



Sputtering of a polycyclic hydrocarbon molecule: TOF–SIMS experiments and molecular dynamic simulations

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Abstract

This study focuses on the desorption and ionization processes of an aromatic molecule containing several phenyl rings, 1,2,3,4-tetraphenyl-naphthalene (TPN), adsorbed on a Au surface, via the comparison of experimental secondary ion mass spectrometry (SIMS) data and molecular dynamic (MD) simulations. The mass spectra and kinetic energy distribution (KED) measurements were obtained using both TOF–SIMS and MD simulation methods. For entire TPN molecules, a good agreement is observed between the calculated and experimental KEDs, except for high energies, where they start diverging. This difference is partly caused by the unimolecular dissociation of internally excited molecules over larger time intervals than those considered in the simulation. In turn, using an internal energy threshold to remove the most excited molecules from the calculated KEDs provides a better agreement with the experiment. The MD simulations also show that molecules surrounding the impact point of the projectile are sputtered with more kinetic energy and shorter emission times than molecules located farther away from it. The distinct emission mechanisms inducing these different energy spectra are identified by the analysis of the simulation results.

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1. Introduction

Secondary ion mass spectrometry (SIMS) is widely used for the analysis of organic surfaces thanks to its chemical information and high sensitivity, but the quantitative interpretation of the data is still restricted and requires an improved understanding of molecular ion emission processes. Computational methods such as molecular dynamics (MD) simulations appear well

suitable for this purpose. Through the careful choice of initial conditions and, sometimes, realistic data correction procedures, a very good agreement with experiments is often attained [1].

This article focuses on the comparison between the MD model and the experimental SIMS data for a system consisting of polycyclic hydrocarbon molecules adsorbed on a metal surface under keV projectile bombardment. The success and challenges of the method are illustrated by experimental and calculated mass and kinetic energy spectra. Alternative theoretical routes aimed at improving the explanation of the results are suggested.

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2. Methods

The secondary ion mass analyses were conducted using a PHI-EVANS time-of-flight SIMS (TRIFT1) equipped with a 15 keV Ga⁺ beam (FEI 83-2 liquid metal ion source; 600 pA dc current; 22 ns pulse width; 11 kHz repetition rate) [2]. The experimental setup has been described in detail elsewhere [3]. The mass spectra were obtained from 180 s acquisitions on a 120 μm × 120 μm sample area, which corresponds to a fluence of 1.1 × 10¹² ions/cm², ensuring static bombardment conditions. An aromatic molecule containing several phenyl rings, 1,2,3,4-tetraphenyl-naphthalene (TPN), adsorbed on a gold surface has been chosen as model sample because it exhibits a fairly high and clear signal for both the molecular TPN ion (M⁺) and the gold-cationized TPN molecule (Au + M)⁺. The TPN sample was dissolved in toluene (1 mg/ml) and spin-coated on a gold covered silicon substrate. The metallized substrates were prepared by first evaporating a 5 nm titanium adhesive layer and then a 100 nm gold layer onto clean silicon wafer.

The MD simulations were performed with the SPUT2000 software developed at Penn State University [1,4]. They involved the 5 keV Ar bombardment of a sample comprised of 16 TPN molecules on a 5000 Å² gold (1 1 1) surface. The different conditions used in the simulation with respect to the experiment were aimed at limiting the computational costs. In addition, it has been shown that the kinetic energy distributions (KEDs) of molecular ions exhibit a negligible dependence on the primary ion nature and energy for bombardment conditions encompassing those described here [3]. The chosen set of argon aiming points partly covers the four central TPN molecules (c-TPN) and does not touch the peripheral molecules (p-TPN). A total of 200 trajectories were computed for a maximum duration of 4 ps each. All the trajectories were initiated using a fresh undamaged sample. Open boundary conditions were used for the system. Experimentally observable properties such as the yield and kinetic energy distributions were calculated from the final positions, velocities, and masses of all of the ejected species. The energy and forces in the system were described by many-body interaction potentials. For Au–C and Au–H interactions, pairwise additive Lennard–Jones (L–J) potential functions were applied. To model the Au–Au interactions, we used the

molecular dynamics/Monte Carlo-corrected effective medium (MD/MC-CEM) potential [5]. The Ar–C, Ar–H, and Ar–Au interactions were described by purely repulsive Moliere potential functions. The AIREBO [6,7] potential, including long-range (van der Waals) forces, was used to describe the C–C, C–H and H–H interactions.

