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Reaction Dynamics Following keV Cluster Bombardment

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The nature of the regions that are favorable for chemical reactions has been investigated for a pure amorphous water ice substrate following energetic bombardment by C_{60} and Au_3 cluster projectiles using molecular dynamics (MD) simulations. The simulations show that both projectiles, especially C_{60} , produce regions where a plethora of reactions occur at elevated densities indicating that multiple atoms or molecules are involved simultaneously in the reactions initiated by cluster bombardment. The total number of reacted water molecules is significantly less than the total sputtering yield, which confirms that both cluster projectiles are useful for molecular depth profiling experiments.

1. Introduction

The use of cluster beams has reinvigorated the experimental approach of secondary ion mass spectrometry (SIMS) of molecular solids.^{1–5} The cluster beams eject more material per incident ion than atomic particles. In addition, there appears to be less chemical damage left in the sample, thus presenting the possibility of performing molecular depth profiling experiments.^{6–9} Concomitant with the increased experimental interest in cluster bombardment has been a bevy of computer simulations aimed at understanding crater formation,^{10–14} ejection mechanisms,^{15–18} ejection yields,^{11,12,19–23} substrate mixing,^{19,20,22,24,25} and projectile energy deposition.^{13,23,26–29} The majority of these computational studies have been aimed at elucidating the physical processes that occur for atomic solids.

The exciting applications in cluster SIMS, however, revolve around molecular substrates that can undergo chemical transformations due to the bombardment events. There have been only a small number of simulations of cluster bombardment on molecular solids. The studies by Krantzman et al.³⁰ and Smiley et al.³¹ confined their simulations to cluster beams with less than 500 eV because it was not computationally tractable to use sufficiently large samples to contain all the motion associated with cluster beams of several kiloelectron volts. In the case of C_{60} bombardment of benzene, the energy of 500 eV is insufficient to dissociate the C_{60} molecule,³¹ and thus the motion cannot be extrapolated to higher incident energies. An estimate of damage was made for simulations of fullerene bombardment of a coarse-grained model of benzene.³² In this case it was found that the ratio of ejected intact yield to the number of damaged molecules was about 5 ± 1 , a value in reasonable agreement with experimental data.⁸ No detailed analysis of the reaction events due to cluster bombardment was made, however.

The challenge of modeling cluster bombardment to extract chemical effects with computer simulations such as molecular dynamics (MD) is daunting, as one needs an interaction potential that realistically models the chemistry and can be evaluated in a reasonable time. One potential that incorporates realistic ground state chemistry for hydrocarbon species is the AIREBO potential³³ that is based on the Brenner REBO potential.³⁴ The

largest C_{60} cluster bombardment simulation to date using this potential was limited to only 500 eV bombardment because of sample size constraints and still took 6 months to calculate.³¹ Even though the REBO/AIREBO potential may include reasonable ground state chemistry, no excited states are included in the description.

The objective of the simulations presented here is to elucidate the nature of the reaction environment for C_{60} and Au_3 cluster bombardment of molecular solids. The system of interest is water ice as MD calculations of the sputtering process for C_{60} and Au_3 bombardment have been previously performed for a system in which the molecules are rigid.^{26,35–37} The previous calculations show that the majority of the energy of the beam is deposited within a fraction of a ps and in a volume that is ~ 2.5 nm wide on the surface. Computationally then, we can focus our studies on the initial stages of the event using shorter time scale simulations and a smaller system size than used previously in which a full trajectory at 5 keV bombardment took several months of CPU time.

As previously discussed, the motion of the projectiles into the substrate is quite different.³⁵ The Au atoms, since they are much more massive than the water molecules, traverse a near straight line trajectory into the solid, coming to rest at about 10 nm for 5 keV bombardment. The C atoms in the C_{60} cluster have less energy per particle than the Au atoms in Au_3 , and they have nearly the same mass as the water molecules; thus, all the C atoms lose most of their energy and stop within 4–5 nm of the surface. The spatial distribution of the energy loss is quite different, and so there is the possibility for differences in the nature of the reaction environments.

There is no known potential for any molecular system that fully describes all the possible chemistry for ground and excited-state reactions. We thus chose a potential that has a high activation for dissociation in order to test the upper energetic limits of types of reactions that are possible. This potential has previously been used to describe for collision induced dissociation of water molecules into ions.³⁸ The high activation energy of 17.2 eV for this process acts as an indicator for the wide range of reactions and electronic events that are energetically accessible during the cluster bombardment process. It is within these limitations that we use this dissociation potential as a guide

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for defining the differences in reaction events in energetic C_{60} and Au_3 bombardment of a molecular solid.

