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Molecular-dynamics simulation of prompt sputtering of a molecular solid at high excitation densities

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Prompt sputtering from a weakly bound, amorphous solid at high excitation densities is simulated with use of molecular dynamics in order to understand the ejection of a volume of material by fast heavy ions—the process thought to be responsible for ejection of whole organic molecules from a solid. Ejection of diatomic molecules from a solid was calculated as a response to a large amount of energy deposited in the vibrational excitation of those molecules within a narrow cylinder: the incident ion's "track." Calculations were performed for two modes of vibrational excitation and for samples with different geometries, number densities, cohesive energies, thicknesses, and boundary conditions. For high excitation densities, rapid ($\sim 10^{-12}$ sec) energy transfer takes place between the internal energy and the center-of-mass motion, resulting in molecular ejection. The yield for prompt sputtering is found to be independent of the molecular mass for a given excitation density and has a steeper than cubic dependence on the energy density deposited in the solid for the energy densities studied, exhibiting a "threshold" at the lowest excitation densities. The scaling with excitation density found is close to that calculated earlier for structureless particles and to the pressure-pulse model but disagrees with the standard "shock" models.

I. INTRODUCTION

Electronic sputtering of molecules from condensed samples has become important for materials modification. Recently, progress has been made in delineating aspects of this process when the excitation density is high.[1] "Late," sublimationlike ejection dominates the sputtering by MeV helium ions of low-temperature, condensed-gas solids made up of small molecules.[1,2] On the other hand, "prompt" ejection due to the production of a steep pressure gradient induced by a fast heavy ion causes the ejection of a volume of whole organic molecules.[1,3] Here we examine the latter process using molecular dynamics, which is appropriate for studying molecular motion over short-time periods.

The penetration of a molecular solid by fast, heavy ions causes electronic excitation of molecules and ionization accompanied by secondary-electron production. These interactions can cause the ejection of ions or neutral molecules from the surface of the solid. Although the details of the transfer of energy from electronic excitation to sputter ejection is not certain,[4] vibrational motion is readily excited in large molecules either directly or on electronic relaxation.[4,5] Therefore, we examine the consequences of large amounts of energy being deposited in vibrational excitation of molecules within the "track" of a fast ion. This leads to a net expansion in the average size of the molecules,[5] producing a net repulsion between molecules in the track. If the excitation density is high, the internal energy may be rapidly converted to center-of-mass motion so that a "pressure pulse"[1,3,6–9] is produced. This causes the surface molecules to experience an outward transient force, which can result in ejection.

Molecular-dynamics (MD) simulations can provide a detailed understanding of the sputtering process. Lee and Lucchese[10] studied the desorption of a species from a solid surface due to vibrational excitation using a one-dimensional chain of atoms. They found that the rate of conversion of internal energy into center-of-mass energy, mainly due to anharmonicity of potentials, controls the ejection process, as suggested by Williams and Sundqvist.[5] Feynö *et al.*[6] assumed that the effect of vibrational excitation in a three-dimensional sample was a net expansion in the molecular size of the molecules in the ion's track. Those calculations gave a roughly cubic dependence of the total yield on the energy density deposited in the solid, consistent with an analytic model[1] and with the measurements Hedin *et al.*[11] for a sample of condensed leucine. Because no internal degrees of freedom were incorporated into their simulations, the conversion of internal energy to center-of-mass motion could not be studied. As realistic organic molecules are compressible and possess complex structures, it is important to understand how the internal modes of a molecular solid excite the center-of-mass motion when the solid is subjected to rapid vibrational excitation. Therefore, Cui and Johnson[7] calculated yields for molecules with one internal degree of freedom. Calculations were performed for a diatomic, amorphous solid with a rectangular shape and vacuum boundary conditions. In this paper we extend those preliminary calculations, considering cylindrical samples, variations in sample size, and the role of a substrate. (We also correct certain publication errors in Ref. 7.) In addition, samples with different number densities, cohesive energy, atomic mass, and thickness were used to study the energy transfer and subsequent ejection in response to a high density of vibrational excitation. The molecules in the track are excited by an initial expansion or by giving each pair of nuclei an equal but opposite momentum. After so exciting the molecules, they are allowed to relax and the motion of every atom in the solid is followed via classical dynamics.

