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Molecular SIMS for organic layers: new insights

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Abstract

Static SIMS is intensively used for molecular surface characterization. In the case of polymers and organic adsorbates, large characteristic fragments and intact parent ions are detected and used for analytical purpose. However, the exact nature of the mechanisms leading to large molecule emission and ionization is still debated. Recently, owing to comparisons between experiments (ion yields, kinetic energy distributions and disappearance cross-sections) and molecular dynamics (MD) simulations, progress has been made in the understanding of molecular fragment and parent molecule emission under ion beam bombardment. In this paper, we review some of the results obtained in this context. Remarkably, MD simulations allow us to confirm that the emission of large intact molecules can occur via collision cascade mechanisms. This involves a cooperative uplifting process, in which substrate recoil atoms with similar momentum push the molecule upward.

Keywords: Secondary ion mass spectrometry; ToF-SIMS; MD simulation; Ion emission; Kinetic energy distribution; Disappearance cross-section; Ejection radius; Polymer

1. Introduction

Nowadays, static SIMS is routinely used for the chemical characterization of molecular surfaces. However, some fundamental questions about the basic processes are still under investigation. In the case of a thin organic layer deposited on a substrate, the exact mechanisms of molecular fragment and intact molecule emission are not completely clear. It is indeed amazing that a single ion impact can induce the emission of intact polymer macrochains up to $m/z \sim 10^4$, allowing the direct detection of the molecular weight distribution in the case of low molecular weight polymers [1]. Up to now, the interpretation was mainly based on the precursor concept already proposed two decades ago by Benninghoven [2] to explain the emission of adsorbed molecules. This model is based on the energy density deposited at the surface by the collision cascade. The energy density decreases with the radial distance from the impact point. In this framework, the emission of intact molecules is possible only where the deposited energy density is sufficient for desorption but low enough to prevent fragmentation.

Can we have an experimental or theoretical confirmation of this model in the case of large organic molecules and polymers? To address this issue, we initiated a comparative study between ToF-SIMS experiments and molecular dynamics (MD) simulations. The aim of this paper is to review some of the main results recently obtained in this context.

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For given primary ion bombardment conditions, experiments can provide information on the emitted species detected in the mass spectra (fragments and parent-like ions), their ion yield, their kinetic energy distribution (KED) and their disappearance cross-section. A direct comparison with the MD computer simulation results, however, is not possible for all of these data. First, MD trajectory calculations have to end after interaction times typically lower than 10 ps in order to keep computer running time to a reasonable value. In comparison, the ions are detected only after μs flight time in ToF mass spectrometers, allowing fragmentation and reorganization reactions to occur in the vacuum before detection. The fact that only the charged fraction is experimentally detected in SIMS, while MD simulations do not account for the charge state of the emitted particles at all, constitutes another limitation. Concerning the KED of the different fragments, ToF-SIMS and MD simulations can be directly compared if it is assumed that the KED is not influenced by the particle charge state. The disappearance cross-sections cannot be inferred from the simulations because that would require huge samples, a high number of projectile impacts and an accurate description of the sample relaxation over a long timescale. Nevertheless, MD can provide important information about the distance of ejection with respect to the impact point for a given fragment. Moreover, MD allows us to follow the time evolution of the sputtering process.

After a brief presentation of the model sample used in the simulations (polystyrene (PS) tetramers deposited on an Ag substrate), we discuss the comparison between calculated and experimental KEDs. Afterwards, the experimental disappearance cross-section and radius are compared to the calculated mean ejection radius, allowing us to derive an indirect information concerning the local energy density deposited by the cascade around the projectile impact point.

2. MD simulation model

The model sample consists in five *sec*-butyl terminated PS tetramers deposited on the {1 1 1} surface of an Ag substrate constituted of nine layers of 156 Ag atoms each. Four thousands Ar projectiles (500 eV) are fired at normal incidence. Details about the model and the different interaction potentials can be found in Ref. [3]. Long-range Van der Waals interaction forces are not taken into account in these simulations. It is worth mentioning that, in these simulations, the collision cascade develops only in the Ag substrate. The processes can be different when it develops in the organic material [4].

3. Comparison between experimental and calculated KEDs

The experimental KEDs were measured on PS thin film samples using a PHI-EVANS TRIFT1 system with a 15 keV Ga^+ beam, according to a procedure described in detail in Ref. [5]. The energy passband is close to 2 eV. The samples were prepared by spin casting from a solution onto a Si wafer. Although the primary bombardment conditions are different in the simulation and the experiment, the comparison is valuable because we demonstrated that the KEDs are almost independent of the primary beam energy and nature [6].