2. Computational Details

MD simulations were performed to model the reaction dynamics of pure amorphous water ice following C_{60} and Au_3 bombardment. As mentioned above a potential originally designed for modeling the dissociation of water into ions was used for the water–water interactions.³⁸ The remainder of the interaction potentials are the same as in the previous simulations of C_{60} and Au_3 bombardment of rigid water.^{26,35,37} The interactions between the projectile atoms and the substrate atoms were described using Molière potentials. The Au–Au interactions were described using potential energies and forces from the embedded atom method (EAM) potential,³⁹ and the C–C interactions were described using the REBO potential of Brenner designed for hydrocarbons.^{34,40}

A 15 nm × 15 nm × 15 nm sample containing 298 545 atoms (99 515 water molecules) was equilibrated to ~200 K, and rigid and stochastic layers were employed along the bottom and sides of the substrate in order to prevent the reflection of pressure waves during the collision cascade.⁴¹ Trajectories using projectile kinetic energies of 2.5, 5, 10, and 15 keV were performed for both C_{60} and Au_3 . Each projectile was aimed normal to the surface, and each simulation was run for 3 ps with the exception of 15 keV C_{60} bombardment which was extended to 5.7 ps. The time scale of these simulations will be discussed later in the Results and Discussion section. Briefly, we have determined that 3 ps is sufficient for our analysis which focuses strictly on the reaction dynamics of pure amorphous water ice. There are other areas of interest following energetic particle bombardment such as emission yields, ejection mechanisms, and projectile energy deposition, which may require a larger time scale, but these topics have been addressed previously for simulations similar to those discussed here.^{26,35–37,42,43} Therefore, we will not reiterate those studies.

3. Results and Discussion

The dissociation of an OH bond is chosen to be the indicator that a reaction has occurred. A conservative definition has been applied, namely that the OH separation distance must be at least 2.29 Å, where the value in intact water is 0.96 Å. According to the model, dissociation is complete when the separation distance is greater than 2.46 Å; thus, there must be almost complete dissociation for a bond to be considered broken in our analysis. The total number of OH bond cleavages is shown in Figure 1 for the simulations for 15 keV bombardment. The largest rate of increase of broken bonds occurs at ~100 fs, and then the rate of increase of the number of bond cleavages diminishes above about 500 fs; thus, both cluster beams create the majority of the broken bonds at the initial stages after impact.

An overview of the trajectories illustrating the fragmented molecules is given in Figure 2 for a time of 0.5 ps, a value chosen from Figure 1 as when the majority of reaction events have occurred. The gray dots represent intact water molecules in a 2 nm slice of the sample through the center of the substrate below the projectile impact. The colored spheres represent all the ions that have formed, regardless of whether they are in the 2 nm slice or not. The fragmented species are placed graphically at their original position in the sample. The positions where the reaction events occur follow the motion of the respective projectiles.³⁵ For Au_3 bombardment, as the kinetic energy of the cluster increases, the penetration depth of the Au atoms increases. The fragmented molecules occur along the motion

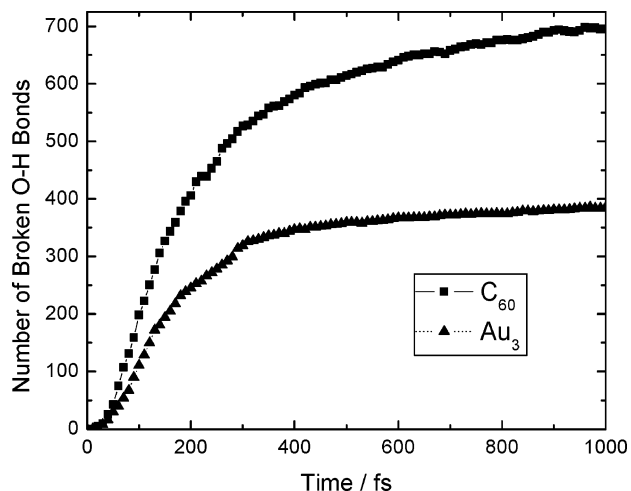


Figure 1. The number of broken O–H bonds as a function of time for 15 keV C_{60} and Au_3 bombardment of pure amorphous water ice.

of the Au particles. There are many occurrences of individual dissociated molecules although there are some regions in which several nearby molecules have fragmented. The Au_3 bombardment shows a near linear increase in the number of broken O–H bonds observed as a function of the incident projectile kinetic energy as seen in Figure 3. In contrast to the Au atom motion, the C atoms from the fullerene cluster stop within 4–5 nm of the surface. Thus, the reaction events are confined to a very dense region near the point of impact as shown in Figure 2. The number of broken O–H bonds exhibits a nonlinear increase as a function of increasing projectile energy (Figure 3), indicating that there is cooperation among the motions of the C atoms in terms of influencing the reaction probability. The nature of the reaction environment for C_{60} bombardment, especially at the higher incident energies, warrants a closer examination.

