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A microscopic view of organic sample sputtering

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Abstract

Molecular dynamics simulations are performed in order to understand the fragmentation and emission mechanisms of kDa chain segments when a polymer (polystyrene) is bombarded by a keV particle (Ar). The calculated energy spectra of small fingerprint fragments and kDa chain segments are compared to experimental distributions. The results show that the ejection of small fragments is primarily induced by interatomic collisions. In contrast, vibrational excitation of the polymer plays a major role in the emission of kDa chain segments.

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1. Introduction

Modeling the bombardment of bulk organic materials via classical molecular dynamics (MD) simulations is now feasible [1], owing to the recent development of a realistic potential for hydrocarbon interactions [2,3]. Using an implementation of this potential (AIREBO) in the MD scheme, we study the sputtering of a 7.5 kDa polystyrene oligomer under 500 eV Ar bombardment. On the grounds of the calculated quantities and the snapshots of the trajectories, we compare the emission mechanisms of small fragments and kDa chain segments.

2. Materials and methods

The Ar bombardment of a *sec*-butyl terminated polystyrene oligomer comprising 61 styrene repeat

units ($C_4H_9[C_8H_8]_{61}H$) adsorbed on a Ag(1 1 1) surface is modeled using MD computer simulations. The MD model, the chosen potentials and the polystyrene sample have been described in extensive detail elsewhere [4]. Beside the traditional Brenner potential [3], we used the adaptive intermolecular potential, AIREBO, developed by Stuart et al. [2] to model the C–C, C–H and H–H short- and long-range interactions. About 300 trajectories (respectively, 1000) were calculated with our PS molecule in the AIREBO (respectively, REBO) potential. For comparison, sub-monolayers of deuterated PS oligomers ($M_n = 5300$ Da) have been analyzed and the kinetic energy distributions (KEDs) of the sputtered fragments were measured [5] using a PHI-EVANS time-of-flight SIMS (TRIFT 1) with a 15 keV Ga^+ beam (FEI 83-2 liquid metal ion source) [6].

3. Results

The theme of this paper is the identification of the mechanisms by which small fingerprint fragments

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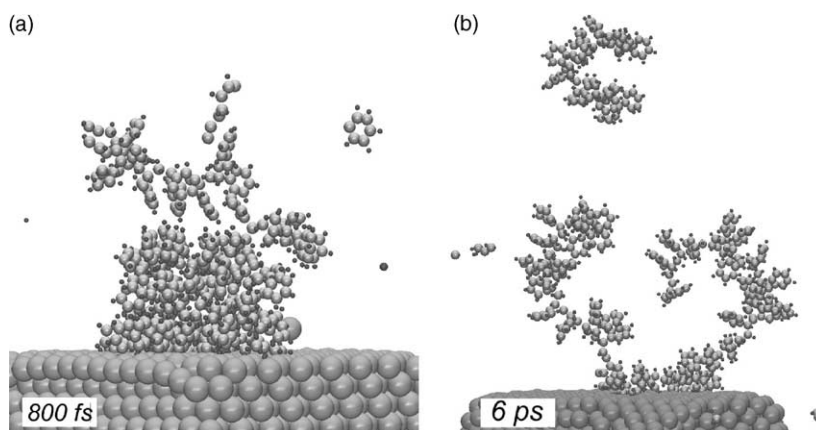


Fig. 1. Movie snapshots of the MD for two trajectories involving PS61.

and kDa chain segments are sputtered from a polymer sample. Two examples of trajectories are illustrated in Fig. 1. In the first vignette, one notices the emission of small fragments, including a phenyl ring (C_6H_5), after less than a picosecond. The second vignette shows a trajectory where the whole molecule unzips, leading to the ejection of a large chain segment, $C_{106}H_{106}$ (1.4 kDa), after 6 ps. Beside the characteristic ejection time, the sputtering of fingerprint fragments and large chain segments exhibit other differences. These mechanisms are investigated on the grounds of energy and velocity distributions.

