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Molecular dynamics simulations to explore the effect of projectile size on the ejection of organic targets from metal surfaces

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Abstract

Experiments have shown that cluster projectiles as compared to atomic projectiles enhance the secondary ion emission of organic molecules. The yield depends nonlinearly on the number of constituent atoms in the primary ion cluster. In this paper, we describe molecular dynamic simulations aimed at determining the fundamental mechanisms responsible for the enhancement in emission yield. 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 Cu_n clusters with $n = 2-4$ and kinetic energies from 0.050 to 0.100 keV per atom are brought in at 45° incidence. The emission yield of the biphenyl molecule increases nonlinearly with the number of atoms in the cluster. Several parts of the biphenyl molecule must be hit in order for it to be ejected intact. A monatomic projectile initially strikes one atom in the top surface layer, while a polyatomic projectile initially strikes two or more atoms. Therefore, with the cluster projectile, there will be a greater probability of two or more collision cascades that are adjacent in time and space and can collaborate to eject the molecule from the surface. © 1998 Elsevier Science B.V.

Keywords: Molecular dynamics simulations; Cluster projectiles; Atomic projectiles; Emission yield

1. Introduction

Secondary ion mass spectrometry (SIMS) can be used to identify nonvolatile high molecular weight organic compounds that cannot be analyzed by other means [1–5]. The sensitivity of this technique can be improved by increasing the secondary ion emission yield of molecules. Therefore, there has been considerable interest in the use of cluster projectiles, which have been shown to produce an enhanced yield compared to single atom projectiles [6–14]. Experimentally, the emission yield increases nonlinearly with the number of atoms in the

cluster. For a homonuclear cluster, the yield is said to be nonlinear 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. For example, the emission yield with a dimer would be more than two times greater than the yield with a single atom projectile at the same velocity. The primary aim of this paper is to understand the reasons for the nonlinear dependence on cluster size in terms of the atomistic mechanisms leading to ejection of molecules from the surface.

Appelhaus and Delmore developed the use of polyatomic ion beams in static SIMS for the analysis of molecular samples [6–8]. They developed a SF₆⁻ ion beam and determined that the

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secondary ion sputtering efficiency is greater with the polyatomic ion beam than with a Cs^+ atomic ion beam [6]. More recently, Applehans and co-workers have performed experiments with a ReO_4^- primary ion beam, which is especially useful for the analysis of environmental samples [7,8].

Other experimental work has been done to study systematically the effect of cluster size on the secondary ion emission yield with a variety of different targets and projectiles [9–14]. The largest nonlinearities are found with heavier atom projectiles on organic molecular solids. For example, in one set of experiments most relevant to our current simulations, an organic layer of phenylalanine was bombarded with Au^+ and Au_n^{p+} clusters [9–12]. Clusters ranging in size from $n = 2$ to 5 and a charge, p , of $+1$ and $+2$ were used with energies of 10–40 keV per Au atom. The yield depends nonlinearly on the number of atoms in the cluster, and the nonlinear enhancement increases with cluster size. The largest jump in enhancement for a single atom increase, i.e. M_n^{p+} to M_{n+1}^{p+} , is between atomic and diatomic projectiles.

Previous theoretical molecular dynamics simulations have been performed to study the bombardment of metal atom targets with metal atoms and metal atom clusters [15–21]. A goal of these studies has been to examine the breakdown of Sigmund's linear cascade theory [21], which occurs when moving atoms collide with moving atoms. Features unique to cluster projectiles are compression of the cluster atoms upon impact, collisions between atoms in the cluster, and target atoms hit by more than one projectile atom. In addition, a clearing-the-way mechanism is important with very large clusters in which the earlier impacting cluster atoms clear the target atoms out of the path of the cluster projectile atoms that follow [14,17]. The common nomenclature is that enhanced yields are caused by regions of high collision density called spikes.

Garrison and collaborators have used molecular dynamics simulations to study Ar bombardment of organic films on metal substrates

[22–31]. Their simulations with single atom projectiles suggest that mechanisms leading to the ejection of intact organic molecules and molecular fragments from organic films are different than with metal atom targets. The earlier simulations used simple pairwise potentials and showed that it is possible to eject a molecule intact from the surface even though the kinetic energy of the bombarding particles is greater than the bond energies within the molecule [22–25]. The first simulations studied the bombardment of a $c(4 \times 4)$ overlayer of benzene on a Ni(001) substrate with 600 eV Ar particles [22–24]. Simulations with other molecular overlayers were also performed [25]. Three factors are identified as important to the ejection of intact organic molecules rather than fragments. First, most of the energy of the incident particle is dissipated into the solid so that the organic molecule is hit with much less energy than that of the incident Ar particle. Secondly, a large molecule has many internal degrees of freedom and, therefore, absorbs excess energy without fragmenting. Thirdly, several parts of the molecule are struck by the substrate atom (or atoms), which leads to a concerted motion of the molecule as it desorbs from the surface. Nickel is larger than carbon and, therefore, one Ni substrate atom may strike several parts of the molecule. Additionally, two Ni atoms may collide with different parts of the benzene molecule. With larger organic molecules, two or three Ni substrate atoms collide with different parts of the molecule to initiate the concerted motion lifting the adsorbate off of the surface.