Snapshots of the positions of the atoms in a 2 nm slice of the sample at the time when the reaction rate is greatest for 15 keV bombardment are given in Figure 4. The particles shown as fragmented are only those that dissociated during the 10 fs interval centered about 95 fs and only those within the 2 nm slice. The C_{60} projectile has moved through ~3 nm of material creating a crater. The molecules initially in the volume where the crater has formed have been compressed into the bottom and sides of the crater forming a dense region. It is within this dense region that multiple and adjacent molecules are reacting. In contrast, for Au_3 bombardment the crater that eventually forms^{26,35} is not yet apparent. The reaction events are more isolated although there are a few regions where multiple reactions have occurred. In order to assess the completeness of reactions for C_{60} bombardment at 15 keV, we estimate the center of origin of dissociated molecules to be about 2.4 nm deep. The fraction of molecules that reacted was determined as a function of distance from this point and is shown in Figure 5. For molecules that were originally in the center of this region, virtually all of them reacted. Moreover, the reactions are confined to a region with a radius of approximately 1.5 nm.

The reaction region needs to be put in perspective with respect to the total volume of material that ejects. In addition, an assessment is featured of how much larger the reaction volume might be if reactions with lower activation energies are included. In a previous study, we have used the mesoscale energy deposition footprint (MEDF) model and short-time MD simulations to analyze the region where the energy is deposited in the sample and the volume of ejection.^{26,37} For 15 keV C_{60}

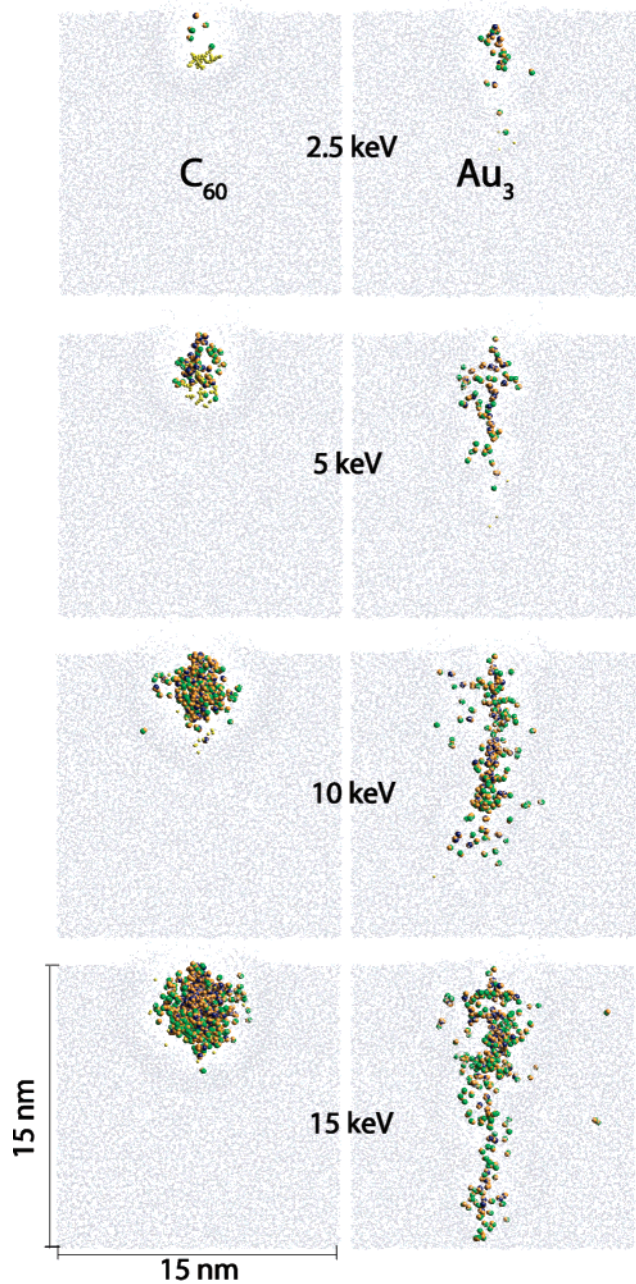


Figure 2. Time snapshots of 2.5, 5, 10, and 15 keV C_{60} and Au_3 bombardment of pure amorphous water ice. Gray and yellow spheres represent intact water molecules and projectile atoms, respectively, within a 2 nm slice through the center of the substrate at 0.5 ps. Orange, green, and blue spheres represent the fragment species placed back in their initial positions and overlaid on the substrate at 0.5 ps.