The motivation for conducting these studies is to understand the volume ejection process, presumed to be responsible for ejection of whole organic molecules, and to obtain a picture of the energy-transfer rates at high excitation densities. In doing this we, in effect, test the simpler calculations of Fenyö *et al.*[6] for structureless particles and the analytic models based on fluid dynamics[12] referred to as a pressure-pulse[1] or a "shock"[3] model. The calculational method and sample preparation are first discussed.

II. CALCULATION

The solution of Newton's equations of motion is carried out using a fourth-order predictor-corrector algorithm.[7] The predictor consists of the computation of positions, momenta, and derivatives of each particle at time $t+\Delta t$ from the positions, momenta, and their derivatives at time t using a Taylor expansion (see Ref. 13). The predicted positions, momenta, and their derivatives are used in the corrector step to evaluate $d\mathbf{r}/dt$ and $d\mathbf{p}/dt$ at $t+\Delta t$ utilizing Newton's equations of motion, which incorporate interatomic and intramolecular forces.

All interactions between the atoms in the solid are assumed to be pairwise. The calculations performed here are for a "model diatomic" in which the Lennard-Jones potential is used to describe the interactions between atoms in different molecules:

$$\varepsilon\left[\left[\frac{\sigma}{R}\right]^{12}-\left[\frac{\sigma}{R}\right]^{6}\right] . \qquad (1)$$

The parameters chosen, for convenience, are those for α-phase solid oxygen, $\varepsilon=0.004\,99$ eV and $\sigma=2.372$ Å, and the potential is truncated at 9 Å. For describing the interaction between two atoms of the same molecule, a Morse potential is used:

$$D_e\exp[-\alpha(R-R_e)]\{\exp[-\alpha(R-R_e)]-2\} . \qquad (2)$$

The parameters appropriate for oxygen would be $\alpha^{-1}=2.958$ Å, $D_e=5.19$ eV. However, we found earlier[5] that extremely large internal excitations are required in a *realistic oxygen sample* in order to cause sputtering (i.e., O_2 must be energetically dissociated as predicted[14]). Here we are only concerned with the diatomic as the simplest molecule having an internal degrees of freedom (compressible). Therefore, the typical sets of values used here are $D_e=0.25$ and 0.50 eV and $\alpha=2.37$ Å. Because the energy-transfer *rate* depends on the size of the mismatch between the internal and external modes and on the size of the anharmonicity,[5,10] using a much smaller well depth D_e allows us to calculate the rapid ($<10^{-11}$ s) transfer of *intermolecular* energy into *intramolecular* energy, which is thought to drive prompt ejection.[1,4] for samples of organic molecules, the molecular dimensions are generally large compared to the molecular separations. Therefore, many low-energy vibrational excitations could cause sputtering, a process difficult to simulate by molecular dynamics at the present time.

An *amorphous* solid was first prepared from a monoclinic crystalline oxygen[4,14] of dimensions $25.73\times13.61\times14.87$ Å^3, having a cohesive energy of 0.088 eV, containing 300 molecules. The sample is subjected to periodic boundary conditions on all sides, and the kinetic energy of each atom is raised to 0.5 eV, (well above the sublimation energy of solid oxygen). The intramolecular distance is kept fixed[15] in order to increase the efficiency of integration. Each pair of atoms in the system is allowed to move from its equilibrium position in the crystalline solid, and the system behaves like a dense gas. After a sufficient period of time (~1.4–2 ps), the system reaches equilibrium at the new temperature and the crystalline structure is lost. An amorphous structure is obtained by repeated cooling of the sample, extracting the kinetic energy until a new equilibrium is reached with a residual kinetic energy less than 1% of the cohesive energy.[14] The periodic boundary conditions were removed after this preparation, and the coordinates of the 300 molecules are used to generate larger rectangular boxes or thicker samples.