3. Results and discussion

3.1. Mass spectra

The experimental and calculated mass spectra are presented in Fig. 1a and b, respectively. The experimental mass spectrum is dominated by the molecular ion ($m/z = 432$) and its Au-cationized homologue ($m/z = 629$). Gold monocations ($m/z = 197$) are present with a lesser intensity. In addition to small hydrocarbons below $m/z = 100$, there is also a series of characteristic polycyclic fragments in the region $250 < m/z < 400$.

Remarkably, the calculated mass spectrum (Fig. 1b) exhibits many of the peaks observed in the SIMS spectrum: Au atoms and clusters, intact TPN molecules, Au–TPN clusters and small hydrocarbon fragments. With respect to the experiment, the gold and TPN peaks are dominant, but the relative intensity of the Au–TPN cluster peak is much weaker. Larger molecule–metal clusters are observed, but few large fragments are produced in the simulation.

The absolute and relative yield differences can be understood considering the absence of charge exchange processes in the simulation, which is the factor conditioning the absolute intensities in experimental SIMS spectra. In the MD simulations, virtually all the sputtered species, including neutrals as well as positive and negative ions, are counted as yield. Since less than 1% of the sputtered species are expected to undergo ionization, it is not surprising to observe much lower yields in the experiment. Describing ionization in the frame of classical MD simulations is a difficult task. One way to do it would be to identify the relevant ionization channels and their associated probability using first principle (“ab initio” [8]) calculations and, then, to implement the corresponding ionization criteria in the model. For example, we recently tested, via this method, an associative ioniza-

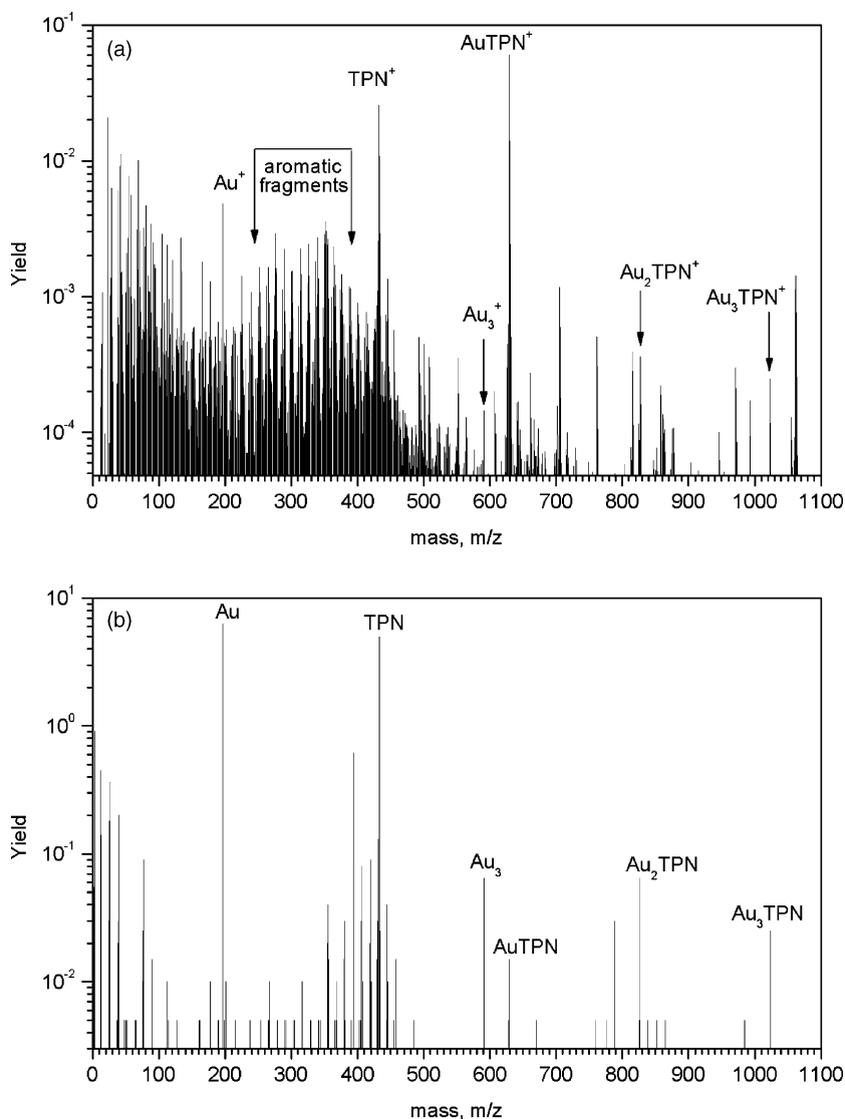


Fig. 1. Experimental (a) and calculated (b) mass spectra of TPN molecules cast on a gold-metallized silicon wafer.

tion mechanism for benzene molecules encountering metal atoms in the vacuum [9].

