

MOLECULAR DYNAMICS SIMULATIONS OF ORGANIC SIMS WITH CLUSTER PROJECTILES

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1. Introduction

Experiments have shown that cluster projectiles compared to atomic projectiles enhance the secondary ion emission of organic molecules [1-3]. For a homonuclear cluster, the yield is said to be nonlinearly enhanced when the yield with a cluster projectile containing n atoms is greater than the yield obtained from n trials with a monatomic projectile at the same velocity as the cluster [3]. Previous molecular dynamics simulations to model organic SIMS with atomic projectiles have shown that several parts of the molecule must be struck in order to initiate the concerted motion of the carbon atoms that lifts the intact molecule off the surface [4]. The recent development of many-body empirical potentials for metals and hydrocarbons provides the means for more realistic simulations of dynamics on systems containing metals and organic molecules [5]. Taking advantage of these potentials, we perform molecular dynamic simulations aimed at determining the fundamental mechanisms responsible for the enhancement in emission yield with cluster projectiles.

2. Method

Our model system, a biphenyl adsorbate on a Cu(001) surface, is chosen as a prototype of the experimental systems of interest. Cu atoms and randomly oriented Cu_n clusters with $n = 2$ to 4 and kinetic energies from 0.050 to 0.100 keV per atom are brought in at 45 degrees incidence. A potential developed with De Pisto's MD/MC-CEM approach is used for the Cu-Cu interactions [6], the Brenner many-body hydrocarbon potential is used for the C-H, C-C and H-H interactions [7] and Lennard-Jones Cu-C and Cu-H potentials are used to describe the copper-hydrocarbon interactions. A more complete description of the system is given elsewhere [8].

3. Results

a. Emission Yields

The secondary ion emission yield is calculated as the number of ejected biphenyl molecules out of a total of 150 trajectories. The results of the simulations indicate that cluster projectiles nonlinearly enhance the emission yield compared to

atomic projectiles. For Cu at 0.100 keV, 6 biphenyl molecules are ejected; for Cu₂ at 0.200 keV, 41; for Cu₃ at 0.300 keV, 57; and for Cu₄ at 0.400 keV, 72. The degree of nonlinear enhancement for each cluster can be quantified by the enhancement factor. Mathematically, the enhancement factor is defined as $Y_n(E)/nY_1(E/n)$ where $Y_n(E)$ is the yield for the homonuclear cluster at energy E and $Y_1(E/n)$ is the yield for the atomic projectiles at the same velocity. If the yield depends linearly on cluster size, then the yield with a Cu₂ cluster at twice the energy would simply be twice the yield with Cu at that energy and the enhancement factor would be one. At 0.100 keV per atom, the yield with Cu is 6 and the yield with the randomly oriented Cu₂ is 41. Therefore, the enhancement factor for Cu₂ compared to Cu is $41/(2 \times 6) = 3.4$. The yield with Cu₂ is 3.4 times more than would be expected with twice as many Cu atoms at the same velocity. The Cu₃ and Cu₄ clusters also show a comparable nonlinear enhancement in yield compared to Cu.

b. Mechanisms for Ejection

The simulations have been used to determine the atomistic mechanisms responsible for the ejection of intact organic molecules, and, therefore, help us understand the reasons for the nonlinear dependence on cluster size. The central issue is that several parts of the molecule must be struck so that the carbon atoms move in a concerted motion to lift the entire molecule off of the surface. How is this accomplished? One copper substrate atom may collide with different parts of the biphenyl molecule; however, usually two different copper substrate atoms are necessary. This is more easily achieved when there are two adjacent collision cascades which can collaborate to gently lift the intact molecule off of the surface.

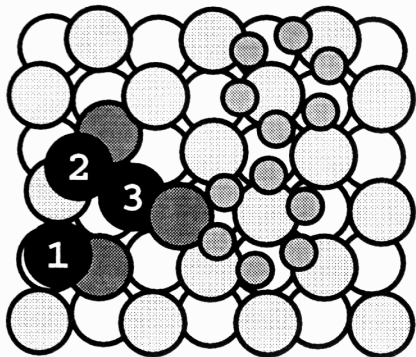
A polyatomic projectile initially impacts more than one copper substrate atom, and therefore, has a greater probability of initiating two or more adjacent collision cascades. Those cascades that would be ineffective with a single atom projectile can collaborate to eject the molecule off of the surface. By working together, the atoms in the projectile nonlinearly enhance the emission yield.

Figure 1 is a schematic diagram that shows one such example of the collaborative mechanism with a Cu₃ projectile at an incidence energy of 0.100 keV per atom. The trajectories of the atoms involved in collisions are superimposed on top of the initial positions of the non-colliding atoms in the surface. Atoms that are a part of the collision sequences that lead to ejection of the biphenyl are shaded grey, while the cluster atoms are in black. For a clearer illustration, only the region around the biphenyl molecule and only the carbon atoms of the biphenyl molecule are included.