Because of the time for calculating a yield is determined by the number of molecules in the sample, a cylindrical sample is more efficient since the region excited by a fast, heavy ion is cylindrical. A sample of such geometry is obtained by scooping out a volume of radius 19.3 Å and height 14.87 Å from a rectangular box of dimensions $38.59\times40.82\times14.87$ Å^3. In our earlier work[7] vacuum boundary conditions were used on all sides, giving a thickness dependence to the yield for small thicknesses. In addition to using thicker samples, reflecting substrates are also used. As the excited cylindrical region is normal to the substrate, this, in effect, increases the sample thickness. The reflecting boundary condition at the base was produced by reversing the z component of momentum when the center of mass of a molecule reaches the substrate.

III. SIMULATION OF SPUTTERING

Simulation of prompt molecular ejection as a result of vibrational excitation around an ion track was performed using a track defined by a cylindrical volume of radius 7.1 Å *within* each sample. Two modes of excitation were used, one of which consisted of giving the same internal expansion along the axis of each molecule in the track and then letting the molecules relax, while the other consisted of imparting the same internal kinetic energy to each track molecule. The second type of excitation was done using twice the well depth $D_e=0.5$ eV, and the mass of the molecules was also changed for one case.

Seven samples were used: *S*1, *S*2, and *S*7 were rectangular samples of different thicknesses and consisting of atoms of different masses, subjected to free boundary conditions on all sides, whereas *S*3, *S*4, *S*5, and *S*6 were cylindrical samples of different thicknesses and number densities subjected to reflecting boundary conditions at the base and free boundary conditions on all other sides (Table I). The average cohesive energy of these samples ranged between 0.015 and 0.029 eV, less than the magnitude of the average cohesive energy of a perfectly crystalline sample. This additional potential energy is available when the lattice is disturbed by excitations but does not significantly affect sputtering.

The molecules within the track were excited after 20 time steps (1 time step $=1.39\times 10^{-15}$ s), to allow additional relaxation, and the subsequent molecular motion was followed for 3500 time steps ($\sim$4.9 ps). Observations were made up to and after this time to check the distances of the atoms of these molecules from the surface, their kinetic energies, and binding energies to the solid. When the z coordinates (being the cylinder axis) of the atoms are much larger than that of the upper surface, the binding with the solid is negligible, and the center-of-mass (c.m.) kinetic energy of the molecule is greater than the cohesive energy of the solid, then the molecule is considered to be sputtered. The values of the z coordinates of "ejected" surface atoms in an earlier time step (3000th time step) are compared with those of the final time step to confirm escape. The yield Y is the total number of such molecules ejected in the time period of interest. Dissociation of the molecule occurs when the intramolecular distance between the two atoms is greater than the cutoff for the Morse potential.

IV. RESULTS

We found that 3500 time steps (4.9 ps) was, roughly, the time required for prompt sputtering to be completed for the samples and excitation densities considered. Figure 1 exhibits results for three different kinetic energies (0.4 eV/molecule for *S*5, 0.6 eV/molecule for the thin sample *S*1, and 0.5 eV/molecule for the thicker sample *S*2) out to 4000 time steps, depicting the time evolution of the total c.m. energy per molecule and the number of ejected molecules. Following a few rapid oscillations in

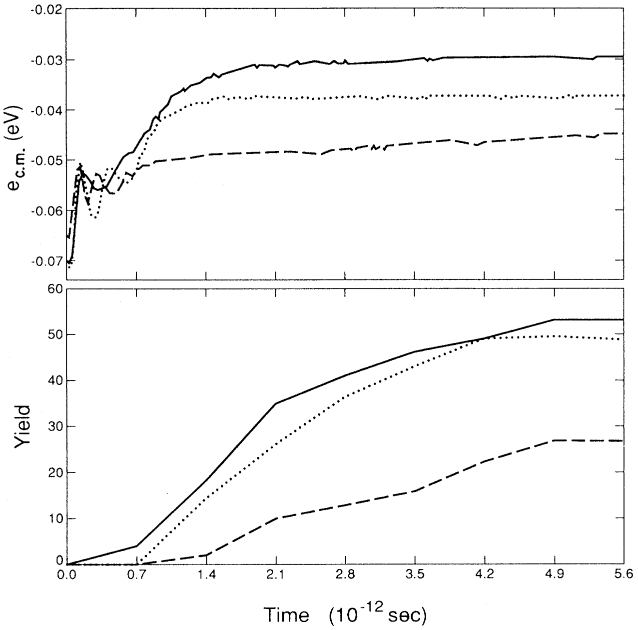

FIG. 1. Yield vs time and average c.m. energy ($e_{\text{c.m.}}$) per molecule in the whole sample vs time for excitation of track molecules with three different kinetic energies (Table III); sample *S*5, 0.4 eV per molecule (dashed); sample *S*2, 0.5 eV per molecule (dotted); sample *S*1, 0.6 eV per molecule (solid).

