

MOLECULAR DYNAMICS SIMULATIONS OF REACTIONS BETWEEN MOLECULES: HIGH ENERGY PARTICLE BOMBARDMENT OF ORGANIC FILMS

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1. Introduction

The ability to model using molecular dynamics (MD) simulations the particle bombardment process and to make quantitative predictions of energy and angular distributions and ejection mechanisms of neutral atoms and small clusters from single crystal metal and semi-conductor surfaces has become virtually routine [2]. Unfortunately, modeling organic and biological systems at the same level of accuracy has been hindered by the lack of an interaction potential that describes the multitude of chemical reaction channels. Initial MD simulations of organic overlayers on metal surfaces were restricted to properties of the intact molecule or a fragment that ejected but not to specific reaction events [3]. Recently an empirical many-body potential energy function has been constructed for studying reactive dynamics [4]. Specifically bonds can be broken and reformed. We have incorporated this potential into our MD model for examining the energetic particle bombardment process.

2. Results

Ethylidyne, C_2H_3 , on Pt{111}

As an initial test system we investigated the 500 eV Ar bombardment of ethylidyne, C_2H_3 , on Pt{111} [5]. This specific system has been studied experimentally by White and co-workers using SIMS [6]. We modeled both 0.25 and 0.50 monolayer ethylidyne coverages in order to test density effects. We find that approximately 80% of the ejected hydrocarbon species originate from a single C_2H_3 adsorbate, while the others result from reactions between two C_2H_3 adsorbates. A study of the internal energies of all of the ejected hydrocarbon aggregates reveals that those originating from a single C_2H_3 adsorbate are generally stable to any further fragmentation or rearrangement.

Ejection of a Portion of the Intact Adsorbate: The most common mechanism of ejection observed in these calculations is the fragmentation of a single C_2H_3 adsorbate. This process usually results from the direct collision of either the bombarding particle or a moving C_xH_y or Pt particle with an C_2H_3 adsorbate.

Alternatively the moving particle such as a Pt atom may eject the intact C_2H_3 molecule. This event is characterized by a collision where the C_2H_3 molecule is rolled off the surface. In contrast, when the momentum of the ejecting Pt atom is directed toward the C_2H_3 adsorbate, the molecule usually undergoes fragmentation and/or rearrangement. The fragments observed include CH_3 , CH_2 , CH and H .

Unimolecular Dissociation and Rearrangement: Often before reaching the detector, ejected CCH_3 clusters undergo rearrangement and/or fragmentation to yield products such as H_2 , CCH_2 , CCH , $HCCH$, or H_2CCH . Although the potential energy function used to describe the hydrocarbon interactions in these calculations may not predict the correct energy barrier for these reactions, the potential does allow classical dynamics simulations for the first time, to be used in the qualitative study of the occurrence of unimolecular dissociation/rearrangement-type reactions in the kiloelectronvolt particle bombardment of an organic film. These rearrangement processes occur within the first few hundred femtoseconds of the collision cascade. By examining the internal energies of the ejected molecules we can estimate the number that will further dissociate during the flight to the detector [5].

Reactions between Molecules: The calculations also predict the occurrence of molecules like methane which cannot form from a single C_2H_3 adsorbate. These reactions are exemplified by a hydrogen abstraction-type mechanism in which a free H atom is channeled across the surface and subsequently abstracts another H atom from an undisturbed C_2H_3 adsorbate to form H_2 . Alternatively, a CH_3 radical is channeled across the surface where it collides with an undisturbed C_2H_3 adsorbate. The collision results in the abstraction of a H atom from the C_2H_3 adsorbate. The final products are a free CH_4 molecule and an adsorbed C_2H_2 species. In this example the attacking CH_3 radical is oriented such that the C atom end collides with the C_2H_3 . When the angle of the attacking CH_3 molecule is such that a H atom is the first to react with the C_2H_3 adsorbate, H abstraction does not occur. Instead, depending upon the energy of the incoming CH_3 radical, the $C-H$ bond on the C_2H_3 adsorbate may break to create a free H atom or the $C-C$ bond might break to give a second CH_3 species.

Substrate Effect

The second investigation is the effect of substrate and binding energy of the molecule to the substrate [7]. Experimentally for a combinatorial library of peptides covalently bound to polystyrene beads, no parent peak was observed [8]. Yet, when the covalent linker bond was clipped using trifluoroacetic acid vapor, such that the peptide was instead physisorbed to the bead, the parent peak appeared in abundance. To understand the energy flow in these systems we modeled the bombardment of a pentylidyne (C_5H_9) film adsorbed on $Pt\{111\}$ and diamond $C\{111\}$ with molecular dynamics simulations. When the binding energy of the film to the substrate is lowered from 2.7 eV to 0.6 eV the total yield of ejected particles

is found to increase. The bombardment of the more tightly bound film results in considerable fragmentation of the C_5H_9 adsorbate while the bombardment of the more weakly bound film results in the scission of the Pt-C bond and desorption of the intact molecular adsorbate. Moreover, we find that the yields from the Pt substrate are larger than from the C substrate. We performed additional simulations and determined that the light ^{12}C mass is insufficient to redirect the primary ^{40}Ar beam in an upward direction and consequently the yields are low.

Molecular Size Effect

Experimentally it has been observed that for small adsorbates that the mass spectrum gives a direct indication of the surface species [9]. As the adsorbates get larger, the dominant peak in the mass spectrum is often smaller than the adsorbate molecule [6,10]. In order to understand these observations, we modeled the bombardment of overlayers of CH , CH_2 , CH_3 , C_2H_3 , C_3H_5 and C_5H_9 on $Pt\{111\}$ [11]. The simulations predict the occurrence of considerable lateral motion of particles in the region right above the surface. For adsorbates such as CH_x , the dominant ejected species are an H atom or the intact adsorbate as there are only two unique bonds to sever. Molecules that extend further above the surfaces are exposed to more collisions from laterally moving particles and consequently there is more fragmentation and the dominant ejected species is usually not the original adsorbate.

3. Summary

The results to be presented are from massive molecular dynamics calculations aimed at describing unknown *reactive* dynamics among a multitude of atoms in a complex environment. The strength of the molecular dynamics approach for examining the initial stages of the bombardment process is the microscopic detail that arises from the atomic positions as a function of time. Hopefully these concepts will aid in the interpretation of previous experimental results and perhaps inspire new experiments.

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