Fig. 1 shows the KEDs of two fragments and of the Ag cationized parent molecules. The agreement between experiment and simulation is very good for the small C_2H_2 fragments and for the parent molecules. For C_7H_7 fragments, there is a disagreement concerning the apparent negative energy tail in the experimental KEDs and the high-energy tail in the calculated one. Both effects are related to the same process, not taken into account in the MD model, i.e., the unimolecular dissociation of highly excited species in the vacuum. Since internal and kinetic energies are correlated [3,7], the high-energy part of the experimental distribution is depleted from the highly excited species undergoing unimolecular decomposition. When an internal energy (IE) threshold, above which fragments decompose, is included in the simulation, the agreement between experiment and simulation becomes excellent. This threshold is fragment dependent and can be reasonably estimated with the RRK theory of unimolecular dissociation. The apparent negative energy part in the experimental KEDs is related to the daughter ions generated by parents undergoing metastable decay in the spectrometer. Well-defined peaks appearing in this negative region allowed us to identify H and H_2 loss reactions [5]. The fraction of fragments formed by dissociation of excited species in the vacuum is

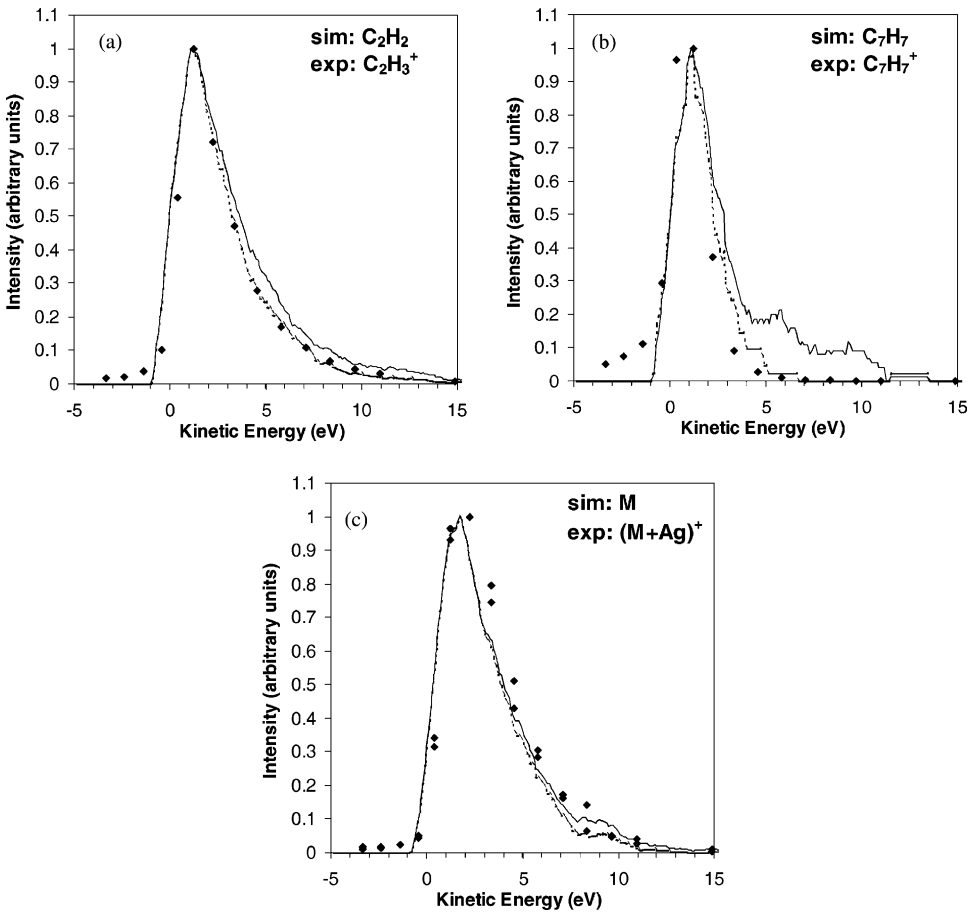

Fig. 1. KEDs of selected fragments sputtered from PS tetramers. Black dots: SIMS experiments; lines: MD simulations; dashed line: effect of the IE threshold for dissociation. Reprinted with permission from Ref. [3]. Copyright American Chemical Society (2000).

significant and represents up to 15% of the total intensity in the positive spectrum of PS.

In general, the kinetic energy of fragments decreases with increasing fragment size and this effect is well predicted by the MD simulation if dissociation reactions are taken into account (Fig. 1). Moreover, within a given hydrocarbon (C_nH_x) series, fragments containing less hydrogen atoms have a broader KED in the experiment. A periodic KED pattern is observed for the different C_nH_x series. This "unsaturation" effect is explained by the fact that precursor fragments can have an excess of IE that can be released by H elimination. The higher the IE of the precursor, the larger the number of H atoms eliminated. Because there is a correlation between kinetic and IE, the number of H atoms released after emission is also proportional to the kinetic energy of the precursor. In addition, the daughter ion KE is not strongly modified by the relaxation process, because the mass of H atoms is almost negligible [8].

