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Modeling the dissociation and ionization of a sputtered organic molecule

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Abstract

The evolution of an organic molecule after sputtering from a gold surface has been analyzed by classical molecular dynamics and ab initio calculations to gain insight into the ionization and fragmentation processes occurring in SIMS. The calculated ionization potential (6.2 eV) of the tetraphenylnaphthalene (TPN) molecule has been found to be close to the unimolecular dissociation energy (5.4 eV) of the most favorable reaction channel involving the loss of a phenyl ring. On the other hand, our calculations show that the internal energies of sputtered TPN molecules can be significantly larger than 5–6 eV. Therefore, it appears energetically possible to relax such excited molecules via both fragmentation and ionization.

We propose to virtually decompose the TPN molecule into its basic fragments. The rationale is that, if the molecule is very excited, then separate parts (e.g. pendant phenyl rings) can interact with each other almost independently. The analysis of the molecular motion after emission shows that the oscillations along the phenyl-naphthalene bond direction, expected to induce the molecule fragmentation by the loss of a phenyl ring, are relatively small (they store only about 0.2 eV). On the other hand, the relative energy stored in the inter-phenyl interactions, modulated by their bending and responsible for ionization according to our hypothesis, oscillates over a range of 6–7 eV and favors ionization.
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1. Introduction

Understanding the fate of sputtered molecules is an important fundamental issue in SIMS. Quantitative SIMS is under development and requires going a step further to take into account all the relaxation processes, which may influence quantitative data. In addition, the relaxation pathways of organic molecules are interesting not only for SIMS but in many other areas, for instance, in nanotechnology, where the behavior of a single molecule determines the properties of an entire device.

Internally excited molecules have different vibration modes, which may favor either dissociation or ionization. Because of the computational cost it is still unreasonable to calculate the time-evolution of a large organic molecule such as tetraphenyl naphthalene from first principles. Nevertheless classical MD can provide structural data, which can be used in "ab initio" calculations to estimate the overlap of electronic orbitals of the phenyl rings constituting the molecule. A joint theoretical approach combining fast MD simulations, supplying the spatial information, and "ab initio" methods, used for electronic structure calculations, appears to be the most tractable procedure to unravel molecular ionization at this point in time.

2. Methods

An aromatic molecule containing several phenyl rings, 1,2,3,4-tetraphenylnaphthalene (TPN), adsorbed on gold was selected as the model. The analysis of the evolution of sputtered molecules (32 trajectories, each of 7 ps duration) was done using classical MD simulations (the SPUT2000 code [1]). The interatomic potentials and the initial conditions for the calculations, as well as the experimental equipment and methods of sample preparation have been described in detail elsewhere [2].

The total energies of the TPN molecule and its constituents were also calculated from first principles using the ABINIT

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code [3], which is based on pseudopotentials and planewaves. Goedecker-Teter-Hutter (hydrogen) and Hartwigsen-Goedecker-Hutter (carbon) potentials were applied. The investigated systems consisted of particles placed in a big box (16 Å × 16 Å × 16 Å) with a maximal plane-wave kinetic cut-off energy of 800 eV. The ionization and fragmentation potentials were calculated as the energy excess in the ground states between either the neutral and charged molecules or the entire system and its constituents.

3. Results and discussion

To estimate the rate of molecular excitation, we analyzed the translational kinetic (KED) and vibrational internal (IED) energy distributions of the sputtered TPN molecules obtained from the MD simulations (Fig. 1a). For the system under consideration, both distributions appear to be wide enough to permit energy dissipation channels involving bond-scission or ionization reactions (molecules have up to 15 eV of internal energies).

The energy-selected mass spectra obtained by varying the target potential in a range of values exceeding the regular acceleration voltage (to detect molecules formed at some distance above the surface and having energy deficit) are illustrated in Fig. 1b. The measurements show large amounts of molecules fragmented after sputtering. The mass spectrum of Fig. 1b (last frame) indicates that the most favorable fragmentation pathway is the ejection of a phenyl complex.

The next step of our investigation is to estimate the energetics of fragmentation and ionization.

