

# A Molecular Dynamics Study of Ejection of Molecules from a Vibrationally Excited "Track" in an Amorphous Solid

S. T. CUI and R. E. JOHNSON

*Department of Nuclear Engineering and Engineering Physics, University of Virginia,  
Charlottesville, Virginia 22901*

## Abstract

A molecular dynamics program is developed to study the ejection of molecules from a weakly bound, amorphous solid made up of diatomic molecules. The ejection is calculated in response to an amount of energy deposited, presumably by an incident fast particle, in vibrational excitation of the molecules within a cylindrical volume about the particle's "track." The anharmonic distortion of the "excited" molecules in the "track" can lead to rapid energy transfer to the center of mass motion producing sputtering. When the level of vibration excitation is small, nearly harmonic motion, virtually no energy transfer occurs in the time scales of interest. At the larger energy depositions considered, the number of molecules ejected vs. energy deposited per unit path length is consistent with recent simulations using structureless particles and with an analytic model for ejection due to a "pressure pulse."

## Introduction

The excitation of molecular solids by fast heavy ions induces a variety of interactions by producing ionization, secondary electrons, and electronically excited molecules [1]. These interactions may eventually lead to the ejection of ions or neutral molecules from the surface of the solid [2,3]. When a fast heavy ion is incident on a solid, various models have been proposed to describe the ejection of intact, large molecules and to predict the ejection yield (the number of such molecules ejected per incident ion) [1,3]. Of particular interest to this paper is the role of vibrational excitation. In the model considered, energy deposited by a fast ion penetrating the solid is assumed to rapidly excite the internal vibrational modes of large molecules in the "track" of the ion, as described earlier [1,4]. The excitation of the internal vibrational modes leads to an expansion in the average size of the molecules due to the anharmonicity of the interaction potentials. This in turn leads to a net repulsion between molecules in the "track" region so that the material experiences a "pressure pulse" [5]. As a result, the transient force on the molecules at the surface region is outward, which may cause molecules to be ejected.

Molecular dynamics simulations provide a useful tool for *quantitatively* understanding this ejection process which has been described, roughly, by an analytic model [6]. Recent molecular dynamics calculations by Fenyo et al. [7] employ an expandable sphere and the Lennard-Jones potential to simulate the excitation of

and subsequent ejection of large organic molecules following the passage of a heavy fast ion. Their results showed the interesting cubic dependence of yield vs. the energy density deposition in the solid first observed experimentally by Hedin et al. [8]. However, that model contained no internal degrees of freedom. Lee and Lucchese [9] used a one-dimensional chain of atoms to describe aspects of the desorption of a species from a solid surface due to a vibrational excitation. Their calculations show that the conversion of the internal vibrational energy into center of mass energy can play a major role in causing the ejection of the molecules due, primarily, to the anharmonicity of the potentials. Therefore, it is important to understand how the incorporation of the internal modes into a three-dimensional molecular solid affects the yield when the solid is subject to rapid vibrational excitation.

In this paper, we use the simplest molecular system (i.e., diatomic) to study the ejection of molecules from the solid surface in response to vibrationally exciting (expanding) molecules in the "track." Different amounts and modes of energy depositions are employed in these calculations, stretching the intramolecular distance or by giving molecules internal kinetic energy. That is done in order to investigate the energy transfer between the internal motion and the center-of-mass motion of molecules which is an important factor in causing the sputtering. The calculations are first described and then the results are reported and discussed.