TABLE I. Properties of samples used.

Sample[a]	Thickness in layers[b]	Mass of atoms ($g\times 10^{-23}$)	Radius (Å) or length × width (Å^2)	Number density (No./cc) × 10^{22}	Cohesive energy U (eV)	Boundary conditions	No. of track molecules
*S*1 (902)	(5)	2.6559	38.5×27.2	5.77	0.070	free on all sides	135
*S*2 (1364)	7.5	2.6559	38.5×27.2	5.77	0.071	free on all sides	197
*S*3 (947)	5	2.6559	19.3	5.44	0.071	reflecting at base	137
*S*4 (1190)	7.5	2.6559	19.3	5.44	0.068	reflecting at base	172
*S*5 (817)	5	2.6559	19.3	4.70	0.065	reflecting at base	138
*S*6 (1016)	7.5	2.6559	19.3	4.70	0.059	reflecting at base	183
*S*7 (902)	5	5.32	38.5×27.2	5.77	0.070	free on all sides	135

[a] Quantities within parentheses denote number of molecules in the sample.

[b] Five layers = 14.87 Å; 7.5 layers = 22.31 Å.

the total c.m. energy (potential plus kinetic), a large fraction of the internal energy is seen to be transferred to c.m. energy in 1.5 ps, producing sputtering which is complete in about 5 ps. We refer to this as "prompt" sputtering. Because of limits on computer time and on sample size, we are not able to follow the behavior of the energy to describe the "late" sublimationlike process sustained by the spreading local temperature.[1,2]

In Fig. 2 the time evolution profiles of the total c.m. energy for the two types of excitation used here are compared at early times. It is seen that excitation by expansion produces a large initial c.m. potential energy, which is converted almost totally into internal energy in about 0.2 ps, after which the two modes of excitation become similar. The general behavior is roughly independent of sample thickness for a given excitation, but fluctuations with time are larger for samples with lower cohesive energy and lower molecular number density The transfer of energy subsequently slows down to a "quasiequilibrium" c.m. energy. However, at this time the energy is not yet dispersed significantly in the radial direction.

Table II lists the increase (ΔE) in the internal (int) and center-of-mass (c.m.) energies initially "deposited" and their corresponding values at the end of 3500 steps. These are divided by the number of molecules in the track. The total ΔE changes somewhat ($\sim 1-8\,\%$ over the full integration time, depending on the sample). Increasing numerical accuracy was shown not to affect the sense of the results below. It is seen from Table II that the internal motion and c.m. motion roughly share the total energy at the higher excitation densities studied. The rapidity of the energy transfer between the internal motion and c.m. motion occurs since the molecules interact strongly with each other because of the significant anharmonicity of the molecular binding potentials for these highly excited species and high excitation densities. (In our earlier work[7] the legend for time evolution profiles of the c.m. energy was inverted; i.e., the graph for expansion is actually kinetic energy and vice versa in Fig. 1.)

The effect of sample thickness is checked using samples *S*2, *S*4, and *S*6, which are 1.5 times as thick as *S*1, *S*3, and *S*5, for both sets of studies. Larger yields are found for the thicker samples as expected from the analytic model.[1,16] In addition, comparison of the yield of *S*1 with *S*3 and *S*2 with *S*4 for the same expansion indicate a 60–80 % increase in yield for a reflecting boundary at the base (a substrate). This is due to prevention of energy loss through the base and is equivalent to having a sample roughly twice as thick for the geometry used. On the other hand, comparison of rectangular and cylindrical samples having the same boundary conditions indicates that sample geometry has little effect on the calculated sputtering yield.