In order to understand the dissociation process, the energies of some fragmentation channels of the TPN molecule were calculated from first principles. The most probable analyzed channel (requiring the least energy) was found to be the ejection of a phenyl complex, requiring 5.4 eV. This energy is lower than the width of the IED. Thus, the fragmentation of TPN via the ejection of a phenyl radical is energetically possible. Ab initio calculations also show that the ionization energy of the TPN molecule (6.2 eV) is not much larger than the dissociation threshold. Both processes, metastable decay and ionization, have similar energy requirements. A significant number of ejected molecules have enough vibrational energy to overcome either the 6.2 eV ionization barrier or the 5.4 eV phenyl complex ejection threshold. Because there is no clear proof regarding the energy of the most favorable dissipation channel, we decided to define a criterion of choice based on the type of vibrational motion in the sputtered molecules. Our hypothesis is that the inter-phenyl interaction is responsible for the ionization of a molecule, and the phenyl-naphthalene interaction for the fragmentation (by the ejection of a phenyl complex). The initial electronic gap of the organic materials like TPN is about 2 eV [4] and they can be referred to as organic semiconductors, containing extended π-electron systems, which can be changed into the conducting state by increasing the temperature (excitation of molecules). In the case of close proximity of the rings, quasi-resonant electronic
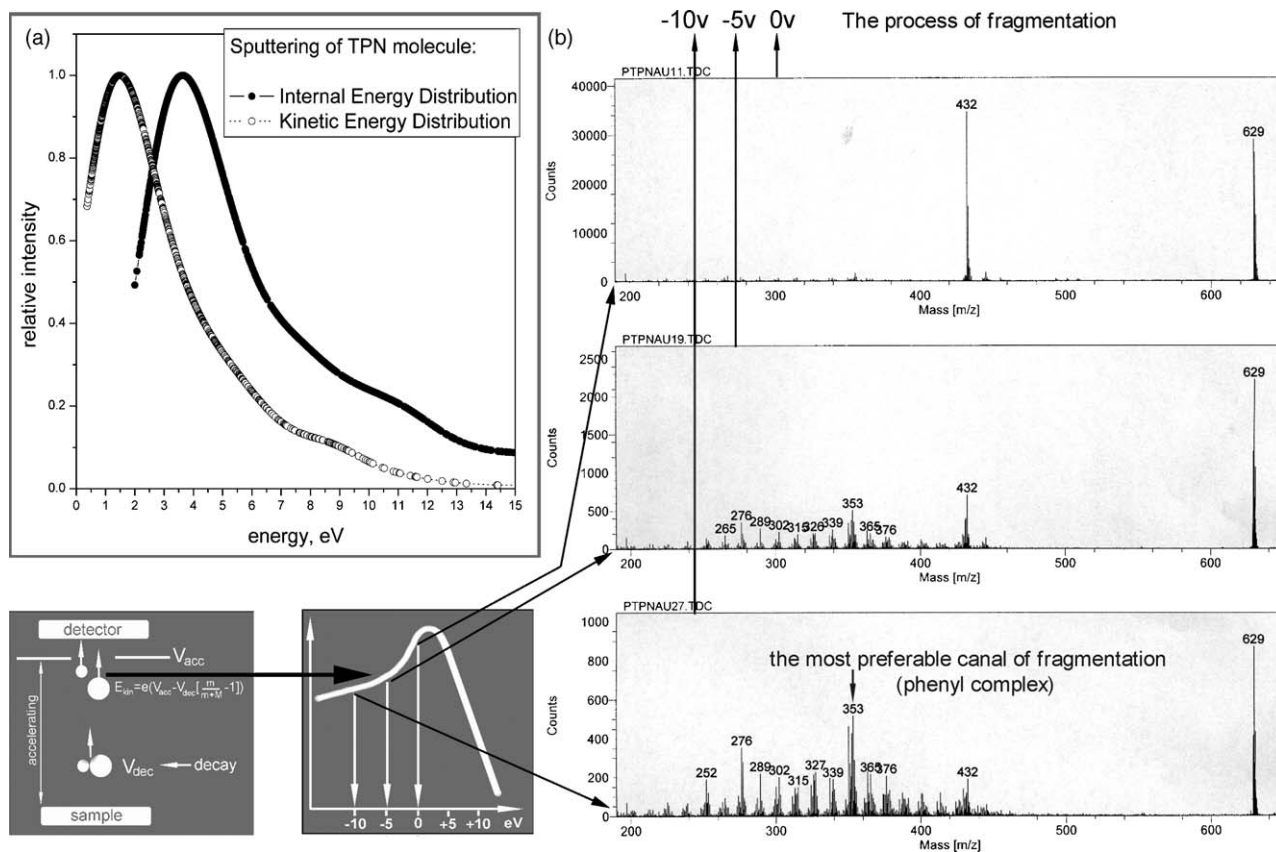