The calculated and experimental KEDs of polymer fragments are shown in Fig. 2a and b, respectively. The KED of C_6H_5 is compared to the cumulated KED of fragments in the range 1000–1500 Da (for a good signal/noise ratio). The calculated distribution of C_6H_5 (Fig. 2a) is displayed: (i) with a 0.5 eV energy passband (open triangles), to reveal the ‘exact’ distribution, and (ii) with a 2 eV passband (full circles) in order to mirror the experimental resolution. With the correction (2 eV passband), the measured and calculated KEDs of C_6H_5 are very similar, which confirms the quality of the MD model.

For C_6H_5 , the average kinetic energy per constituent carbon atom is high, ~ 0.25 eV. Such an emission mechanism in which a relatively large momentum is transferred to the center-of-mass of the fragment can be categorized as collisional. The KED of large kDa segments, broader than that of the phenyl, peaks

around 4 eV in the simulation and the experiment, which corresponds to an average center-of-mass kinetic energy per C atom close to 0.05 eV, i.e. five times less than the phenyl. Another observable of interest, the internal energy of the fragments, is provided by the MD simulation. The average internal energy of phenyl fragments is ~ 6 eV, i.e. 1 eV per C atom, whereas that of fragments in the range 1000–1500 Da is ~ 27 eV, i.e. $\sim (1/3)$ eV per C atom.

The *velocity* distributions of sputtered fragments (Fig. 2c and d) provide us with complementary information related to the chronology of the emission. In Fig. 2c, we show the calculated velocity distributions of C_6H_5 (triangles) and the cumulated distribution for fragments in the range 1000–1500 Da (full line). The dashed line corresponds to the distribution deduced from the *corrected* KED of C_6H_5 using Eq. (1). In parallel, the velocity distributions deduced from the experimental KEDs via Eq. (1) are displayed in Fig. 2d.

$$\frac{dI}{dv} = \frac{dI}{dE} \frac{dE}{dv} = \frac{dI}{dE} (2mE)^{1/2} \quad (1)$$

$$v = \left(\frac{2E}{m} \right)^{1/2} \quad (1')$$

In this figure, the ‘experimental’ velocity spectrum of kDa fragments is represented by a range of distributions (dashed area) because of the range of masses considered in the KED (see Eqs. (1) and (1')). For C_6H_5 , the calculated and experimental velocity spectra