The atomic mass was doubled for the molecules in sample *S*7, and the yield was compared with an identical run for *S*1 with energy deposited as initial kinetic energy. It was found that the yield (see Table III) is roughly independent of the molecular mass, as in the analytic model.[1]

In Fig. 3 we display the yield versus energy deposited per unit path length using the dimensionless quantity $\Delta E/(n_m^{1/3}LU)$ suggested by the analytic model, where ΔE is the total energy deposited per molecule in the track, U is the cohesive energy of the solid, n_m is the molecular number density (so that $n_m^{-1/3}$ is the molecular dimension), and L is the sample thickness.[6] Results for

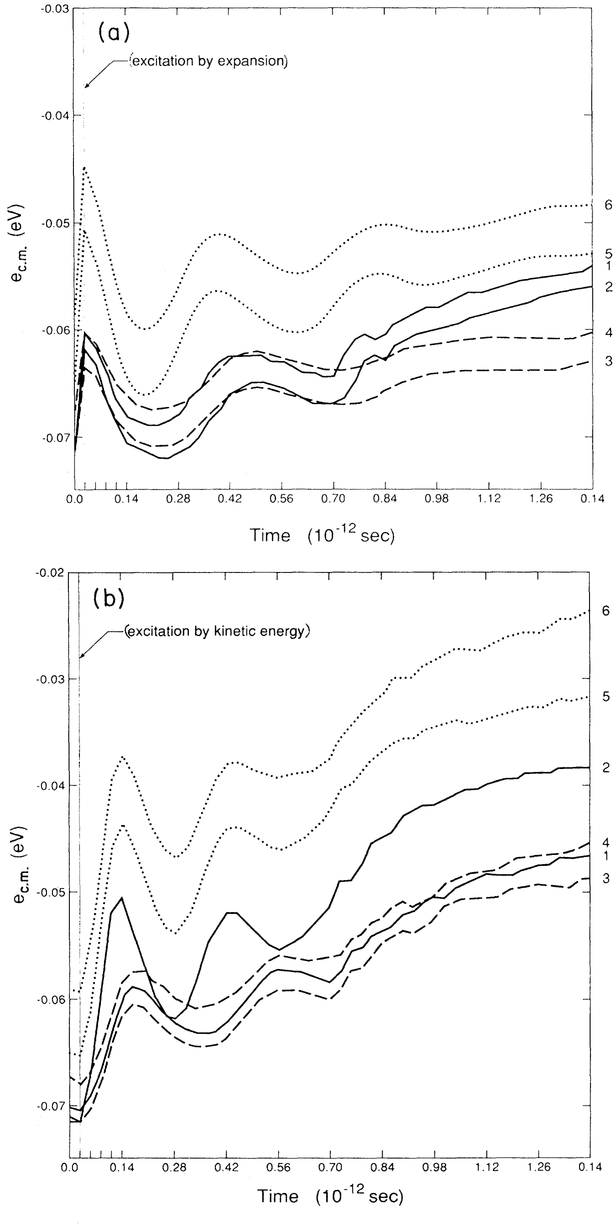

FIG. 2. (a) Time evolution profile of average c.m. energy per molecule for various samples as labeled (parameters given in Table I). Results are for track molecules undergoing an initial expansion for an density of energy deposited at 0.25 eV/molecule in the track. (Note that calculations for samples *S*1 and *S*2 are from Ref. 7; the times have been corrected by dividing by $\sqrt{2}$.) (b) Time evolution profile of total c.m. energy for various samples as labeled (parameters given in Table II). Results for track molecules with an initial kinetic energy for density of energy deposited at 0.5 eV/molecule in track.