Fig. 1. Kinetic and internal energy distributions of TPN molecules calculated by MD simulations (a), and energy selected mass spectra of TPN (for particles with 0, 5 and 10 eV energy deficit) obtained by SIMS (b).

exchange processes between neighboring phenyl rings can give rise to local excitations. After intra-molecular $\pi \rightarrow \pi^*$ excitation, the de-excitation process may pump an electron from the π^* level into the vacuum and cause a positive ionization of the entire molecule.

Because the TPN molecule remains a large system to perform ab initio calculations, we propose to virtually decompose the molecule into its fractions and analyze them separately. The underlying hypothesis is that, if the molecules are highly excited (as is the case after sputtering in SIMS), then the component parts (phenyl rings) can interact with each other more or less independently.

The evolution of a typical TPN molecule having a sufficiently high internal energy (6.3 eV) and located at 15 Å from the impact point of the primary beam can be traced from the MD simulations (Fig. 2). The analysis of the inter-phenyl interaction (Fig. 2a) indicates a very strong variation in the distance between the centers of mass of neighboring phenyl rings. It causes considerable energy fluctuations inside the subsystem of two phenyls. The close proximity of the rings results in an exponential increase of their total energy. The energy magnitude for the extreme positions of oscillation reaches 6 eV (MD calculations) or 7 eV (calculated from first principles). The similarity of the two values justifies the use of the MD-calculated molecular configurations as input values for the ab initio energy determination. It confirms the accuracy of the MD AIREBO [5] potential to describe hydrocarbon interactions in organic molecules. The quantity of internal energy stored by the interacting phenyl rings is of the same order as the ionization potential of the TPN molecule.

On the other hand, the phenyl-naphthalene vibration mode thought to induce the decomposition of the TPN molecule by a phenyl loss does not show strong oscillations (Fig. 2b). The <0.2 Å magnitude of oscillation causes a very small change in the total energy of the entire TPN molecule. The energy difference reaches 0.5 eV (MD calculations)/0.25 eV (calculated from first principles). The applied MD potential is more rigid than the one used for "ab initio". In any case, this quantity of energy is insufficient to decompose the molecule. In other words, there is a negligible probability of collecting enough vibrational energy on the phenyl-naphthalene bond to overcome the 5.4 eV dissociation barrier.

Finally, there is a third degree of freedom that could influence the ionization process indirectly. It is the torsion oscillation of phenyl-naphthalene bonds. The analysis of the angle evolution between separate phenyl rings in TPN molecule shows that the angles lie in the range of 20°–40° (Fig. 2c). The "ab initio"-calculated total energy varies linearly with the angle and is negligible up to 60°. The magnitude of the energy oscillations between the extreme positions of the phenyl rings is found to be about 0.25 eV. Again, it appears too small to induce either molecular dissociation or ionization.

