

## MODELING SPUTTERING OF ORGANIC MOLECULES

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Molecular dynamics simulations of keV particle bombardment of organic systems are described including the Brenner hydrocarbon potential that mimics chemical reactions. Cooperative uplifting as a key mechanism of organic molecule ejection from metal surfaces is highlighted.

## INTRODUCTION

One successful approach for understanding collision cascades or atomic motions in solids subsequent to bombardment by very energetic particles is molecular dynamics (MD) computer simulation [1, 2]. One of the predictions of the MD simulations for atomic solids is that the ejection of particles due to the collision cascade predominantly occurs on the sub-picosecond timescale. This fast timescale opens the possibility for large organic and biological molecules being ejected from a surface without reaching thermal equilibrium and decomposing. In fact, the analytical techniques of Secondary Ion Mass Spectrometry (SIMS) and Fast Atom Bombardment Mass Spectrometry (FABMS) [3, 4] do successfully employ keV particle beams to eject molecules. Although the experimental techniques are quite mature, the interrelationships between the motions in the solid that result in liftoff of intact molecules and the final experimental spectra remain elusive.

Can MD simulations therefore be used to understand organic SIMS, where the ejected species are molecular ions and molecular ion fragments? Certainly describing chemical specificity of fragmentation, formation of ions and possible electronic effects in the collision cascade are beyond the capability of classical mechanics. On the other hand, some experimental data indicate that collision cascades play a major role in the ejection of molecules [5–7]. Regardless of the importance of phenomena we cannot model, there must be a collision cascade present. Thus, we feel that it is important to understand the predictions of the motion of the atoms on the ejection of molecules.

## 1. COMPUTATIONAL APPROACH

Briefly, the MD approach involves integrating the classical equations of motion for all the particles in the solid [8, 9]. The results of the simulation provide the positions and velocities of all the atoms in the system as a function of time. From the final velocities, measur-

able quantities such as energy and angular distributions can be calculated. From the time development of the atomic positions, a microscopic picture of the important motions can be visualized. In addition, the microscopic mechanisms can be identified with specific quantities that can be measured.

The MD approach needs as input a force field or interaction potential among the atoms. A great advance in the past decade has been the development of many-body potentials for describing extended systems [10]. For example, the Brenner potential initially developed [11] for modeling chemical vapor deposition of diamond films has provided insight into a number of different reactive scenarios involving hydrocarbon systems [9]. Based on a form developed by Tersoff [12] to model covalent solids, this potential function gives the binding energy  $E_b$  in a form reminiscent of a pair potential

$$E_b = \sum_{i=1}^{N-1} \sum_{j=i+1}^N [V_R(r_{ij}) - b_{ij}V_A(r_{ij})],$$

where  $r_{ij}$  is the distance between pairs of atoms,  $V_R$  represents the repulsion between atomic cores,  $V_A$  represents the attraction due to valence electrons, and  $b_{ij}$  represents a bond-order function that modulates the bonding according to the local environment of each atomic pair. Based on chemical pseudopotential theory, this form assumes that the core–core repulsion and the bonding due to valence electrons are both pair additive and independent of atomic hybridization. All many-body effects, including rehybridization due to bond breaking/forming, are incorporated in the bond-order function,  $b_{ij}$ .

The central properties that determine the value of the bond order function  $b_{ij}$  are local atomic coordination and bond angles. A functional form is used for  $b_{ij}$  so that its value decreases as the local coordination increases. Consequently, the attractive term weakens to model the finite number of valence electrons available for bonding. The bond-order function is also parameterized so that its value increases with increasing bond angles. Bond angles of 180°, 120°, and 109.5° for 2-, 3- and 4-fold coordination are favored, in agreement with the expected hybridizations. The value of the bond or-

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der also depends on the presence of radicals, whether unsaturated bonds are part of a conjugated system, and the value of the dihedral angle for rotation about double bonds.

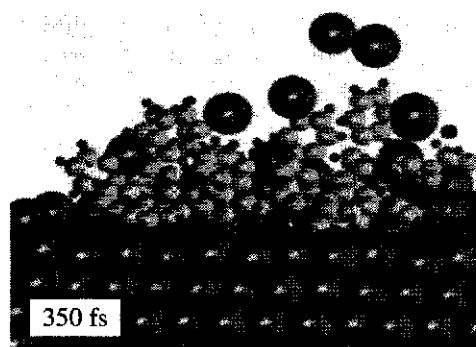
Parameters in the potential have been fitted to a variety of solid-state and molecular properties. A complete description is given in the original paper by Brenner [11]. The unique feature of this potential is that atomic hybridizations are not explicitly specified; instead the bonding characteristics are all determined by the local environment through the bond-order function coupled to highly transferable pair terms. This feature, which is absent in more traditional force fields, provides not only a good description of the structure and energetics of carbon in a variety of hybridizations with a single functional form, but it also allows bonding characteristics to change as bonds are formed and broken. This flexibility of the potential has made it an extremely useful tool for modeling a wide variety of phenomena as presented in [8]. For our simulations of modeling sputtering of organic molecules, the potential by Brenner underpins all our work.

## 2. RESULTS

The simulations provide both mechanistic insights into the bombardment process as well as predictions of quantitative distributions of the ejected species [13, 14]. Highlighted here are extended molecular systems in which there are multiple contacts to a metal substrate. Examples of such systems include benzene on Ni [15, 16] and Ag [17, 18]; biphenyl on Cu [19, 20] and Si [21, 22]; coronene on Ni [23]; ethylene on Ni [24], and polystyrene on Ag [25–27]. The question addressed is how do molecules eject with sufficiently low internal energy such that they reach the detector intact?

The predominant ejection mechanism for molecules with multiple contact points to the surface is one in which several substrate atoms hit different parts of the molecule resulting in a cooperative uplifting of the intact unit [13–17, 19–21, 23–27]. This process is illustrated in Figure 1 for a polystyrene tetramer on Ag. The imparted upward energy to the molecule in this case comes from several gentle collisions rather than one violent collision. Of course, if the collisions are more energetic, fragmentation may occur. In some cases, there are even collisions in which one substrate atom can eject the intact molecule.

Ejection of a molecule from the substrate requires that there be momentum directed towards the vacuum above the surface. The momentum of the primary particle, on the other hand, is initially aimed into the solid. Is there some way to enhance the chances of several substrate atoms moving upward underneath the molecule on the surface? One approach to coordinating subsurface motion uses polyatomic projectiles [28–31] such as metal or  $SF_5^+$  clusters. Our calculations clearly



Cooperative uplifting mechanism for a polystyrene hexadecamer on Ag. The Ag atoms are represented by large spheres and the C and H atoms by smaller and lighter spheres.

show that the polyatomic projectiles, in fact, do increase the probability of having several substrate atoms cooperatively uplift a molecule from the surface [19–22].

## 3. PROSPECTS FOR THE FUTURE

These studies of modeling energetic particle bombardment of organic films were initially undertaken as a calculated risk. Some predictions from the calculations have been confirmed by experimental data. A key aspect for future calculations, then, is to continue to refine the model so that it becomes feasible to predict larger portions of the mass spectrum. Part of this goal involves incorporation of ionization processes that are still problematic to model. Finally, it is essential to extend these ideas to the study of the condensed films of organic molecules, polymers, and biochemicals that are critically important to a wide community of experimentalists [32, 33]. Henceforth we move in this direction.

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