Since the earlier simulations, the development of many-body potentials, such as those for metals based on the embedded atom method [32] and corrective effective medium theory [33–35] and the Brenner empirical potential for hydrocarbons [36,37] has made it possible to perform more realistic simulations of the high energy bombardment of organic films. Recently, Taylor and Garrison have blended the empirical many-body Brenner and EAM potentials with Lennard–Jones [38] and Molière potentials [39] to model the

high-energy bombardment of hydrocarbon films with Ar ions [26–30]. By using a many-body potential for the hydrocarbons, reactions between the adsorbate molecules can be simulated. In addition, Liu, Vickerman and Garrison have used a blend of many-body and pairwise potentials to model the bombardment of deuterated alkanethiol chains on a gold surface by high-energy Ar particles [31].

In this work, we describe simulations to study the nonlinear effect of cluster size on the secondary emission yield of organic molecules. We focus here on the fundamental atomistic mechanisms that lead to a nonlinearly enhanced yield with cluster projectiles. Our model, a biphenyl molecule adsorbed on a Cu(001) surface, is chosen as a prototype of the experimental systems of interest. Cu atoms and Cu_n clusters with $n = 2\text{--}4$ and kinetic energies from 0.050 to 0.100 keV per atom are brought in at 45° incidence. In this preliminary study, our model system of a small crystal with one adsorbate molecule is used in order to better focus on the atomistic mechanisms leading to the ejection of a molecule. In the near-threshold energy region, where yields are very small with Cu projectiles, the simulations will be most sensitive to the size of the clusters. Therefore, at lower energies, we are able to obtain the most insight into the fundamental mechanisms responsible for the observed nonlinearity.

Our calculated emission yield of the biphenyl molecule increases nonlinearly with the number of atoms in the cluster. In agreement with previous molecular dynamics simulations, the simulations show that several parts of the biphenyl molecule must be hit in order to be ejected intact. A monatomic projectile initially strikes one atom in the top surface layer, while a polyatomic projectile initially strikes two or more atoms. Therefore, with the polyatomic projectile, there is a higher probability of two or more adjacent collision cascades in the surface region, which can each lead to collisions with carbon atoms in different regions of the biphenyl molecule. Those

cascades that would be ineffective alone can work together to eject the molecule off the surface.

In this paper, we first discuss the methodology used in the simulations including a description of the model system and the interaction potentials used. Next, we discuss the quantitative results of the simulations that demonstrate how the yield depends on the kinetic energy and size of the cluster. Additionally, different orientations of the dimer are used in the simulations to determine the effect of dimer orientation on the emission yield. The atomic mechanisms leading to ejection of an intact biphenyl molecule are described and used to explain the observed enhancement in emission yield and the dependence of yield on the orientation of the dimer.

2. Description of the calculations

The classical method of molecular dynamics simulations is used to study the system of interest and the details of this method are described extensively elsewhere [40–42]. Once the initial conditions of the system and the potential energy function to describe the interactions between the atoms are specified, Hamilton's equations of motion are integrated to determine the position and velocity of each atom as a function of time. From the final positions and velocities of the atoms, the identity and kinetic energy of all ejected species can be calculated. Additionally, the atomic motions leading to the ejection of the molecule may be analyzed.

The model system is a single biphenyl molecule adsorbed on a copper substrate, which is represented by a Cu(001) microcrystallite of 1260 atoms arranged in nine layers of 140 atoms. The position of the biphenyl adsorbate is determined by allowing the adsorbate to equilibrate at 0 K on the Cu(001) surface using an algorithm based on the generalized Langevin equation (GLE). Fig. 1(a) and (b) illustrate side and top views of the model system. Cu and Cu_n

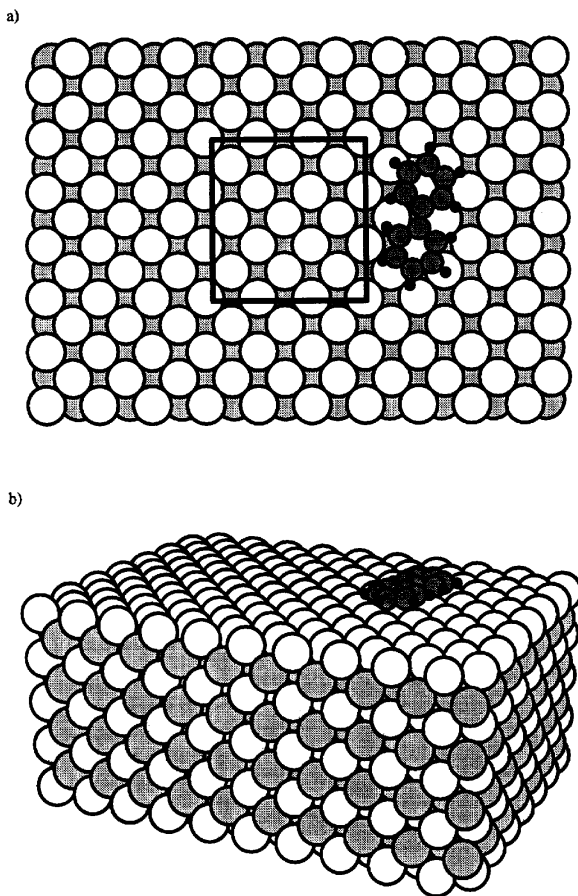


Fig. 1. Model system used in the simulations. The Cu(001) microcrystallite is composed of 1260 atoms arranged in nine layers of 140 atoms. A biphenyl molecule is adsorbed on the surface. (a) Top view. The impact zone for the incoming projectiles is outlined. The second layer of copper atoms is shaded a darker gray. (b) Side view.

