

Molecular desorption in bombardment mass spectrometries

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Abstract

Molecular dynamics simulations have been performed to gain microscopic insight into those factors which influence the ejection due to ion bombardment of molecules adsorbed on solid substrates. The specific system modeled is a pentylidyne (C_5H_9) film adsorbed on Pt{111} and C{111}. Lowering the binding energy of the film to the substrate from 2.7 to 0.6 eV increases the total yield of ejected particles. The bombardment of the film bound by 2.7 eV results in considerable fragmentation of the C_5H_9 adsorbate while the bombardment of the film bound by 0.6 eV results in the desorption of the intact molecular adsorbate.

1. Introduction

The molecular-level characterization of molecular surfaces is receiving increased attention. Energetic particle bombardment [1–11] offers intriguing possibilities in this regard since mass spectral information can often be acquired directly from the matrix by analyzing the ejected material. Most recently, the molecular ion yield for adsorbed small peptides has been shown to be related to the bond strength to the surface [12]. For a combinatorial library of peptides covalently bound to polystyrene beads, no parent peak (the molecule \pm a proton) was observed. 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. For further progress, it is essential that the dynamics of energy flow which leads to these observations be understood on a firm basis.

Molecular dynamics computer simulations offer a powerful approach for disentangling the various factors which might influence the probability of intact molecular desorption [13–20]. Calculations of this sort are feasible for the first time because of the recent development of many-body potential functions which describe the forces between hydrocarbon species [21,22] and fcc metals [23]. Although it is important to emphasize that these classical calculations do not generally include ionization or unimolecular gas phase decay, they can provide a clear representation of what is expected to occur as a result of the bombardment-induced collision cascade. In particular this generation of interaction potentials is capable of describing bond energies. Moreover, the potential allows all C–H bonds to be broken and reformed if the dynamics so indicate. In this letter, we report the results of large-scale molecular dynamics calculations of the high energy bombardment of a pentylidyne (C_5H_9) film (Fig. 1a) adsorbed on both

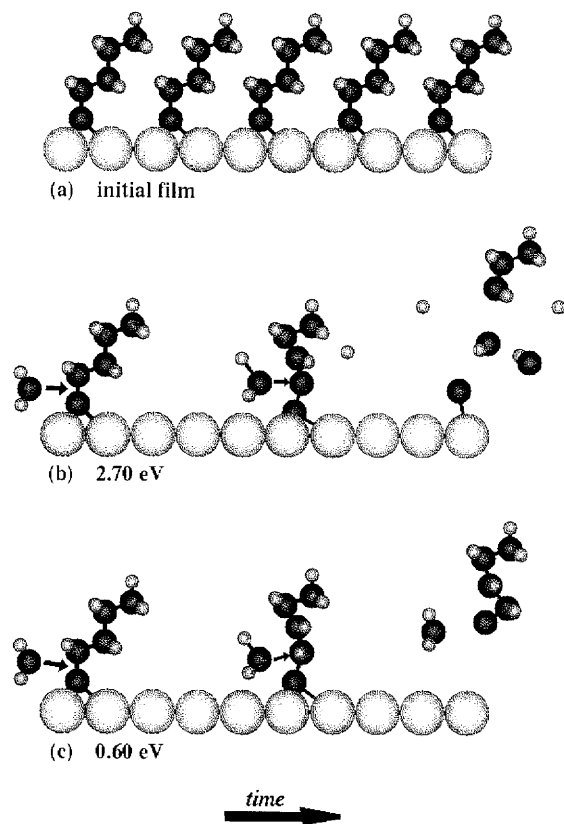
C₅H₉/Pt(111)

Fig. 1. C₅H₉ bound in fcc threefold site on Pt(111): (a) initial array; (b) Scenario for ejection of the C₃H₇ fragment from C₅H₉ film bound by 2.70 eV on Pt(111); (c) Scenario for ejection of the C₅H₉ molecule from C₅H₉ film bound by 0.60 eV on Pt(111). In (b) and (c), the time progression is from left to right across the crystal. See text for an explanation of the collisional events. The large light gray spheres represent Pt atoms, the medium sized dark spheres represent C atoms, and the small spheres represent H atoms.

a platinum and a diamond surface. A major dynamical factor identified in the simulation is that lateral motion of pieces of the organic overlayer is observed during the collision cascade. As shown in Fig. 1b, if an energetic fragment (e.g. CH₂) strikes a molecule bound to the surface by 2.7 eV, bond rupture occurs near the point of impact. If, on the other hand, the surface bond is only 0.6 eV, the whole molecule can be propelled from the surface as shown in Fig. 1c. The mass of substrate atoms is also found to influence the dynamics.