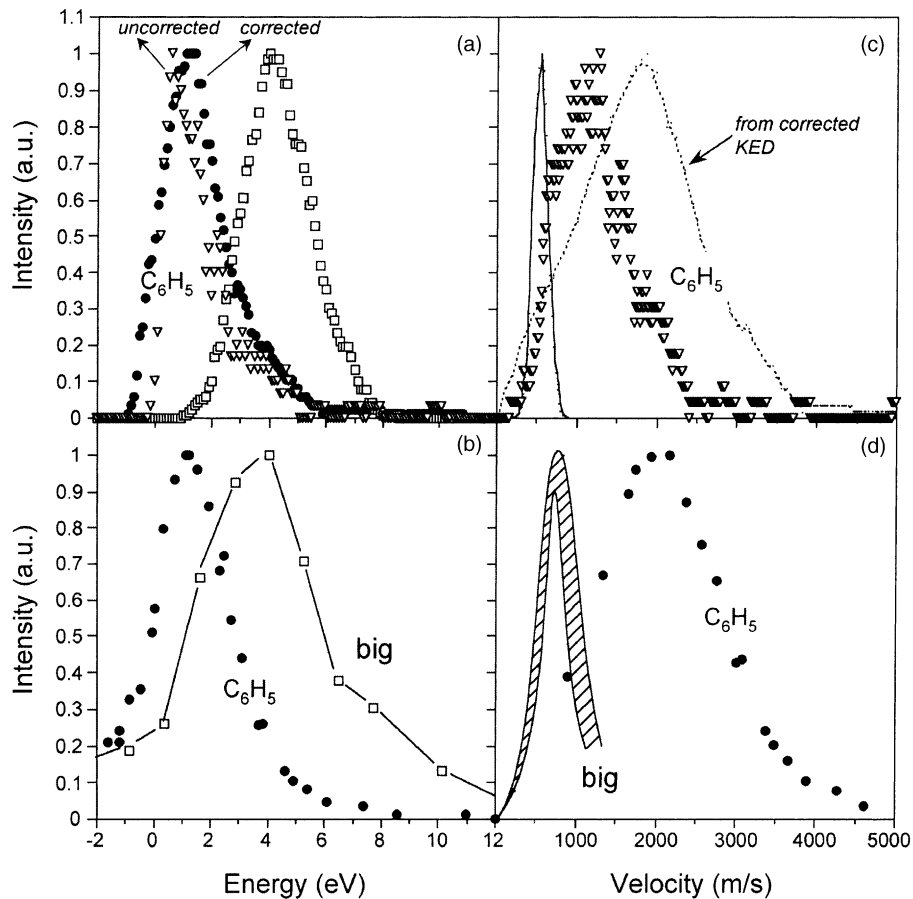


Fig. 2. Energy and velocity distributions of fragments: (a) calculated KEDs; (b) measured KEDs; (c) calculated velocities; (d) measured velocities.

deduced from the KEDs appear significantly broader than the 'exact' distribution obtained from the velocities at the end of the MD simulations (triangles in Fig. 2c). The reason is that we introduced an error by deriving velocity distributions from KEDs obtained with a limited resolution. Therefore, it can be considered that the velocity spectra directly given by the MD model are more realistic.

The average velocity of phenyl fragments is 2.5 times higher than that of kDa fragments and their velocity spectrum is much broader. Better than the characteristic energies, the different ejection times and velocities of fingerprint and kDa fragments allow us to categorize the sputtered species in two groups, with a time of ~ 1 ps and a velocity of ~ 1 km/s as characteristic transition values.

4. Discussion

Fingerprint fragments in the range 0–150 Da such as C_6H_5 , with ejection times smaller than 1 ps and velocities greater than 1 km/s, constitute the first batch of ejected species in the chronology of the sputtering processes. The MD simulations indicate that they are mostly formed as a result of the direct interaction between the primary particle and a close neighbor C atom of the nascent fragment, inducing a bond-scission and the subsequent ejection of the fragment in a classical action–reaction scenario.

The kDa chain segments belong to the second batch of sputtered species, with characteristic emission times larger than 1 ps and velocities lower than 1 km/s. According to the computed trajectory movies,

the first step of their formation is also a bond-breaking caused by the primary particle. Nevertheless, the reaction energy transferred in this collision is insufficient to unzip and eject a heavy chain segment. With time, the atomic collision cascade cools down and the cascade energy is mostly stored in the C–C bonds of the molecule. When a large amount of vibrational energy concentrates in the loosely bound chain segment, it can detach from the rest of the molecule and depart in the vacuum. As a consequence of the energy dissipation in the organic medium, corresponding to later times in the trajectories, the average kinetic + internal energy per atom for kDa fragments is several times lower than that calculated for small fingerprint fragments.

5. Conclusion and outlook

The bombardment of a polymer by keV particles leads to the sputtering of fingerprint fragments and kDa chain segments. MD simulations show that these species are characterized by different emission processes, i.e. collision-induced ejection (small fingerprint fragments) and vibration-induced desorption (kDa chain segments). The characteristic velocity and energy distributions of the respective fragments keep the memory of these two distinct mechanisms. The microscopic view revealed by the MD model is strongly supported by the similarity between the experimental and calculated energy distributions of the sputtered species. In ongoing and future simulations, we are interested in modeling a bicomponent

system consisting of 2 kDa styrene oligomers embedded in a low molecular weight matrix (trimethylbenzene). With this system, we investigate a new route to enhance the yield of large analyte molecules in SIMS.

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