($n = 2-4$) clusters are brought in at 45° incidence at kinetic energies ranging from 0.01 to 0.100 keV per atom. The positions of the Cu atoms within the cluster are determined by quenching to 0 K [43]. In order to simulate experimental conditions, the results must be averaged over a set of trajectories that sample a region of the surface. A set of 150 aiming points are evenly distributed over the impact zone outlined in Fig. 1(a) and the results with each cluster at each incident kinetic energy are averaged over the set of 150 trajectories, each with a different

aiming point. The impact zone is chosen so that all of the aiming points leading to the ejection of the molecule are included for the Cu and Cu₂ clusters. At higher kinetic energies with the Cu₃ and Cu₄ clusters, the impact zone does not include all of the trajectories which eject the molecule. The model system, however, is too small for a larger impact zone. Therefore, the results of these simulations for $n > 2$ are considered to be preliminary and will provide the groundwork for future studies with a full monolayer adsorbate overlayer.

The forces among the atoms are calculated using a potential energy function, which is a combination of potentials to describe the various interactions in the system. A potential developed with DePristo's MD/MC-CEM approach is used for the Cu–Cu interactions [33–35] and the Brenner many-body hydrocarbon potential is used for the C–H, C–C and H–H interactions [36,37]. The Brenner potential was not developed to describe the repulsive forces between atoms when hard collisions occur. Therefore, a Molière pairwise potential [39] is used in the repulsive region. A linear interpolation scheme used by Taylor and Garrison connects the repulsive and many-body attractive potentials and is described in detail elsewhere [27]. Lennard–Jones Cu–C and Cu–H potentials [38] are used to describe the copperhydrocarbon interactions. This potential is written as $V(r) = \epsilon[(\sigma/r)^{12} - 2(\sigma/r)^6]$. The parameters for the interactions are as follows: for Cu–H, $\epsilon = 0.01$ eV and $\sigma = 2.3$ Å; for Cu–C, $\epsilon = 0.05$ eV and $\sigma = 2.3$ Å. With these parameters, the biphenyl adsorbate is bound to the surface with 1.7 eV of energy.

3. Results and discussion

In the following sections, we discuss the emission yield of ejected biphenyl molecules and the atomic mechanisms for ejection. The emission yield of the biphenyl molecule is determined as a function of the number of atoms and the

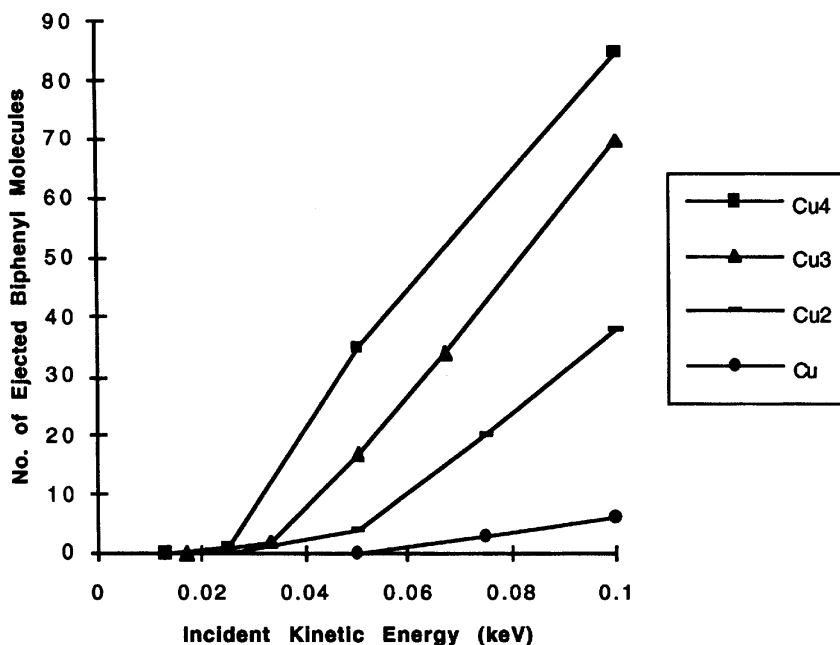


Fig. 2. Emission yield as a function of kinetic energy per atom for Cu and Cu_n ($n=2-4$) projectiles. The emission yield is the number of ejected molecules out of 150 trajectories.

incident kinetic energy of the cluster. In addition, we discuss the effect of the orientation of the dimer on the emission yield. The enhancement factors are calculated at 0.100 keV per atom and show that the yield depends nonlinearly on the number of atoms in the cluster. This nonlinear dependence can be explained in terms of the atomic mechanisms for ejection. We show schematic diagrams to illustrate the collision cascades leading to the ejection of the molecule with the atomic and diatomic projectiles.

3.1. Molecular emission yield

The emission yield is calculated as the number of biphenyl molecules ejected out of the 150 trajectories sampled over the impact zone. The simulations use a fixed orientation of each cluster and are calculated for a range of incident kinetic energies. In order to visualize the dependence on the kinetic energy per atom, Fig. 2 shows a plot of the emission yield (number of ejected biphenyls in 150 trajectories) as a function of kinetic energy

per atom for Cu and Cu_n ($n=2-4$) projectiles. As the number of constituent atoms in the projectile increases, the threshold energy per atom needed to eject the molecule decreases. For example, the threshold energy is ~ 0.075 keV per atom with the Cu projectile, whereas at a lower energy of 0.05 keV per atom, there are 35 biphenyl molecules ejected with the Cu_4 projectile.