TABLE II. Energies and yields in sputtering as a result of initial expansion.[a]

Sample	Percent expansion	$\frac{\Delta E^0_{\mathrm{int}}}{UN_T}$ [b]	$\frac{\Delta E^0_{\mathrm{com}}}{UN_T}$	$\frac{\Delta E^f_{\mathrm{int}}}{UN_T}$	$\frac{\Delta E^f_{\mathrm{com}}}{UN_T}$	Yield	Ratio[c]	Dissociation (quantities in parentheses are sputtered) species
$S1$[a]	50	2.31	0.52	1.58	1.31	6.5	0.49	0
	52	2.34	0.6	1.6	1.54	7	0.50	0
	55	2.50	0.72	1.7	1.57	10	0.49	0
	60	2.62	0.99	1.74	1.91	16.5	0.53	1(0)
	65	2.74	1.32	1.95	2.15	22.5	0.54	4(1)
$S2$[a]	52	2.37	0.50	1.64	1.30	9	0.43	0
	60	2.61	0.96	1.80	1.83	18	0.53	6(2)
	65	2.74	1.36	1.84	2.31	29.5	0.60	8(3)
$S3$	52	2.32	0.56	1.54	1.39	9	0.48	0
	57.5	2.49	0.79	1.72	1.61	19.5	0.49	$2(\frac{1}{2})$
	65	2.68	1.25	1.87	2.09	34	0.53	4(3)
$S4$	52	2.49	0.54	1.72	1.35	10	0.45	1(0)
	57.5	2.67	0.78	1.84	1.65	21	0.48	$5(3\frac{1}{2})$
	65	2.87	1.24	1.99	2.14	40	0.52	10(5)
$S5$	42	2.19	1.33	1.94	1.62	23	0.46	0
	45	2.33	1.58	1.52	1.94	31	0.41	1
	50	2.54	2.08	1.95	2.70	45.5	0.58	4(2)
	55	2.72	2.73	2.24	3.26	62	0.60	9(4)
$S6$	42	2.41	1.37	2.06	1.76	19	0.47	0
	45	2.57	1.62	2.25	1.99	27	0.42	2(1)
	50	2.80	2.14	2.21	2.76	50	0.56	2(1)
	55	3.0	2.8	2.53	3.35	77	0.58	12(7.5)

[a] Results from Ref. 7.

[b] ΔE is energy added; N_T is number of track molecules; change in total ΔE indicative of overall accuracy (~1–8 %).

[c] Ratio of $(\Delta E^f_{\mathrm{com}}/U)/[(\Delta E^0_{\mathrm{int}}/U)+(\Delta E^0_{\mathrm{com}}/U)]$.

the same samples are connected by lines, and the previous calculations[7] are also displayed. (Note that in Fig. 2 of Ref. 7 the x axis should be multiplied by 10^8.) Also, here we have averaged the yield for ejection from the "top" and "bottom" surfaces when there is no substrate which changes the lowest data point in Ref. 7. The higher yields seen in Fig. 3 for the excitation by an initial expansion are due primarily to the smaller D_e used and in part due to the initial repulsion (viz., Fig. 2).

The range of ΔE values for each sample in Fig. 3 is not large because of the limit on the size of the samples for which a calculation can reasonably be carried out. However, the yields in Fig. 3 can be roughly represented by

$$Y \approx C\left[\frac{\Delta E}{n_m^{1/3} LU}\right]^n . \tag{3}$$

Here $n=3.3\pm0.04$ for excitation by expansion, $n=3.4\pm0.03$ for kinetic-energy excitation, and C depends on sample properties other than n_m and U (e.g., thickness). The average n over the range shown is somewhat steeper than the cubic dependence found by Fenyö *et al.*[6] and the pressure-pulse model[1] for an infinite track. However, it is much larger than the three-halves power predicted in the standard "shock" model.[3,17] In Fig. 3 it is seen that the slopes, hence n, tend to decrease at the largest energy depositions, becoming more consistent