### Calculations

A molecular dynamics method is used to keep track of the trajectories of 902 or 1364 diatomic molecules in an amorphous solid. Before making the solid amorphous, the system used is based on the  $\alpha$ -phase solid oxygen, which has a monoclinic crystal structure with the axes of the oxygen molecules all in the direction perpendicular to the rectangular plane. The equilibrium separation between the two atoms constituting the  $O_2$  molecule is 1.2 Å. The other parameters of the oxygen solid are lengths  $a = 5.403$  Å,  $b = 3.429$  Å,  $c = 5.086$  Å, and angle  $\beta = 132.53^\circ$ . The potential for describing the interaction between the atoms in different molecules is the Lennard-Jones potential,  $\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$ . For solid oxygen, these parameters are  $\epsilon/k = 58$  K and  $\sigma = 2.988$  Å, where  $k$  is the Boltzmann constant. This potential is truncated at 9 Å in the calculations. The potential used for describing the interaction between the two atoms in the same molecule is the Morse potential,  $D_e \exp[-\alpha(R - R_e)] [\exp(-\alpha(R - R_e)) - 2]$ . The parameters appropriate for oxygen are  $\alpha = 2.958$  Å<sup>-1</sup> and  $D_e/k = 60320$  K. However, to obtain a calculable yield and to test the effect of the coupling of the internal and external modes, a smaller well depth  $D_e$  is used in the calculations so that the diatomic species is only "oxygen-like." Most of the sputtering yield calculations are carried out with  $D_e/k = 2900$  K to give a reasonable yield and for integration efficiency and with  $\sigma$  about 2.37 Å. This value of  $D_e$  results in an internal potential with a well depth ( $\sim 0.25$  eV), which is 50 times the external well depth above. The molecular density is twice that of oxygen and the net cohesive energy of this solid is 0.088 eV.

The first step of the calculation is to prepare an amorphous solid starting with the monoclinic crystalline oxygen sample. Periodic boundary conditions are used

for this purpose. This is done in a manner used earlier for solid Ar [10]. The kinetic energy of each atom is raised to 0.5 eV, which is well above the sublimation energy of solid oxygen, but the intramolecular distance is kept fixed in order to increase the efficiency of the integration. Each pair of atoms in the system can then move far from its equilibrium site in the crystalline solid and the entire system acts like a dense gas. After a sufficient period of time, the system reaches equilibrium at the new temperature and the crystalline structure is lost. Amorphous solid oxygen is obtained through the cooling of this system by extracting residual kinetic energy. This is done by setting the kinetic energy of the molecules to zero and then letting the system relax to a new equilibrium. The procedure is repeated until the residual kinetic energy is negligible, which in our case is less than 1% of the cohesive energy. In the above process, the separation of the atoms in the molecule is fixed at 1.2 Å by integrating the equations of motion derived using Gauss' principle of least constraint [11]. By the proper choice of tolerance, the accuracy of the calculation can be controlled. Our calculations keep the deviation of nuclear distance from 1.2 Å at less than 0.003 Å. After obtaining an amorphous solid this constraint is released so that molecules can vibrate. After the preparation step, the boundary condition in the  $z$ -direction is removed to allow the surfaces to relax until equilibrium is reached. The  $x$ ,  $y$ -boundary conditions are then removed for the sputtering yield calculation so that the calculations are carried out on a sample surrounded by a vacuum.

To simulate the molecule ejection resulting from vibrational excitation around an ion track, a cylindrical volume of radius 7.1 Å is chosen, a typical "track" size [2]. Each molecule within this volume is given the same internal expansion along its axis or the same internal kinetic energy. The size of these quantities are not chosen to relate to "true" excitation conditions, but rather are chosen large enough to lead to ejection. The size of the radius of the cylinder which is excited can be compared with the size of the sample, which is  $38.5 \times 27.2 \text{ Å}^2$ . A test calculation using a sample size of  $38.5 \times 19.8 \text{ Å}^2$  gives essentially no difference in the sputtering yield which indicates that the effect of the vacuum on the side is negligible but we use the larger sample in any case. After the initial excitation the molecular motion is followed for  $\sim 10^{-11}$  s of real time, after which the sputtering is essentially complete. At the end of the calculation, the distances of the molecule from the surface, its center of mass energy, and the binding energy to the solid are checked. A molecule which has moved sufficiently far from the surface that its binding energy becomes zero is counted as a sputtered molecule. For a molecule which still has a small binding to the surface, a check on its center-of-mass kinetic energy and binding energy is used in order to decide whether to count it as a sputtered molecule.