The simulations are also performed with three orientations of the Cu_2 projectile, shown in Fig. 3, in order to determine how the emission yield depends on orientation. In orientation a, the dimer is in a plane parallel to the surface and is brought in with its internuclear axis oriented parallel with respect to the biphenyl molecule. In orientation b, the dimer is in a plane parallel to the surface and is brought in with its internuclear axis perpendicular to the biphenyl molecule. In orientation c, the dimer is brought in with its internuclear axis perpendicular to the plane of the surface. Table 1 lists the results of the simulations. The dimer with orientation b produces an emission yield that is lower than the other

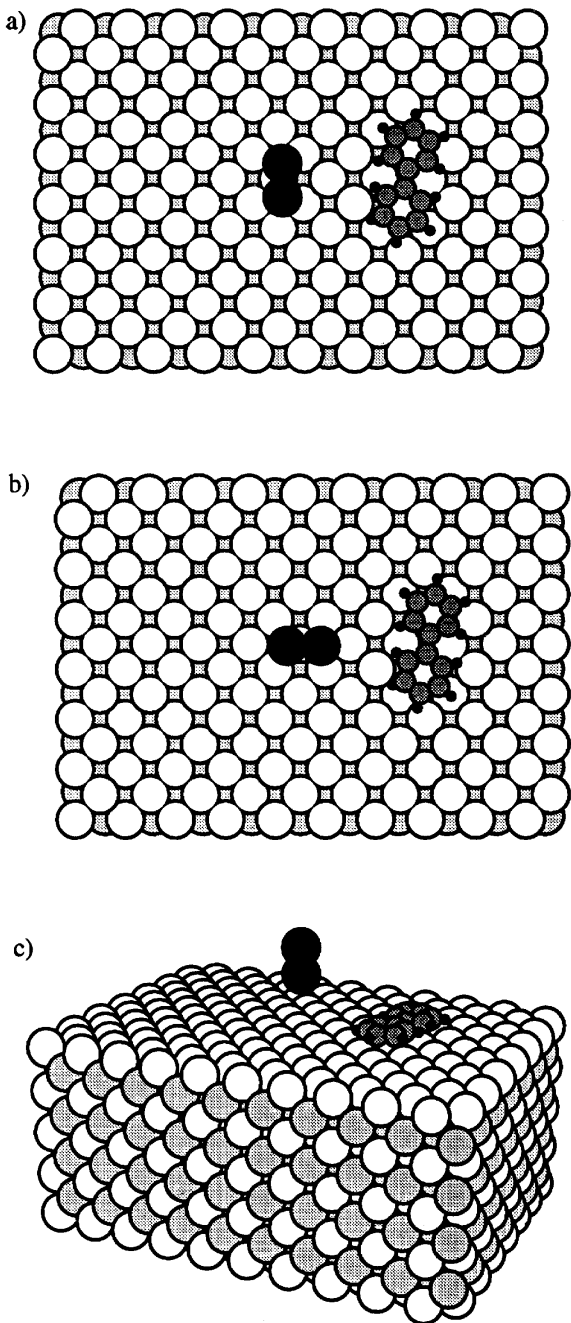


Fig. 3. Dimer projectile. (a) Orientation a, dimer is in a plane parallel to the surface and its internuclear axis is parallel to the biphenyl molecule, top view. (b) Orientation b, dimer is in a plane parallel to the surface and its internuclear axis is perpendicular to the biphenyl molecule, top view. (c) Orientation c, dimer's internuclear axis is perpendicular to the surface, side view.

Table 1

Emission yield with Cu_2 at 0.100 keV/atom as a function of dimer orientation

Orientation	No. of ejected biphenyl molecules out of 150 trajectories
Vertical	38
Horizontal	22
Perpendicular	40
Random	41

orientations. Can we obtain mechanistic insight into why this particular orientation produces a smaller yield of biphenyl molecules?

The degree of nonlinear enhancement for each cluster can be quantified by the enhancement factor. Mathematically, the enhancement factor is defined [9] 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 Cu_2 cluster at energy E would simply be twice the yield with Cu at $E/2$ and the enhancement factor would be 1. In order to calculate enhancement factors at 0.100 keV per atom that can be more realistically be compared with experiment, new simulations for each cluster are performed where the orientation of the cluster is selected randomly oriented for each trajectory. At 0.100 keV per atom, the yield with Cu is 6 and the yield with the randomly oriented Cu_2 is 41. Therefore, the enhancement factor for Cu_2 compared to Cu is $41/(2 \times 6) = 3.4$. The yield with Cu_2 is 3.4 times more than would be expected with twice as many Cu atoms at the same velocity. Table 2 shows the emission yields and enhancement factors for the randomly oriented Cu_2 , Cu_3 and Cu_4 projectiles at 0.100 keV per atom. In agreement with experiment, there is a significant nonlinear enhancement with each of the polyatomic clusters. The total emission yield does increase with cluster size. The magnitude of nonlinear enhancement, however, does not increase with the size of the cluster, which disagrees with experiment. This discrepancy is

Table 2

Emission yields and enhancement factors for randomly oriented Cu_n ($n = 2-4$) clusters at 0.100 keV per atom. See the text for a detailed description of the enhancement factor

Projectiles	No. of ejected biphenyl molecules	Cluster ratio	Enhancement factor
Cu	6		
Cu ₂	41	Cu ₂ /Cu	3.4
Cu ₃	57	Cu ₃ /Cu	3.2
		Cu ₃ /Cu ₂	0.9
Cu ₄	72	Cu ₄ /Cu	3.0
		Cu ₄ /Cu ₂	0.9
		Cu ₄ /Cu ₃	0.9

most likely due to the limitations of the size of the model system; and, therefore, the yields and enhancement factors for Cu₃ and Cu₄ should be considered estimates of the true values.

Enhancement factors between different clusters may be similarly defined and are shown in Table 2. The enhancement factor for Cu₂ compare to Cu is 3.4, while the enhancement factors for Cu₃ to Cu₂ and Cu₄ to Cu₃ are much lower. Therefore, the largest jump in enhancement for a single atom increase in the cluster size is between the monatomic and diatomic projectiles. The question then is whether the simulations can give mechanistic insight into the reasons for the nonlinear enhancement.