Another factor might explain the relatively low yield of Au–TPN clusters in the simulation. The Au–C and Au–H Lennard–Jones potential functions, fit to provide a good description of the binding energy of benzene on a metal surface, do not accurately predict the bonding of a single Au atom to an hydrocarbon molecule in the vacuum. This issue could be solved inside the framework of the model by applying

different L–J potentials parameters for bulk and cluster configurations, or by using a more appropriate metal–hydrocarbon potential, and we plan to recalculate it in future.

Several causes may account for the low yield of polycyclic fragments in the simulation. First, the REBO potential is probably not adequate to describe all types of reactions. Second, the calculated trajectories (4 ps) are very short. It has been shown that internally excited molecules may undergo

unimolecular dissociation over larger time intervals than those considered in the simulation [10]. This fact is experimentally confirmed for TPN samples by energy-selected mass spectra (not shown), which exhibit a large amount of polycyclic fragments resulting from metastable decay reactions in vacuum. The width

of the calculated internal energy distribution of sputtered molecules (about 5 eV) supports the possibility of late fragmentation processes. Theoretically, the main fragmentation channels and probabilities could be calculated ab initio, from the viewpoint of total energy minimization, in order to correct the MD

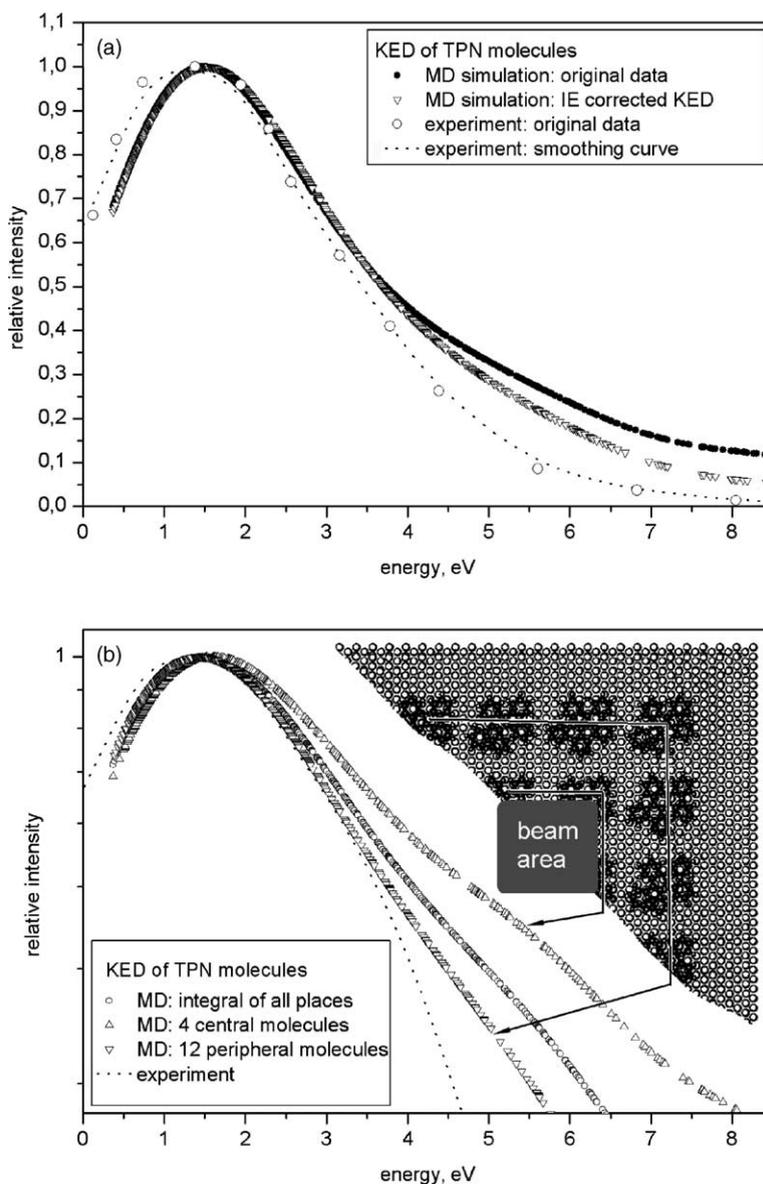


Fig. 2. Experimental and calculated kinetic energy distributions of TPN molecules sputtered from a gold surface: (a) comparison between experiment, raw data from simulation and corrected data from simulation; (b) dependence of the distribution on the ejection site in the MD simulations.

results. Preliminary estimates have been made using the ABINIT software [8] (DFT calculation). They provide a strong indication concerning the favored fragmentation channels (especially the loss of a phenyl residue) for the considered TPN molecule. In the following section, a simpler criterion is used to correct the MD results for such dissociation reactions.

3.2. Energy distributions

Fig. 2a and b presents the experimental and calculated energy distributions of entire TPN molecule. The maxima match and a very good agreement is observed for the main part of the distribution (below 3.5 eV). This fact indicates that, unlike the yields, the energy distributions of entire molecules are not strongly affected by charge transfer processes.

At higher energy, the experimental and calculated KEDs start diverging. One possible reason could be the time restriction of the MD simulations. As mentioned above, energetic clusters may have sufficient internal energy excess to decompose during their flight to the detector, over larger time intervals than those considered in the model. To test this hypothesis, we used a realistic internal energy threshold to remove the most excited molecules from the calculated KEDs (molecules with $E_{\text{int}} > 10$ eV). The result of this method is shown on Fig. 2a (triangles). After correction, the agreement with experimental data is improved.