## Results

The energy transfer between the external and the internal modes is first studied. In Table I we list the average initial internal (int) and center-of-mass (COM) energies "deposited" per molecule in the track and their corresponding values at the time the calculations are stopped. In these calculations, the well depth for the internal

TABLE I. Energies and yields in sputtering calculation.

Percent expansion	$\Delta E_{\text{int}}^0/U^a$	$\Delta E_{\text{COM}}^0/U^a$	$\Delta E_{\text{int}}^f/U^a$	$\Delta E_{\text{COM}}^f/U^a$	Ratio <sup>b</sup>	$E_s/U^c$	$Y$
50 <sup>d</sup>	1.86	0.42	1.20	1.12	0.49	0.29	2
52 <sup>d</sup>	1.91	0.47	1.25	1.19	0.50	0.36	6
55 <sup>d</sup>	1.98	0.58	1.34	1.27	0.49	0.25	8
60 <sup>d</sup>	2.10	0.79	1.39	1.53	0.53	0.40	15
65 <sup>d</sup>	2.20	1.06	1.53	1.76	0.54	0.56	20
0 <sup>e</sup>	2.89	0.0	1.43	1.46	0.51	0.30	8
52 <sup>f</sup>	1.84	0.41	1.27	1.04	0.46	0.45	8
60 <sup>f</sup>	2.02	0.77	1.39	1.45	0.52	0.47	17
65 <sup>f</sup>	2.12	1.09	1.42	1.83	0.57	0.66	28

<sup>a</sup> Average excitation energies of the molecules in the excited cylinder divided by the cohesive energy  $U$  ( $\sim 0.088$  eV): 0, initial;  $f$ , final.

<sup>b</sup> Ratio =  $\Delta E_{\text{ex}}^f / (\Delta E_{\text{int}}^0 + \Delta E_{\text{ex}}^0)$ .

<sup>c</sup> Average COM energy of the *ejected* molecules.

<sup>d</sup> Molecules in cylinder expanded: 902 molecules, "five" equivalent layers.

<sup>e</sup> Atoms in each molecule given a kinetic energy initially for 902 molecule, "five" equivalent layers.

<sup>f</sup> Molecules in cylinder expanded: 1364 molecules in sample, "seven and a half" equivalent layers.

interaction is 50 times the external interaction potential well depth which is a large mismatch. Our results show that the internal motion and the COM motion rapidly share the total initial energy deposition, each approaching about half in the time period of interest for the cases shown. Figure 1 shows the behavior of the total COM energy (potential plus kinetic) vs. time (solid line). After some initial oscillations, the internal motions rapidly lose energy. This process slows down at later times and eventually a stabilized level is reached. The rapidity of the energy transfer between the internal motion and the COM motion shows that the molecules in the system interact strongly with each other due to the significant anharmonicity of the binding potentials for the highly excited species.

We also performed a calculation giving an initial internal kinetic energy to each molecule in the cylindrical volume. Using a total initial kinetic energy equal to that of molecular expansion of 60%, the final energy partition is listed in Table I and the transient state of the COM energy is also plotted in Figure 1 (dashed line). The behavior of the energy transfer between the internal motion and the COM motion is found to be similar to the case of potential energy deposition. However, the sputtering yield is somewhat smaller, reflecting the fact that the initial repulsion plays a role in enhancing the sputtering yield when the molecules are initially stretched. This emphasizes that the sputtering observed is a "prompt" process.