The good agreement between measured and calculated KEDs supports the idea that molecular secondary ion emission is a collisional process well described by MD simulations. The simulations allow us to study the detailed emission mechanisms by looking at the time evolution of the trajectories. For instance, the broader KED observed for entire molecules [1] as compared to fragments (except for the smallest ones [3]), can be explained by differences in the emission mechanisms. In the low energy part of the KED (see Fig. 1), the ejection of the entire PS tetramer is often induced by the isolated action of an energetic upward moving Ag atom of the collision cascade. The result is a low KE

secondary ion with a high IE. A typical trajectory gives KE = 1.9 eV and IE = 11.1 eV. Such a high IE can be accommodated without fragmentation owing to the large number of vibration-rotation modes of PS tetramers. In the high-energy tail of the KED, there is a larger fraction of molecules sputtered via the cumulative uplifting action of several substrate recoil atoms having low but correlated upward momentum, leading to a 'cooler' emission process. A representative trajectory gives KE = 6.7 and IE = 7.1 eV. This second mechanism is not observed for fragment emission, where the first bond breaking is primarily induced by the direct interaction between the primary particle and the polymer chain. The second bond breaking leading to their emission can be induced either by a recoil atom or by IE-driven relaxation.

4. Disappearance cross-section and local deposited energy profile [9]

At first glance, these two quantities do not seem to be related. Indeed, the first one refers to the organic layer degradation while the second one corresponds to a single isolated projectile impact on the surface. MD simulations help us to find a correlation between these two quantities.

The disappearance cross-section σ is deduced from the exponential decay of the secondary ion yield with the primary ion fluence ϕ. This decay is observed for fragment ions that are characteristic and not induced by the beam degradation. Fig. 2 shows σ as a function of the fragment mass. It is seen that σ is fragment dependent, increasing with the fragment mass. This observation is in agreement with the physical meaning of σ, i.e., the average area per incident ion from where the fragment emission is excluded (larger than the fragment size). Moreover, within the same C_nH_x series, σ increases with the number x of H atoms. MD simulation allows us to look at the origin of the emitted species on the surface and to derive the distance between the projectile impact point and the center of mass of the departing fragment, distance defined as the ejection radius. Fig. 3 shows the distribution of the ejection radii for different PS fragments. This distribution broadens and its maximum

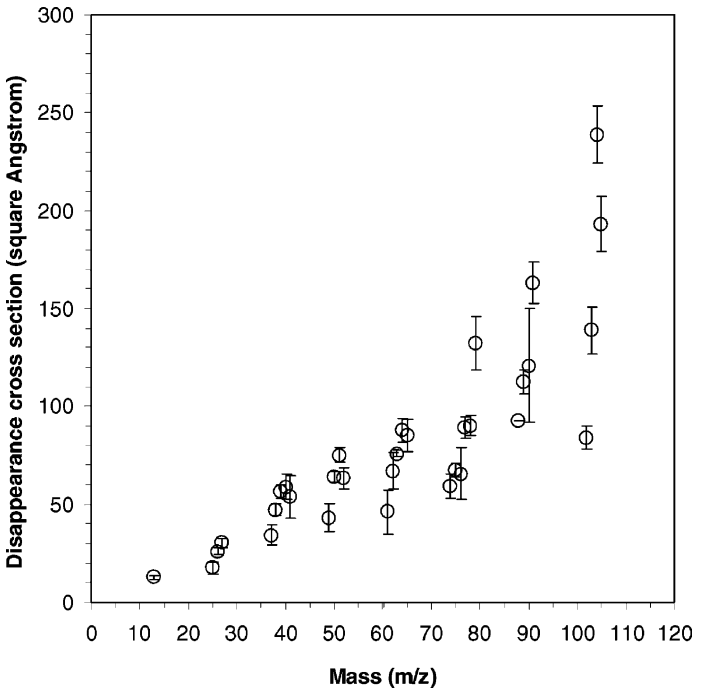

Fig. 2. Disappearance cross-sections (Å^2) of the hydrocarbon fragments sputtered from PS as a function of the fragment mass. Reprinted with permission from Ref. [9]. Copyright Elsevier (2000).