3.2. Atomistic mechanisms for ejection

The simulations have been used to determine the atomistic mechanisms responsible for the ejection of intact organic molecules, and therefore, to help us understand the reasons for the nonlinear dependence on cluster size. After viewing many trajectories, we conclude that our simulations show that the features identified by Garrison in earlier simulations [21–25] are necessary in order to eject an intact biphenyl molecule. The projectile impacts the surface and initiates one or more collision cascades. Most of the kinetic energy from the incident atom or cluster is dissipated into the crystal so that very low energy collisions with carbon atoms in the biphenyl molecule actually cause

ejection of the molecule. Carbon atoms in both rings of the molecule must be hit in order to initiate the concerted motion needed to lift the entire molecule off of the surface. Usually, two or more copper substrate atoms are needed to hit different regions of the biphenyl molecule. The biphenyl molecule absorbs much of the excess energy in its many internal degrees of freedom and leaves the surface vibrationally distorted. However, the molecules do not have enough energy to fragment and will reach the detector intact. For these low incident energies, only the first layer of surface atoms are involved directly in collision cascades that lead to the ejection of the molecule.

We have developed schematic diagrams to illustrate the collision cascades that result in the ejection of a biphenyl molecule. Harrison's original 'lean-on' analysis, which was modified by Sanders et al. [44] for many-body potentials, is used to determine the collision cascades. The cascades are then analyzed to determine which sequences result in a collision with a carbon atom in the biphenyl molecule. In the following schematic diagrams, the trajectories of the atoms involved in collisions are superimposed on top of the initial positions of the non-colliding atoms in the surface. Each atom is shaded a darker gray once it becomes part of a collision sequence that leads to a direct hit of a carbon atom in the biphenyl molecule. For a clearer illustration, only the region around the biphenyl molecule and only the carbon atoms of the biphenyl molecule are included. These particular trajectories are chosen as representatives of the general mechanisms found and illustrate the important characteristics.

3.2.1. Mechanism with Cu

Fig. 4 illustrates the mechanism for ejection with a copper atom at 0.100 keV. Generally, we find that more than one collision sequence is needed to produce two copper substrate atoms that collide with carbon atoms in different parts

of the biphenyl molecule. Initially, at 54 fs, the incoming copper atom (black) hits the surface and collides with a copper substrate atom (dark gray). At 72 fs, the initially struck copper atom collides with two neighboring copper atoms. At 93 fs, each of these copper atoms has initiated a collision cascade. At 139 fs, each of the two collision cascades has resulted in hitting carbon atoms in each ring of the molecule. A side view of the surface in Fig. 4(e) shows how the carbon atoms in each ring move in a concerted fashion as the intact molecule lifts off of the surface. In order for the biphenyl molecule to be ejected intact, the substrate atoms must collide with atoms in both rings of the molecule to initiate the concerted motion.

3.2.2. Mechanism with Cu_2

A similar mechanism occurs with the dimer projectile in which one of the dimer atoms initiates a collision cascade (or cascades) that lead to the ejection of the molecule. Since there are twice as many atoms, there will be double the probability of initiating such a cascade and so the emission yield should be twice that with the atomic projectile. The simulations, however, show that the emission yield is more than two times greater. The simultaneous impact of the two copper atoms nonadditively enhances the emission yield because each of the two atoms initially impacts a copper substrate atom. Therefore, there is a higher probability of initiating two adjacent collision cascades which lead to collisions with carbon atoms in different parts of the biphenyl molecule. Thus, those cascades that would be ineffective with one projectile can collaborate to eject the molecule off of the surface.

Fig. 5 shows the collaborative mechanism for ejection with the Cu_2 projectile at 0.100 keV. First, at 45 fs, the dimer (black) hits the surface and each atom hits a copper substrate atom (dark gray). At 63 fs, each substrate copper atom then goes on to hit a neighboring atom (dark gray). In

the third step at 84 fs, each of the neighboring atoms then collides with two carbon atoms (dark gray) in different rings of the biphenyl molecule. Lastly, at 104 fs, one of these atoms then goes on to strike two more carbon atoms (dark gray) in the ring. In addition, a third collision cascade has branched off from one of the two collision cascades and leads to hitting another carbon atom. Fig. 5(e) shows a side view of the last step in which the concerted motion of the carbon atoms in the two rings lifts the biphenyl molecule off of the surface.

By understanding the mechanism for ejection of intact biphenyl molecule, we can explain the observed results. Generally, two collision cascades are necessary to hit two different parts of the biphenyl molecule and initiate the concerted motion of the carbon atoms. Sometimes one copper projectile can initiate two adjacent collision cascades. Generally two copper projectile atoms, however, are necessary to produce sufficient collisions for ejection. Therefore, with the Cu_3 and Cu_4 clusters, usually only one or two atoms will be directly involved in ejecting the molecule, and this explains why the largest jump in enhancement is between the Cu and Cu_2 projectiles. The collaborative mechanism can also explain why the horizontal orientation of the dimer produces a lower emission yield. With this orientation, the dimer is aligned almost perpendicularly to the biphenyl molecule and cannot initiate parallel collision cascades.