In Table I, we also present the calculated sputtering yields. These are plotted in Figure 2 vs. the energy depositions  $\Delta E/U$ , where  $\Delta E$  is the total energy "deposited" and  $U$  is the cohesive energy of the solid. As a result of the excitations, the internal vibrational level is raised and the center-of-mass motion of the molecules increases due to the repulsion from other molecules caused by the large dislocation from the

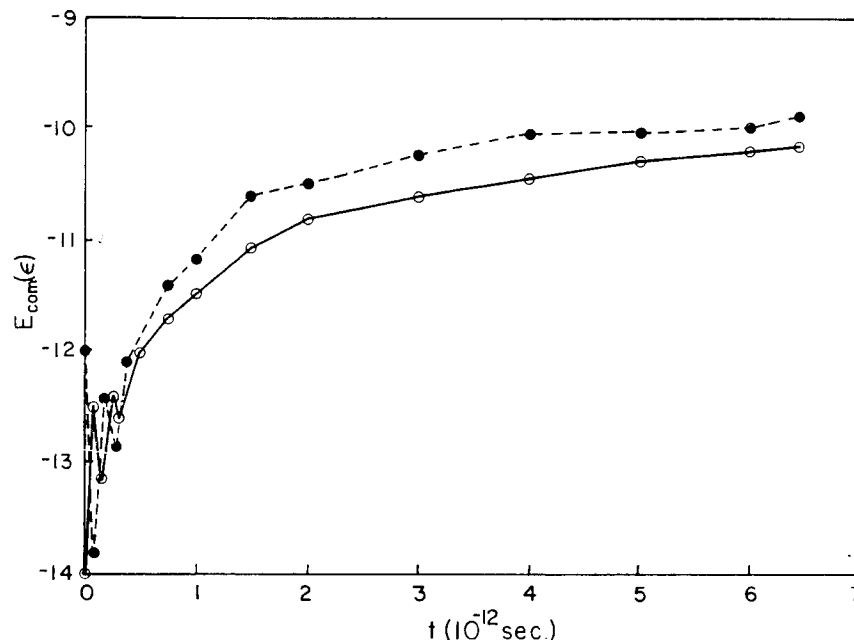


Figure 1. The total center of mass (COM) energy vs. time: (—) excitation by a 60% expansion; (---) excitation by an internal kinetic energy equivalent to the 60% expansion of the molecules:  $\epsilon = 0.005$  eV van der Waals well depth.

equilibrium. Since a large amount of computing time is needed for each calculation, only a few calculations are made on a CRAY. This still allows us to describe the general trend of the dependence of the sputtering yields on the energy deposition. The effect of the thickness of the sample is checked by using a sample of the same dimension in  $x$ - $y$  plane and a thickness of 1.5 times as large. It is seen that for the samples studied there is a thickness dependence. (At the smaller energy depositions for the larger thickness, there are a few loosely attached molecules which cause a large enhancement). However, for both samples and for the larger energy depositions the yield  $Y$  becomes very roughly consistent with the line represented by  $Y \propto (\Delta E/LU)^3 n_M^{-1}$ , the result found in the simulations of Feynö et al. [7] and given by a simple analytic model [6]. Here  $L$  is the sample thickness and  $n_M$  is the molecular number density. For smaller energy depositions, i.e., smaller excitations, the yields drop rapidly to zero as predicted for an excited cylindrical region of finite radius [6]. In Table I it is also seen that the average kinetic energies of the sputtered species tends to increase with increasing excitation densities over the small range of excitation densities studied.

The sputtered species in our calculations are mostly the vibrationally excited molecules which are located within the cylindrical volume before the excitation. Initially unexcited molecules, which reside outside of the excitation volume, were ejected from the solid only for the largest  $\Delta E$  used here. Because of the computational times used no "late" contributions to sputtering occur, for example, due to subli-