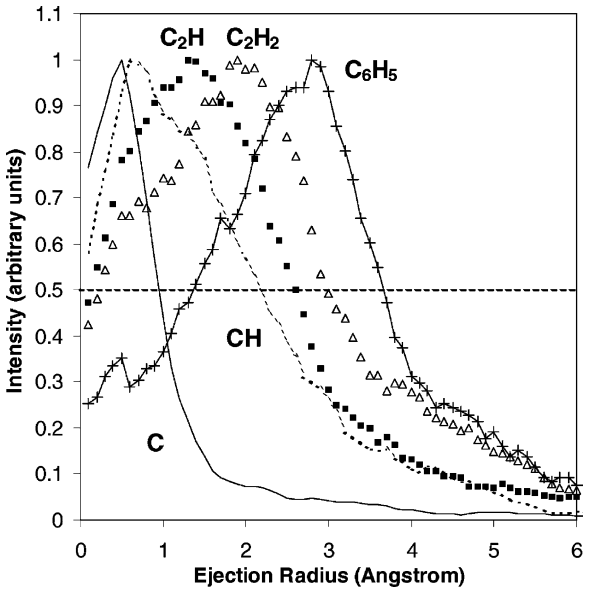

Fig. 3. Calculated distributions of distances between the impact point and the center-of-mass of the nascent fragments obtained from MD simulations. Reprinted with permission from Ref. [9]. Copyright Elsevier (2000).

shifts towards higher distances when the fragment size increases. This indicates, as proposed in Benninghoven's precursor model [2], that large fragments and the entire molecule are emitted at some distance from the impact point. Therefore, the ejection radius at the maximum of the distribution behaves similarly to the disappearance cross-section with respect to the fragment size. Moreover, a good linear correlation can be found between the ejection radius at the maximum and the disappearance radius derived from the disappearance cross-section ($r_{\mathrm{dis}} = (\sigma/\pi)^{0.5}$). This correlation allows us to use r_{dis} as an estimate of the mean ejection radius (in fact r_{dis} overestimates the calculated ejection radius by a factor close to 2 [9]).

On the other hand, the KE of the fragments can be estimated by the full width at half maximum, Δ_{FWHM}, of the distributions. This experimental quantity can also be correlated with the total energy received by the emitted fragment divided by the fragment mass (E/m) in the MD model. Assuming that E/m mirrors the local energy density deposited by the cascade, then the plot Δ_{FWHM} as a function of r_{dis}, as shown in Fig. 4 for PS

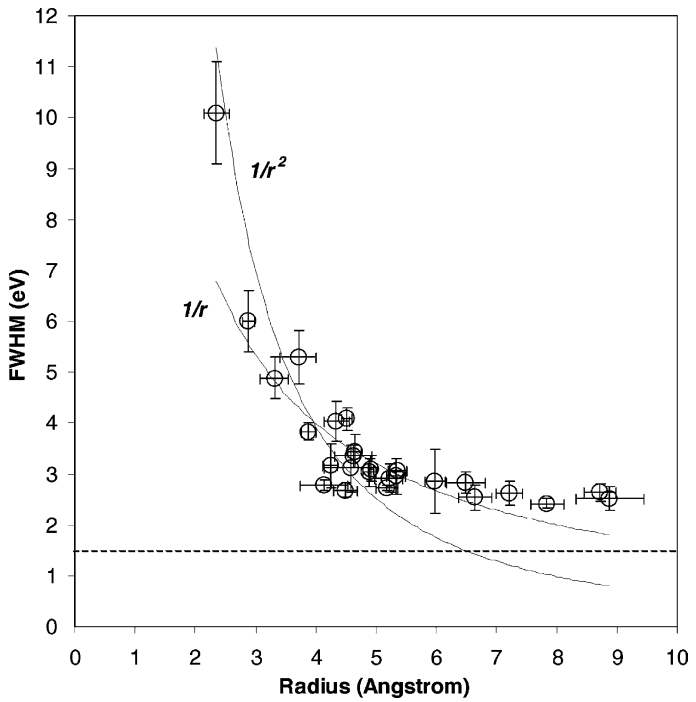

Fig. 4. Correlation between the KED widths and the disappearance radii for PS fragments. Reprinted with permission from Ref. [9]. Copyright Elsevier (2000).

fragments, mirrors the deposited energy density profile at the surface. Fig. 4 shows that Δ_{FWHM} decreases steeply up to 5 Å, then saturates beyond 5 Å with a value close to the energy resolution of the KED measurements. The narrow energy density profile illustrates the limited spatial extent of the emission region.

5. Conclusions

Our results show that there is a good agreement between the experimental and calculated KEDs of PS fragments, provided that IE dependent fragmentation is taken into account in the simulation. Molecular fragments and entire molecules are emitted by collisional processes. MD simulation results highlight the role of the projectile as a trigger of the fragmentation, whereas the experiment shows the importance of metastable decay reactions in vacuum. It is clearly shown that cooperative uplifting by several substrate recoil atoms contributes to intact molecule emission.

In addition, the correlation between the fragment kinetic energies and disappearance radii provides an image of the deposited energy profile at the surface. The exact nature of the ionization mechanisms remains an issue. To explain the metal cationization of intact molecules, we recently proposed the contribution of an associative ionization mechanism in which a neutral organic molecule and a neutral excited metal atom recombine and become ionized above the surface [10,11].

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