bombardment on a sample of water ice using a potential that considers the water molecule to be rigid, we predict that 90% of the energy of the incident particle is deposited in a cylindrical region of radius 2.5 nm and that the ejected material comes from a conical volume with a base radius of 6.2 nm and a depth of 2.5 nm as shown in Figure 6. The predicted volume of ejected material, as illustrated by the red region, is approximately 100 nm^3 and contains 2790 molecules. The number of reacted molecules is 175, which is only 6% of the total volume. If we assume that lower activation energy reactions can occur in the entire energized track, represented by the blue region, then 36% of the ejected molecules would be reacted. Thus, there still remains a considerable number of molecules that can eject intact. A similar analysis for Au_3 bombardment at 15 keV is also shown

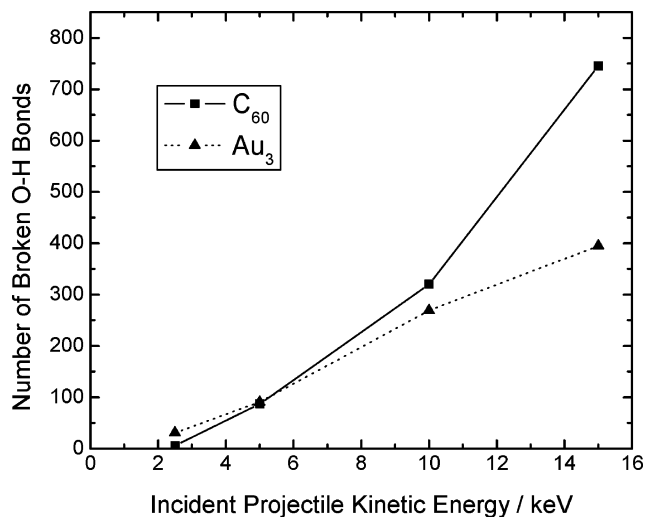


Figure 3. The number of broken O–H bonds as a function of incident projectile kinetic energy for both C_{60} and Au_3 bombardment of pure amorphous water ice.

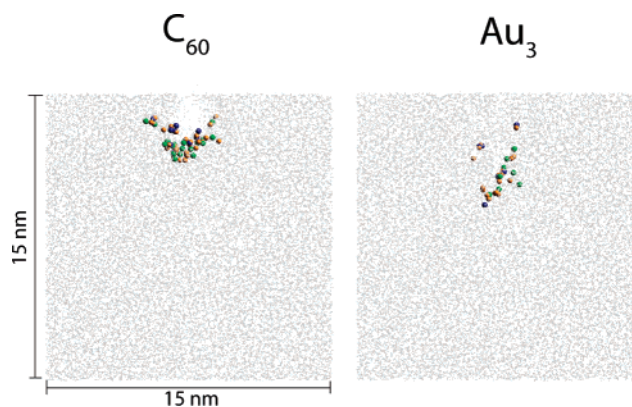


Figure 4. Time snapshots showing species that have dissociated only in a 10 fs interval centered about 95 fs. The color scheme is the same as shown in Figure 2, although the projectile atoms are now gray dots, and only material within a 2 nm slice through the center of the substrate is shown.

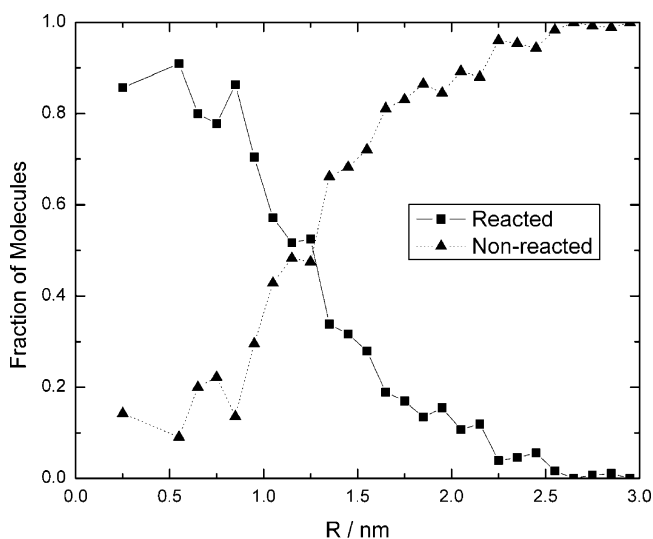


Figure 5. The fraction of reacted vs nonreacted molecules as a function of distance from the center of mass of the reaction zone for 15 keV C_{60} bombardment.