4. Conclusion and perspective

In order to investigate the fragmentation and ionization mechanisms of sputtered tetraphenylnaphthalene by ab initio methods, the molecule was split into its basic fraction, namely the naphthalene core and the four phenyl rings. Our analysis of the energy dissipation channels was based on the hypothesis that fragmentation occurs mainly via a phenyl-naphthalene bond breaking (ejection of the phenyl group), while ionization is the consequence of the inter-phenyl interactions (overlapping electronic clouds). The calculations indicate that the energy stored in the phenyl-naphthalene bond is much smaller than the 5.4 eV energetic barrier of unimolecular dissociation. In contrast, the phenyl-phenyl interaction is able to store up to 6–7 eV of energy. Therefore, we suggest that one electron might
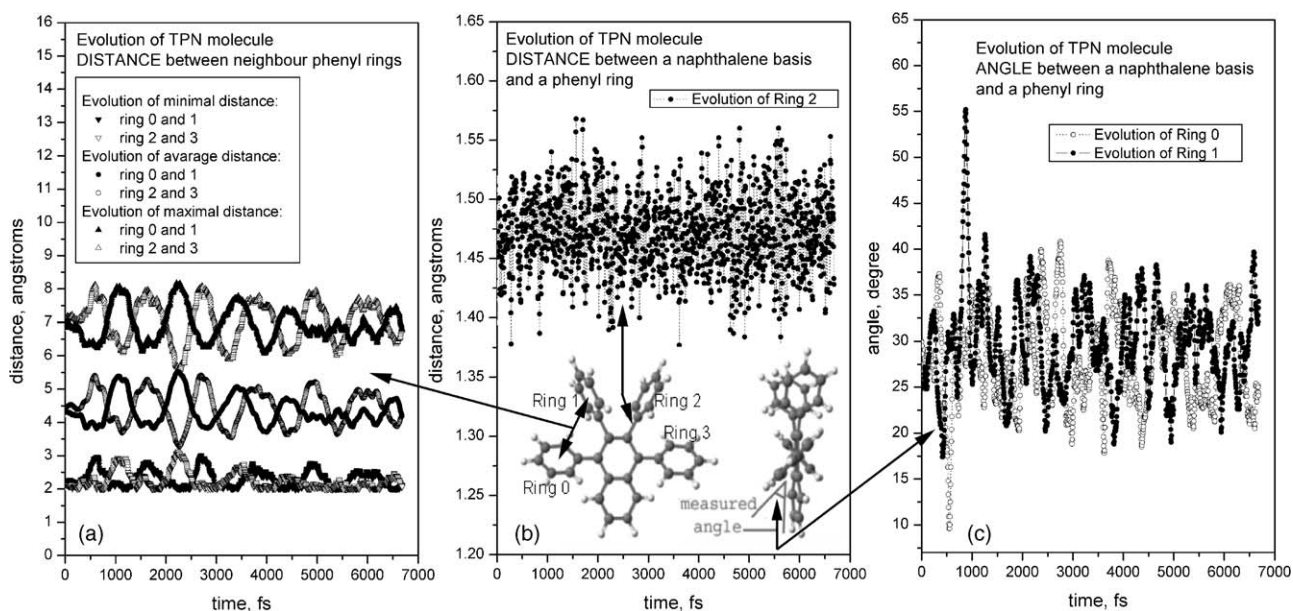

Fig. 2. MD calculated sputtering of TPN molecule from gold surface under 5 keV Ar beam. Evolution of the distance between neighbor phenyl rings of TPN molecule (a), the distance between a naphthalene core and a phenyl ring in TPN molecule (b), the relative angles of separated phenyl rings in TPN molecule (c).

be promoted to the higher energy state of the virtual double-benzene system and then ejected, overcoming the ionization threshold (6.2 eV). This ionization mechanism could partly explain the high yield of molecular ions observed for TPN in SIMS, in comparison with the relatively low yields generally measured for flat polycyclic molecules, where the rings cannot interact in this manner. Our future investigations will aim at identifying alternative energy dissipation scenarios (for instance the ''squeezing'' of a phenyl between two other rings, possibly leading to its ejection) and at understanding the specifics of energy conversion in more details.

Acknowledgements

References

[1] B.J. Garrison, A. Delcorte, K. Krantzman, Acc. Chem. Res. 33 (2000) 69.
[2] V. Solomko, A. Delcorte, B.J. Garrison, P. Bertrand, Appl. Surf. Sci. 231–232 (2004) 48–53.
[3] X. Gonze, et al. Comput. Mater. Sci. 25 (2002) 478.
[4] M. Onoda, et al. J. Phys. D: Appl. Phys. 24 (1991) 1152–1157.
[5] S.J. Stuart, A.B. Tutein, J.A. Harrison, J. Chem. Phys. 112 (2000) 6472.