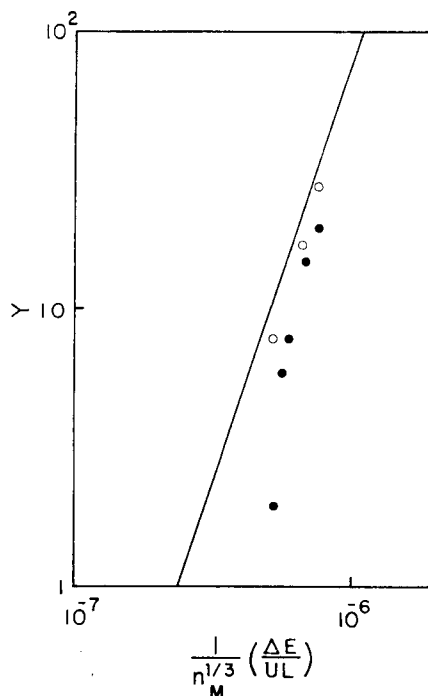


Figure 2. Yield (number of molecules ejected) vs. the total energy deposition per unit path length. This is scaled to the cohesive energy,  $U$ , and the molecular number density,  $n_M$ : (dots) 902 molecules, "five" equivalent layers; (open circles) 1364 molecules, "seven and a half" equivalent layers; (—) predicted cubic dependence for large excitation densities and "narrow" cylinders.

mation of a molecule during the later stages of energy dissipation. Such processes may be important for ices [2,6]. We also find that a few molecules may be dissociated due to the large internal excitations involved. The excitations used raise the vibrational level of a molecule in the cylinder to a position near the top of the potential well and the interactions with other molecules can supply energy or alter the binding leading to the dissociation of the molecule. However, *on the average* the internal excitation energy of the sputtered species decreases from their initial values due to energy transfer to the COM. For example, for a 60% expansion the average  $\Delta E_{\text{int}}/U$  for the sputtered molecules decreases by about 30% of the initial value.

In the calculations of Lee and Lucchese [9], it was shown that the energy transfer process for harmonic potentials is very inefficient when the differences between the strengths of the intramolecular and the intermolecular bonds are large, consistent with the energy gap law [12]. Small initial internal energy depositions are used here to test this effect in 3D. The energies given to each molecule in the cylinder for this test are equal to 0.5 and 0.3 of the well depth of the intramolecular potential, corresponding to the total energy depositions of 16.9 and 10.1 eV. At the end of the calculation, an equivalent of a physical time 5.4 ps, a time in which considerable sputtering could occur, the energy transfer to the COM motion in the former case is 2.6 eV, while it is essentially zero in the latter case.

### Conclusions

Using an amorphous solid of "oxygenlike" diatomic molecules, we showed that rapid excitation of internal modes of a *volume* of molecules can lead to prompt ( $t < 10^{-11}$  s) sputter ejection. In the cylindrical volume studied and for the molecular structures chosen here, significant excitations are required for ejection. The results at the larger excitation energies exhibit a behavior roughly consistent with a calculation of the ejection for expanded, structureless particles [7] and an analytic model [6]. The large vibrational excitations required to achieve sufficient anharmonicity would indicate that the electronic sputtering of a true sample of low-temperature, condensed solid oxygen by fast light ions [13] may require considerable dissociation, as the internal binding is much larger than that used in the model calculations presented here. Such dissociation (which is the extreme case of vibrational "expansion") is expected to occur following electronic recombination for diatomic molecules [2,14]. In a solid of large organic molecules, on the other hand, the molecular volumes are large compared to the separations between their boundaries and, therefore, lower level of vibrational excitations should be effective. The important point for such biomolecules is that the anharmonicity of the interaction potentials can allow *rapid* transfer of internal excitation energy to the center of mass motion without significant dissociation of even very highly excited molecules. This is a situation very favorable to the ejection of a volume of whole, thermally labile biomolecules. In fact the internal motions, on the average, were shown to "cool" slightly during the expansion, as suggested earlier [1], and initially "unexcited" molecules may be ejected from the edges of the cylindrical volume excited *if* the excitation density is large enough [7]. For larger excited volumes than that used here, lower levels of excitations should be sufficient for ejection. Therefore, for laser excitation of a molecular matrix material containing "unexcited" biomolecules [15] the "expansion" of the matrix material can carry off the biomolecules without significant energy transfer into the internal modes. On the other hand, for ejection by fast heavy ions, high levels of internal excitation may be required in the narrow track of the ion.

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