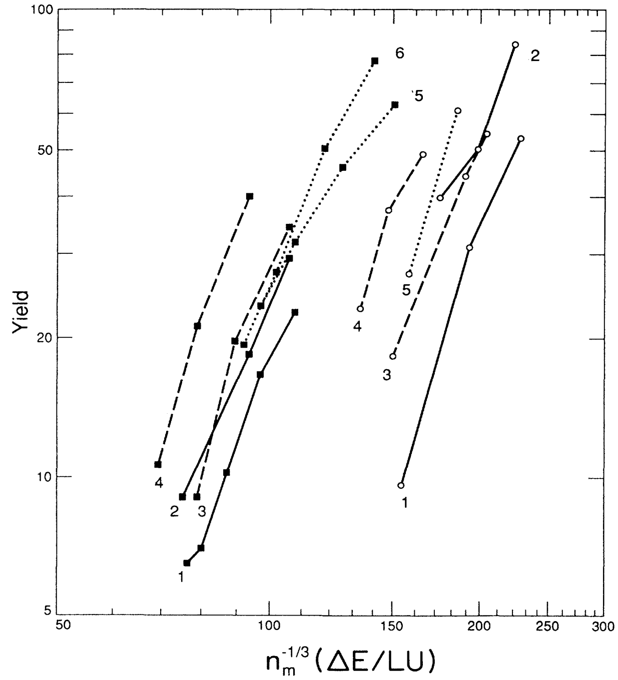

FIG. 3. Yield (Y) vs total energy density deposition $n_m^{-1/3}(\Delta E/LU)$ for initial expansion (solid squares) and initial kinetic energy (open circles).

with the $n=3$ prediction.[1] At low excitation densities the track width is important,[4] consistent with the yields decreasing more rapidly with decreasing excitation density until sputtering essentially ceases. A rough "threshold" value was found below which there is little or no sputtering in the times of interest. This threshold value depends on the strength of the intramolecular Morse potential, sample thickness, and the mode of excitation (viz. Table III).

For the energy densities studied here, ranging from a threshold for sputtering to an energy slightly above the top of the Morse well, the sputtered molecules are mostly vibrationally excited molecules from the cylindrical track. Although these are initially highly excited, only a fraction of the ejected molecules are dissociated (viz. Table II). In the calculations of Fenyö *et al.*,[6] large numbers of nontrack particles are ejected for the largest yields. However, they have also shown that the rate of expansion of the molecules in the track[12,16] significantly affects the yields. Since a large fraction of the initial excitation energy remains in the internal modes *and* because of the finite excitation time (int. to c.m. conversion), the process described here corresponds to the lowest excitation densities of Fenyö *et al.*[6] Since the amount of energy transfer and rate of transfer depend on the excitation density and the potential well shapes, the energy transferred to c.m. is a more relevant quantity for determining the yield than ΔE in Eq. (3).

It is also seen in Fig. 3 that the *shapes* of the curves are not significantly affected by the sample thickness, with the reflecting substate equivalent to increased thickness. Based on Ref. 6, the yield for the thickest samples used here with reflecting boundaries is close to the thick-sample limit.[4,18]

In Ref. 7 the track molecules of sample $S1$ were given an initial kinetic energy of 0.20 eV per molecule, for an intramolecular potential with a well depth which is $\frac{1}{20}$ that of true oxygen. In the calculations here we *doubled* this well depth and found that, for the same level of excitation, the *energy sharing took longer.* This is due to the smaller repulsion (i.e., smaller anharmonicity, excitation energy divided by well depth). This is also indicated by the significant differences in the yield for two different internal well depths in Fig. 3. Not surprisingly, roughly twice the amount of internal energy is required when the well depth is doubled to produce the yield in Ref. 7. Finally, for a kinetic energy of 0.3 eV per molecule (see Table III), for $S5$ there was no sputtering and the energy transferred to the c.m. mode was only 16% of the total in 4.8 ps. This indicates, as stated, the presence of a threshold below which prompt sputtering essentially does not occur.

These results show that "repulsion" between neighbors determines ejection, consistent with the one-dimensional calculations of Lee and Lucchese:[10] i.e., energy transfer increases in efficiency with increasing anharmonicity as suggested by Williams and Sundqvist.[5] Large anharmonicities imply strong interactions with neighbors, so that

TABLE III. Energies and yields in sputtering when track molecules have initial kinetic energy.