4. Conclusions

Molecular dynamics simulations of the bombardment of a biphenyl molecule on a Cu(001) substrate with Cu and Cu_n , $n = 2-4$, projectiles are performed. The threshold energy per atom needed for ejection decreases with an increasing number of constituent atoms in the cluster. Clusters show a nonlinear enhancement in yield compared to the monatomic projectile. The largest jump in yield for a single atom increase in

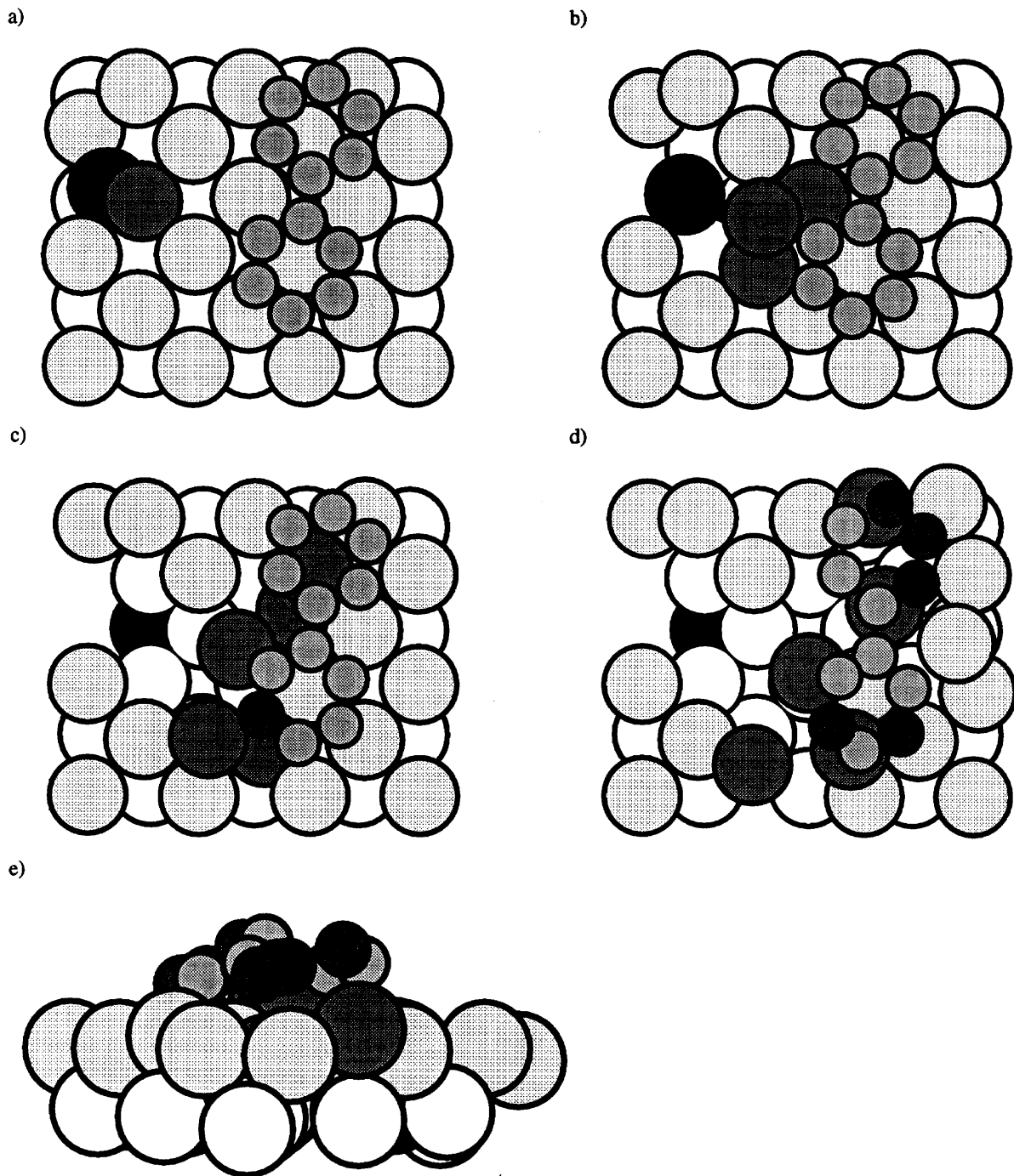


Fig. 4. Schematic diagram illustrating the mechanism for the ejection of a biphenyl molecule with a single atom projectile at 0.100 keV. The incoming atom is black and the biphenyl molecule is shaded gray. As atoms become part of the collision sequence leading to ejection of the molecule, they are shaded a darker gray. The incoming atom initiates two collision cascades that result in hitting a carbon atom in each ring of the molecule. The concerted motion of the carbon atoms lifts the biphenyl molecule off of the surface. Details are in the text. (a) 54 fs, top view; (b) 72 fs, top view; (c) 93 fs, top view; (d) 139 fs, top view; (e) 139 fs, side view.