2. Computational details

Films of C₅H₉ adsorbed on Pt(111) and hydrogen terminated C(111) were chosen as prototypes for the 500 eV Ar beam bombardment studies. This molecule is sufficiently simple so as to be computationally feasible, yet complex enough to identify important factors for intact ejection in the high energy bombardment of molecular films. The Pt–C₅H₉ system is modeled by a finite microcrystallite containing 1998 Pt atoms arranged in six layers and a C₅H₉ film consisting of 77 adsorbate molecules. Each C₅H₉ adsorbate is bound in a fcc threefold site via three Pt–C bonds resulting in a tilt angle of $\approx 35^\circ$ relative to the surface normal. The C–C₅H₉ system is approximated by a diamond substrate containing 2919 C atoms arranged in eight layers and a C₅H₉ film consisting of 67 adsorbates placed in a p(2 × 2) configuration above the atop sites. The remaining 246 surface C atoms are each terminated with a single H atom. Due to the possibility of enhanced reactivity caused by the C₅H₉ species on C(111) being diradicals, calculations with a C₅H₁₁ overlayer in which all C atoms are fourfold coordinated were also performed.

Construction of potential functions is a very complicated procedure and is delineated in detail in a previous study [14,15]. Briefly, the metal interactions are described with an EAM potential and the hydrocarbon interactions by a many-body function developed by Brenner [21,22]. We developed the Pt–C and Pt–H interactions to blend the two functional forms [14,15]. Originally the parameters describing the Pt–C interactions were chosen to reproduce the adsorption energy of C₂H₃ on Pt and resulted in an adsorption energy of 7.35 eV. In this study, we have chosen adsorption energies of the C₅H₉ molecules to the Pt surface of 2.70 and 0.60 eV¹. Both of these energies are smaller than the C–C or C–H bond strengths of 4–4.5 eV.

For each trajectory the Ar particle strikes a fresh undamaged sample. Calculations at normal incidence and 45° with respect to the surface normal were

¹ The values of the Lennard-Jones well depth, ϵ , used are 0.75 and 0.05 eV for the 2.70 and 0.60 eV adsorption energies, respectively.

performed. For the adsorbate overlayers each trajectory requires 12–24 hours of cpu time on one node of an IBM SP1 computer. Generally, about 50 trajectories were recorded for each system under study.

3. Results

Calculated mass distributions are determined by counting the neutral clusters which exist 1–2 ps after the bombardment event and are not adjusted for ionization probabilities, ion stabilities or possible further fragmentation of the larger clusters during their μs flight to the detector. These distributions may then be conveniently plotted as ‘mass spectra’. The low mass regions (< 80 amu) computed for normal incident Ar bombardment of the C_5H_9 films bound to Pt(111) by 2.70 and 0.60 eV and the 45° incident Ar bombardment of the C_5H_9 film bound to Pt(111) by 2.70 eV are shown in Fig. 2. The normalizations of all frames in Fig. 2 are the same so that direct comparisons can be made.

The normal and off-normal Ar bombardment of more tightly bound C_5H_9 on Pt result in the ejection of C_xH_y species which consist primarily of three or fewer carbon atoms (Figs. 2a and 2c). The number of desorbed molecules is low in both cases. To eject an intact C_5H_9 species bound by 2.70 eV the Pt–C bond must be severed – an event that takes just the right set of collisional conditions [24–26]. Bond-breaking collisions at other points of the molecule result in fragmentation near the impact point (Fig. 1b). The total yield of emitted particles, given in Table 1, increases as the angle of incidence is changed from 0° to 45° . The main effect of the off-normal angle of incidence is to increase the initial fragmentation of the film, not to enhance molecular ejection. Fragments created by the beam can then move laterally across the surface and further fragment the film, as shown in Fig. 1b.

In contrast, the most probable desorbed species calculated for the bombardment of the C_5H_9 film bound by 0.6 eV is the parent molecule as shown in Fig. 2b. Here the C–C bond strength (4.3 eV) is much higher than the Pt– C_5H_9 binding energy (0.6 eV). Thus as shown in Fig. 1c, collisions of laterally moving particles and stationary C_5H_9 adsorbates can result in the intact C_5H_9 adsorbate being swept up