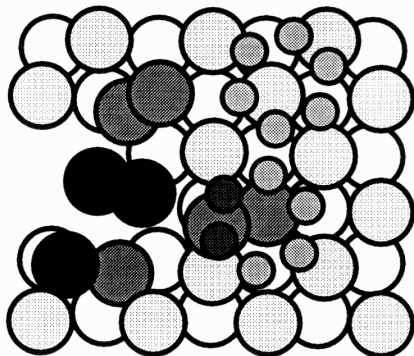
In this example, each of the cluster atoms initiates a collision sequence, which we will refer to as sequence one, sequence two and sequence three. However, only two of the sequences are directly involved in ejecting the molecule from the surface. At 61 femtoseconds, Figure 1a shows that the cluster has collided with the surface and cluster atom one has initiated sequence one, cluster atom two has initiated sequence two and cluster atom three has initiated sequence three. Only 8 femtoseconds later, in Figure 1b, sequences two and three are apparent and sequence three has led to collisions with two carbon atoms in the biphenyl ring. Figure 1c, at 98 femtoseconds, shows the system from a side view in order to illustrate how the copper substrate atoms lift the biphenyl molecule off of the surface. At that point in time, sequence two has reached the other ring of the biphenyl molecule, and therefore, both rings are lifted simultaneously. At 161 femtoseconds in Figure 1d, sequence one has also reached the molecule, but it has little effect because the molecule has already moved off of the surface.

Figure 1: A schematic diagram to illustrate the collaborative mechanism with the Cu_3 projectile at an incident energy of 0.100 keV per atom.

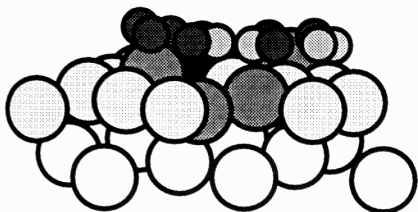
a) 61 fs



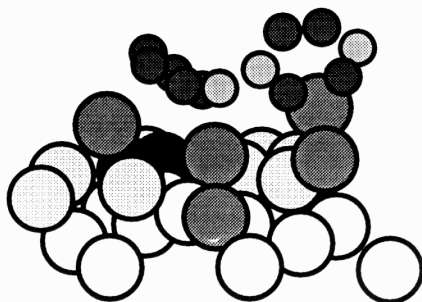
b) 70 fs



c) 98 fs



d) 161 fs



4. Summary

Molecular dynamics simulations of organics SIMS have shown that cluster projectiles produce a nonlinear enhancement in secondary emission yield. The enhancement can be explained in terms of the fundamental mechanism leading to the ejection of intact molecules from the surface. Carbon atoms in more than one part of the molecule must be hit in order to initiate the concerted motion of the entire molecule as it lifts off of the surface. With a polyatomic projectile, there is a higher probability of producing two adjacent collision cascades that can hit different carbon atoms in the molecule and collaborate to eject the molecule from the surface.

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References

- [1] H. Anderson, in *Fundamental Processes in Sputtering of Atoms and Molecules*; P. Sigmund, ed.; The Royal Danish Academy of Sciences and Letters: Copenhagen, 1993; pp.127-153 and references therein.
- [2] A.D. Appelhans and J.E. Delmore, *Anal. Chem.* *61* (1989) 1087; G.S. Groenewold, J.E. Delmore, J. E. Olson, A.D. Appelhans, J.C. Ingram and D.A. Dahl, *Int. J. Mass. Spectrom. Ion Proc.*, in press.
- [3] M.G. Blain, S. Della-Negra, H. Joret, Y. LeBeyec, E.A. Schweikert, *Phys. Rev. Lett.*, *63* (1989) 1625; E.A. Schweikert, M.G. Blain, M.A. Park and E.F. Da Silveria, *Nucl. Instr. and Meth.*, *B50* (1990) 307; M. Benguerba, A. Brunelle, S. Della-Negra, J. Depauw, H. Joret, Y. LeBeyec, M.G. Blain, E.A. Schweikert, G. Ben Assayag, P. Sudraud, *Nucl. Instr. and Meth.*, *B62* (1991)
- [4] B.J. Garrison, *J. Am. Chem. Soc.*, *102* (1980) 6553; B.J. Garrison, *J. Am. Chem. Soc.*, *104* (1982) 6211; B.J. Garrison, *Int. J. Mass. Spectrom.*, *53* (1983) 243.
- [5] R.S. Taylor and B.J. Garrison, *Langmuir*, *11* (1995) 1229; R.S. Taylor and B.J. Garrison, *Int. J. Mass. Spectrom.*, *143* (1995) 225; K.S.S. Liu, J.C. Vickerman and B.J. Garrison, *Radiation Effects and Defects in Solids*, in press.
- [6] M.S. Stave, D.E. Sanders, T.J. Raeker and A.E. DePristo, *J. Chem. Phys.* *93* (1990), 4413; T.J. Raeker and A.E. DePristo, *Int. Rev. Phys. Chem.*, *10* (1991) 1; C.L. Kelchner, D.M. Halstead, L.S. Perkins, N.M. Wallace and A.E. DePristo, *Surf. Sci.*, *310* (1994) 425.
- [7] D.W. Brenner, *Phys. Rev. B*, *42* (1990), 9458; D.W. Brenner, J.A. Harrison, C.T. White and R.J. Colton, *Thin Solid Films*, *206* (1991) 220.
- [8] R. Žarić, B. Pearson, K.D. Krantzman and B.J. Garrison, to appear in the Polyatomic Ion-Surface Interactions Special Issue of *Int. J. Mass. Spectrom. Ion Proc.*