is more complex, dividing in two sub-cascade groups after a head-on collision between the Ar atom and a third layer Ag atom at approximately 10 fs. The primary Ar atom energy is equipartitioned in this collision, so that both atoms carry 2–2.5 keV of kinetic energy after the collision. In the following stages of the cascade, the Ar atom undergoes several violent collisions in the surface region, dissipating the rest of its kinetic energy in a very small volume, while the 2.5 keV silver atom carries its energy deeper in the crystal, generating a more sparse network of sub-cascades. Obviously, the high-energy density region created by the Ar atom in the upper layers of the crystal is the main cause of high sputtering yield in trajectory C. It also explains the ejection of a 2 kDa polystyrene hexadecamer from the same region of our second

Table 1
Ejection of entire molecules. Percentages of trajectories and sputtered yields in each quadrant of the inset of Fig. 2

Quadrant	% of trajectories	% of total yield
I Low action/low yield	61	26
II Low action/high yield	10	20
III High action/high yield	23	50
IV High action/low yield	6	5

sample (Figs. 1(d)–(f)). Trajectory C is not an exceptional case and several trajectories in the third quadrant of the inset of Fig. 2 are capable of ejecting PS hexadecamers. In particular, trajectory labeled E in the inset induces the simultaneous ejection of the two PS hexadecamers present on the sample surface [6]. Finally, trajectory D indicates why high action does not always produce high ejection yields. In this trajectory, after a violent collision transferring ~600 eV to a carbon atom, the Ar atom traverses six layers of silver atoms without significant energy loss. In the seventh layer, it undergoes a head-on collision and starts to generate a dense, downward-directed network of sub-cascades. The high action barely reaches the upper part of the crystal, leaving the surface nearly intact.

As was illustrated in Fig. 2, the genesis of action and sputtering is revealed by the use of collision trees. In particular, our analysis shows that very high sputtering yields, as well as ejection of large organic molecules of more than 1 kDa, are only observed for a particular category of trajectories. In these trajectories, a large fraction of the primary particle energy is quickly dissipated via successive collisions in a small volume close to the sample surface. The high-energy density induces the simultaneous motion of several hundreds of silver atoms. Such collective motions are capable of ejecting heavy molecules with a relatively low internal energy. Therefore, we believe that they are central to the explanation of the ejection process of large organic species such as biomolecules.

4. Summary and outlook

MD simulations show that massive ejection of inorganic and organic material, induced by the simultaneous motion of hundreds of atoms in the sample, occurs in a significant number of trajectories when organic overlayers adsorbed on metals are bombarded by 5 keV atoms. Such events require the formation of a high-energy density volume in the surface region of the sample. In general, the excited volume is the result of a succession of high-energy collisions between the primary particle and substrate atoms in a limited time and space. The induced collective motions are efficient to desorb molecules with a mass of 2 kDa. Our future investigations will focus on the sputtering of larger molecules and bulk organic samples. The ejection of large quantities of organic material from such samples has also been experimentally demonstrated, providing some indirect support to the existence of high action events. Modeling bulk organic samples [9], however, is still a challenge because the need to consider long-range interactions drastically increases computer time requirements, but it is now feasible [10]. Therefore, new results should be obtained soon in that arena.

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