Our simulations indicate that the calculated KEDs are a superposition of distributions corresponding to molecules originating from different locations on the surface (Fig. 2b). The four central molecules (c-TPN), initially close to the impact point, are predominantly sputtered by relatively energetic recoil atoms. The surrounding molecules (p-TPN), farther away from the impact area, experience mostly a soft uplifting by the surface gold atoms as the collision cascade spreads out. On average, as indicated by the partial energy distributions, central molecules are sputtered with a higher kinetic energy (and a shorter emission time) than molecules located in the periphery. In a previous experimental study, the effects of the projectile mass, energy and incident angle on the KEDs have been shown to be negligible in a large range of bombardment conditions [3]. Nevertheless,

we cannot totally dismiss the possibility that the 15 keV Ga^+ bombardment (experiment) might induce a slightly different distribution of the low- and high-energy fractions for this particular system and, thereby, some minor change in the energy spectra.

Finally, the influence of ionization processes on the shape of the energy distributions in the SIMS measurements cannot be completely excluded. For instance, the image charge created in the metal by the departing ions constitutes a supplementary force that is not taken into account in the simulations and could affect the energy spectra.

4. Conclusion and perspective

The comparison between MD simulations and SIMS data shows that, unlike the absolute and relative intensities of sputtered species, the energy distributions of desorbed TPN molecules only exhibit a weak or no dependence on ionization processes. Their KEDs are fairly well described by the model and the use of an internal energy threshold for dissociation in the simulation helps improving the agreement. As shown by the model, the types of mechanisms responsible for molecular ejection depend on the molecule-impact point distance and are reflected by the energy distribution shapes.

The MD model includes a large part of the physics required to explain the sputtering of molecules from organic surfaces. With a careful choice of parameters for calculation, a realistic correction of the data and a sensible interpretation of the results, they provide invaluable insights into the molecular emission processes. Through a detailed comparison between simulation and experiment, this paper pinpoints some challenging issues for future MD simulations and provides some ideas to overcome them. Problems related to the model size and/or the CPU time costs will probably be naturally resolved by the ongoing progress of the microprocessor industry. Other issues, such as the correct description of ionization and fragmentation processes require different approaches. Ionization effects require complex molecular structure calculations based on the first principles.

In future works, we plan to use the internal energy distributions provided by the classical MD model as

inputs for electronic structure computations aimed at testing different ionization mechanisms. In particular, a mechanism in which vibrationally excited neutral molecules de-excite by ejecting an electron will be investigated via first principle calculation.

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