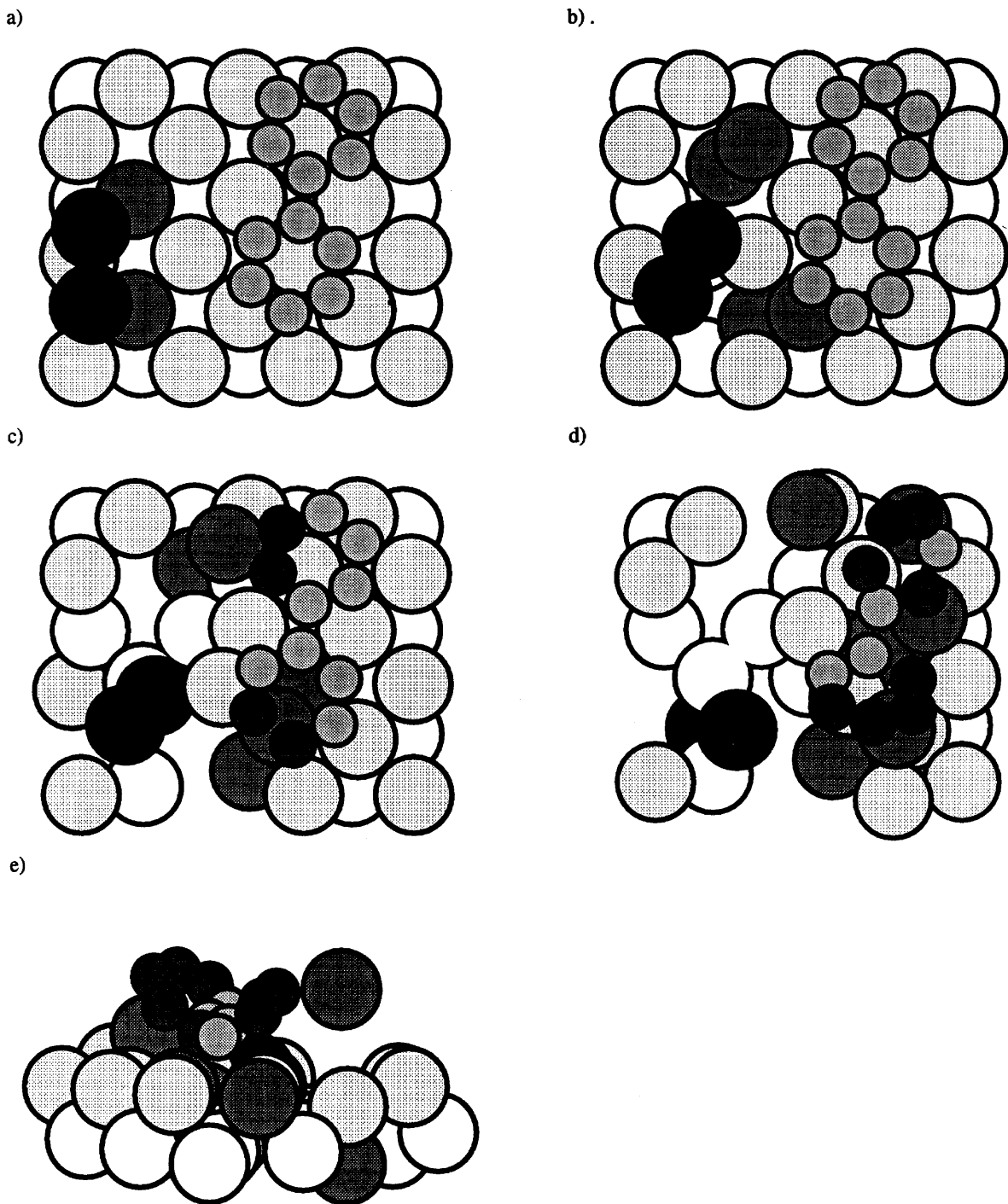


Fig. 5. Schematic diagram illustrating the mechanism for the ejection of a biphenyl molecule with a diatomic projectile at 0.200 or 0.100 keV per atom. The incoming cluster atoms are black and the biphenyl molecule is shaded gray. As atoms become part of the collision sequence leading to ejection of the molecule, they are shaded a darker gray. The two atoms in the dimer act collaboratively to initiate two adjacent collision cascades that lead to hitting carbon atoms in each ring of the molecule. As in Fig. 4, the carbon atoms in each of the rings move in a concerted fashion to lift the molecule off of the surface. (a) 45 fs, top view; (b) 63 fs, top view; (c) 84 fs, top view; (d) 104 fs, top view; (e) 104 fs, side view.

cluster size is between monatomic and diatomic projectiles.

These results 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. This is most likely to occur when there are adjacent collision cascades that can lead to collisions with different parts of the molecule. With a polyatomic projectile, there is a higher probability of producing two adjacent collision cascades that can hit different carbon atoms in the molecule. Therefore, collision cascades that are ineffective alone can work collaboratively to eject the molecule from the surface. Usually, only one or two collision cascades are needed to initiate this motion, and therefore, the largest jump in enhancement will be between the atomic and diatomic projectiles.

Of note is that for these relatively low incident energies, it is possible to clearly distinguish one collision sequence or cascade from another. As the incident energy increases, the collision sequences will become intertwined and indistinguishable. The important issue is that more motion is initiated in the near surface region with cluster projectiles. Since molecular adsorbates need several collisions to eject them, this increased motion in the near surface region enhances the yield nonlinearly.

The details of exactly how the yield changes with cluster size and incident kinetic energy will depend on many factors such as the binding energy of the molecule, and the relative sizes of the molecular adsorbate, substrate atoms and cluster atoms. These model calculations have identified an essential mechanism that is fundamental to a nonlinear dependence of molecular emission yield on cluster size. We believe that the importance of the collaborative mechanism in enhancing the emission yield extends to larger, more realistic systems. Future studies using a system with a monolayer of adsorbates will

enable us to determine enhancement factors that can more realistically be compared with experiment.