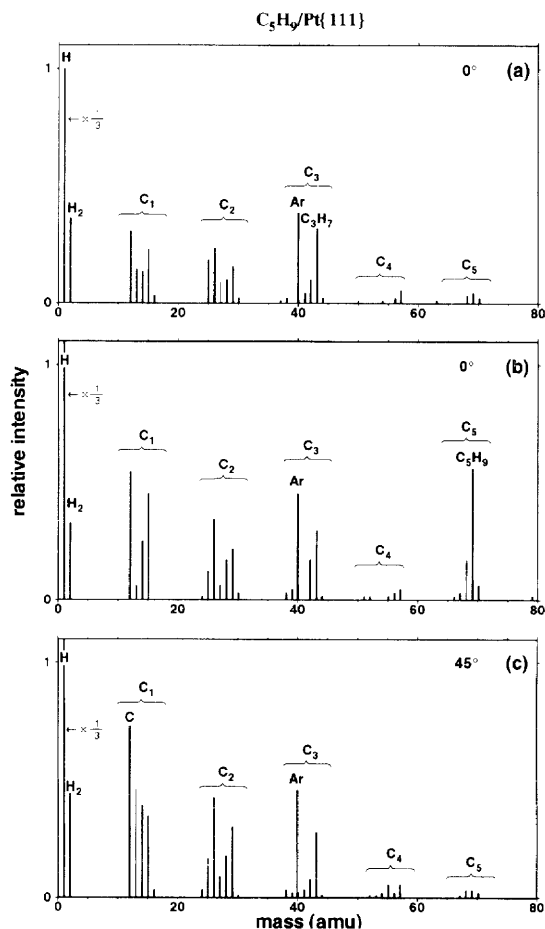


Fig. 2. Low mass regions of the calculated distributions for Ar bombardment of a $p(2 \times 2)$ C_5H_9 film on Pt(111). (a) Normal incidence (0°), 2.70 eV film. (b) Normal incidence (0°), 0.60 eV film. (c) Off-normal incidence (45°), 2.70 eV film.

into the vacuum. A Pt– C_5H_9 binding energy of 2.7 eV, although not as strong as that of the C–C bond strength, is still sufficiently high that the C_5H_9 adsorbate usually undergoes ample fragmentation rather than intact ejection (Fig. 1b). An analytic model for estimating ejection yields developed by Sigmund for atomic systems predicts that the ejection yield should be proportional to the reciprocal of the binding energy [27].

This model assumes that ejection is due to collisions from the bulk that knock off the species. For the two C_5H_9 films investigated here the ratio of the binding energies is 4.5 ($= 2.7/0.6$). The calculated

Table 1
Total atomic yield per incident Ar particle. The total number of trajectories in each case is 50. The yields are reported as integers so as to focus on trends and not specific values

	Angle of incidence	Pt	C	H	Ar
C ₅ H ₉ on ¹⁹⁵ Pt{111}	0°	1	10	23	1
	45°	1	13	31	1
C ₅ H ₉ on ¹⁹⁵ Pt{111} (0.60 eV)	0°	1	20	41	1
C ₅ H ₉ on ¹² C{111}	0°	–	0	2	0
	45°	–		5	16
C ₅ H ₁₁ on ¹² C{111}	0°	–	2	9	0
¹⁹⁵ Pt{111}	0°	2	–	–	1
¹² Pt{111}	0°	1	–	–	0
¹⁹⁵ C{111}	0°	–	1	–	1
¹² C{111}	0°	–	0	–	0

yield enhancement, however, is a factor of 9. This extra enhancement is due to this newly identified mechanism in which a laterally moving species can ‘pull off’ the weakly bound adsorbate molecule.

The ejection yields for the simulations that employ C{111} substrates are given in Table 1. Mass distributions comparable to those shown in Fig. 2 consist of a large H peak and an array of small C_xH_y peaks. The increase in yield at 45° incidence is due to fragmentation of the film, and not to the ejection of the parent species. The difference in the results from the C₅H₉ and C₅H₁₁ films arises because disruption of the diamond substrate allows the diradical C₅H₉ species to strengthen its interaction to the substrate during the course of the collision cascade, thus reducing the yield of desorbed species. The main result shown in Table 1 is that the ejection yield from the C substrate is much less than the yield from the Pt substrate.

The difference in yields observed from Pt (195 amu) and C (12 amu) matrices is due to the inability of diamond to redirect the momentum of the Ar (40 amu) beam in an upward direction. The C atoms are simply too light to turn around the momentum of the Ar atom. To test this idea we performed calculations for clean Pt{111} and C{111} where the mass in each case is artificially switched (i.e. ¹⁹⁵C and ¹²Pt) but the crystal structure and interaction potentials are left unaltered. As shown in Table 1 both crystal structures exhibit a large mass effect in the calculated

yield. The experimental observation that metals provide an excellent substrate for SIMS has been exploited for years as a cationization source although to our knowledge the possible benefit of the heavy metal mass has not been appreciated or systematically tested.

4. Summary

Molecular dynamics calculations have evolved to the point of being able to realistically model reactions among organic molecules on metal and carbon substrates due to keV particle bombardment. The concepts elucidated here provide suggestions for fine-tuning of the experimental design to maximize molecular ion yields. For example, experiments are already in progress to customize the binding agent substrate and analyte so as to enhance molecular ejection [28]. Equally exciting is the prospect of modeling [29] even more realistic molecular biological substrates such as peptides [2,30,31] and membrane analogs such as alkane thiols on metal surfaces [32–34]. In these cases there are chemistry driven fragmentation channels and reactions with metal cations which will also be important factors for determining the mass spectra.

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