in Figure 6. In this case, the volume of the ejection cone is approximately 28 nm^3 containing 811 molecules and has approximately the same width as the energized region. Only

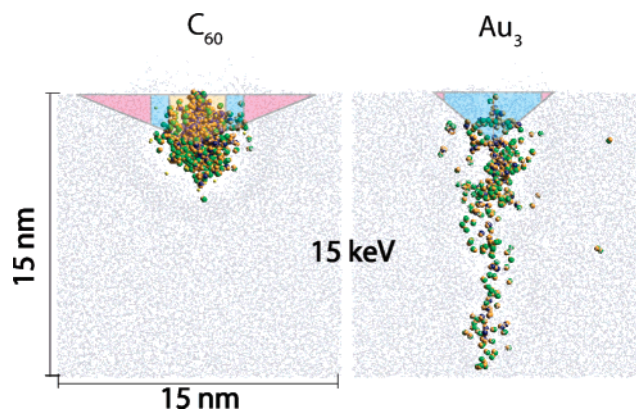


Figure 6. Snapshots of the reaction zones created by 15 keV C_{60} and Au_3 at 0.5 ps. The red triangle outlines the conical ejection region as identified by the MEDF model and implicitly includes the blue and yellow regions. The blue region represents the energized track created by projectile bombardment, and the yellow region is indicative of the reaction region created.

50 molecules out of the 811 are reacted. If and one assumes the reactions are allowed to extend to the edges of the energized (blue) region, most of the ejected material could possibly react. These calculations demonstrate clearly how the damaged fraction of the ejected material can be less than the total ejection yield.

The magnitude of damage, i.e., altered species, left in the solid is important when considering SIMS molecular depth profiling experiments.⁸ From Figure 6, for C_{60} bombardment, most of the reaction products are right at the bottom of the predicted ejection cone and could easily eject if they have high volatility. For Au_3 bombardment there is considerable damage deep in the sample. Experimentally, it is observed that both C_{60}^+ and Au_3^+ bombardment can depth profile through organic solids, and the signal of the molecular species can reach a steady-state value.^{8,44,45} Our calculations indicate that the damage due to Au_3 bombardment should be deeper in the sample than for C_{60} bombardment.

The kinetics of complex reactions is commonly understood and analyzed as a series of simple, elementary reactions.⁴⁶ This approach has been used successfully to describe, for example, chain reactions, explosions, polymerization, and catalysis.⁴⁶ Even the conventional language of electronic effects in sputtering tries to simplify the processes into concepts such as the electron-tunneling model in which 1d drawings are used for illustration⁴⁷ or the bond-breaking model for a single bond.⁴⁸ Ideally, it would be convenient to be able to describe the reactions in cluster bombardment of molecular solids in terms of simple, elementary reactions that we know from gas or liquid-phase chemistry. The simulations presented here strongly suggest, however, that multiple atoms/molecules are simultaneously involved in the reactions initiated by cluster bombardment, especially for C_{60} projectiles. In addition to the compressed geometrical region, the events are occurring in a very short time frame; thus, many non-adiabatic and excited-state reactions are energetically possible. This cauldron of motion could spawn any number of complex reaction events; thus, the concept of discussing the reaction dynamics as a series of possible simple reaction events is not possible. It is problematic to even think about designing an appropriate electronic structure calculation. A new paradigm for conceptualizing and describing this environment therefore needs to be developed. Although Au_3 does not create as large a concentration of reaction events, there are obviously some configurations as shown in Figure 2 where many molecules may simultaneously participate in reactions.

4. Conclusions

MD simulations of C_{60} and Au_3 bombardment of pure amorphous water ice using an interaction potential that incorporates chemical reactions have been performed. The simulations clearly show that a new reaction paradigm exists in which multiple adjacent molecules simultaneously react. In addition, the geometries of the molecules can be compressed, especially for C_{60} bombardment, from that of a normal liquid. Any experiment, theory or simulations aimed at understanding reactions including ionization processes must consider this new reaction paradigm. The total number of reacted molecules is significantly less than the total sputtering yield, indicating less damage to the substrate, and thus confirming the experimental observations that molecular depth profiling is possible with both types of cluster beams.

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