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References

- [1] J.C. Vickerman, in: J.C. Vickerman, A. Brown, N.M. Reeds (Eds.), *Secondary Ion Mass Spectrometry*, Oxford University Press, New York, 1989, pp. 1–71, 149–243.
- [2] N. Winograd, *Anal. Chem.* 65 (1993) 622a.
- [3] A. Benninghoven, B. Hagenhoff, E. Niehuis, *Anal. Chem.* 65 (1993) 630a.
- [4] N. Winograd, B. J. Garrison, in: A.W. Czanderna, D.M. Hercules (Eds.), *Ion Spectroscopies for Surface Analysis*, Plenum Press, New York, 1991, pp. 45–141.
- [5] R. Möllers, A. Schneiders, G. Kortenbrack, A. Benninghoven, in: A. Benninghoven, B. Hasenhoff, H.W. Werner (Eds.), *Secondary Ions Mass Spectrometry, SIMS X*, Wiley, New York, 1997, pp. 943–946.
- [6] A.D. Appelhans, J.E. Delmore, *Anal. Chem.* 61 (1989) 1087.
- [7] G.S. Groenewold, J.E. Delmore, J.E. Olson, A.D. Appelhans, J.C. Ingram, D.A. Dahl, *Int. J. Mass. Spectrom. Ion Proc.* 163 (1997) 185.
- [8] G.S. Groenewold, A.K. Gianotto, J.E. Olson, A.D. Appelhans, J.C. Ingram, J.E. Delmore, to be published in *International Journal of Mass Spectrometry and Ion Processes*.
- [9] M.G. Blain, S. Della-Negra, H. Joret, Y. LeBeyec, E.A. Schweikert, *Phys. Rev. Lett.* 63 (1989) 1625.
- [10] E.A. Schweikert, M.G. Blain, M.A. Park, E.F. Da Silveria, *Nucl. Instr. Meth.* B50 (1990) 307.
- [11] 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. Meth.* B62 (1991) 8.

- [12] K. Boussofiand-Baudin, G. Bolbach, A. Brunelle, S. Della-Negra, P. Håkansson, Y. Le Beyec, Nucl. Instr. Meth. B88 (1994) 160.
- [13] P.A. Demirez, J. Eriksson, R.A. Zubarcv, R. Papaléo, G. Brinkmalm, P. Håkansson, B.V.R. Sundqvist, Nucl. Instr. Meth. B88 (1994) 138.
- [14] H.H. Anderson, in: P. Sigmund (Ed.), *Fundamental Processes in Sputtering of Atoms and Molecules*, The Royal Danish Academy of Sciences and Letters, Copenhagen, 1993, pp. 127–153 and references therein.
- [15] M.H. Shapiro, T.A. Tombrello, Nucl. Instr. Meth. B58 (1991) 161.
- [16] M.H. Shapiro, T.A. Tombrello, Nucl. Instr. Meth. B62 (1991) 35.
- [17] V.I. Shulga, P. Sigmund, Nucl. Instr. Meth. B62 (1991) 23.
- [18] K. Johannessen, Nucl. Instr. Meth. B73 (1993) 481.
- [19] R.S. Averback, M. Ghaly, Nucl. Instr. Meth. B90 (1994) 191.
- [20] Z.Y. Pan, M. Hou, Nucl. Instr. Meth. B102 (1995) 317.
- [21] P. Sigmund, Phys. Rev. 184 (1969) 383.
- [22] B.J. Garrison, J. Am. Chem. Soc. 102 (1980) 6553.
- [23] B.J. Garrison, *Le Vide, le Couches Minches* (Supplement) 201 (1980) 1411.
- [24] B.J. Garrison, J. Am. Chem. Soc. 104 (1982) 6211.
- [25] B.J. Garrison, Int. J. Mass. Spectrom. 53 (1983) 243.
- [26] R.S. Taylor, B.J. Garrison, J. Am. Chem. Soc. 116 (1994) 4465.
- [27] R.S. Taylor, B.J. Garrison, Langmuir 11 (1995) 1220.
- [28] R.S. Taylor, C.L. Brummel, N. Winograd, B.J. Garrison, J.C. Vickerman, Chem. Phys. Lett. 233 (1995) 575.
- [29] R.S. Taylor, B.J. Garrison, Chem. Phys. Lett. 230 (1994) 495.
- [30] R.S. Taylor, B.J. Garrison, Int. J. Mass. Spectrom. 143 (1995) 225.
- [31] K.S.S. Liu, J.C. Vickerman, B.J. Garrison, Radiation Effects and Defects in Solids 142 (1997) 205.
- [32] S.M. Foiles, M.I. Baskes, M.S. Daw, Phys. Rev. B 33 (1986) 7983.
- [33] M.S. Stave, D.E. Sanders, T.J. Raeker, A.E. DePristo, J. Chem. Phys. 93 (1990) 4413.
- [34] T.J. Raeker, A.E. DePristo, Int. Rev. Phys. Chem. 10 (1991) 1.
- [35] C.L. Kelchner, D.M. Halstead, L.S. Perkins, N.M. Wallace, A.E. DePristo, Surf. Sci. 310 (1994) 425.
- [36] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
- [37] D.W. Brenner, J.A. Harrison, C.T. White, R.J. Colton, Thin Solid Films 206 (1991) 220.
- [38] M.P. Allen, D.J. Tildesley, *Computer Simulations in Liquids*, Oxford University Press, New York, 1987, p. 9.
- [39] D.J. O'Connor, R.J. MacDonald, J. Radiation Effects 34 (1977) 247.
- [40] D.E. Harrison Jr, CRC Crit. Rev. Solid State Mater. Sci. 13 (1988) 51.
- [41] B.J. Garrison, Chem. Soc. Rev. 21 (1992) 155.
- [42] B.J. Garrison, N. Winograd, D.E. Harrison Jr, J. Chem. Phys. 69 (1978) 1440.
- [43] A. Wucher, B.J. Garrison, Phys. Rev. B 46 (1992) 4855.
- [44] D.E. Sanders, K.B.S. Prasad, J.S. Burnham, B.J. Garrison, Phys. Rev. B 50 (1994) 5358.