Sample	Kinetic energy per molecule (eV)	$\dfrac{\Delta E^0_{\text{int}}}{UN_T}$ [a]	$\dfrac{\Delta E^0_{\text{com}}}{UN_T}$	$\dfrac{\Delta E^f_{\text{int}}}{UN_T}$	$\dfrac{\Delta E^f_{\text{com}}}{UN_T}$	Yield	Ratio[b]	Dissociation (quantities in parentheses denote sputtered molecules)
$S1$	0.40	5.71	0	4.46	1.69	9.5	0.30	0
	0.51	7.21	0	4.79	2.70	36	0.37	4(2)
	0.60	8.49	0	4.87	3.85	54	0.45	9(9)
$S2$	0.45	6.70	0	4.68	2.35	40	0.35	0
	0.51	7.54	0	4.62	3.24	49	0.43	0
	0.58	8.56	0	4.42	4.43	80	0.52	1
$S3$	0.40	5.50	0	4.13	1.81	18	0.33	0
	0.51	6.96	0	4.35	2.87	43	0.41	0
	0.54	7.48	0	4.24	3.39	54	0.45	6(1.5)
$S4$	0.40	5.93	0	4.52	1.83	22.5	0.31	1(0)
	0.45	6.48	0	4.48	2.33	37	0.36	0
	0.51	7.29	0	4.71	2.84	48	0.39	7(5)
$S5$	0.30	4.66	0	4.18	0.74	0	0.16	0
	0.40	6.21	0	4.77	1.76	27	0.28	0
	0.51	7.85	0	4.69	3.47	60.5	0.44	0
$S6$	0.51	8.63	0	4.97	3.97	60	0.46	1(1)
$S7$	0.45	6.43	0	4.69	2.12	21	0.33	0
	0.51	7.21	0	4.79	2.70	36	0.38	4(2)
$S1$[c]	0.20	2.89	0	1.43	1.46	8	0.51	0

[a] ΔE is energy added; N_T is number of track molecules; change in total gives order of overall accuracy ~ 1–$8\,\%$.

[b] Ratio of $(\Delta E^f_{\text{com}}/U)/[(\Delta E^0_{\text{int}}/U)+(\Delta E^0_{\text{com}}/U)]$.

[c] Results of Ref. 7 (well depth of Morse potential$=0.25$ eV).

efficient energy transfer between "mismatched wells" can occur in spite of the "energy gap law."[16,19] The rate and amount of energy transfer are determined by the density of excitation.

Regardless of the initial mode of excitation of the track molecules, the yield for "prompt" sputtering depends on the energy transfer to the c.m. in times less than about 5×10^{-12} s. There will be, in addition, late contributions for the small molecules caused by sublimationlike processes which occur during energy dispersal.[1] However, the sample sizes are too small and the computation times needed are too large to study this via MD. Such effects, however, are thought to dominate the total sputtering yield of a true oxygen solid.[1,2,13]

V. CONCLUSIONS

For the amorphous diatomic solid constructed here, we find that a high density of the vibrational excitation of molecules in a cylindrical volume can result in rapid energy transfer to center-of-mass motion and prompt ($<10^{-11}$ s) ejection of a volume of molecules. These calculations were performed in order to understand the role of intramolecular-to-intermolecular energy transfer in a highly excited region having a geometry like that produced by a fast, heavy ion penetrating a solid. The results suggest that electronic excitations produced by a fast ion which lead to excitation of internal modes can produce a prompt volume ejection component to the sputtering yield. Such a component was studied by Fenyö *et al.*[6] by physically expanding the particles in the track. Here compressible particles are used.

Significant internal excitations are necessary for ejection to occur for the samples used here. Larger excitation densities are required to obtain yields comparable with Fenyö *et al.*[6] due to the residual vibrational energy and the time for internal to c.m. energy conversion.[16] Over the narrow range of $(\Delta E/L)$ studied for each sample, the yields for all samples show a somewhat steeper dependence on the energy density deposited than that produced by the track of instantaneously expanded, rigid molecules,[6] and steeper than that predicted by the analytic, pressure-pulse model,[1] which assumes instantaneous excitation of point particles in a narrow track. Earlier, it was shown that a finite track width can result in a steeply decaying threshold region at low excitation density.[4] This threshold is also determined by the rate of excitation of c.m. motion. Finally, the yields calculated here were also found to be independent of molecular mass, consistent with the analytic models.[1,3]

Because these studies are roughly consistent with aspects of the analytic model[1,16] and the simpler calculation using expandable spheres,[6] the latter can be used with some confidence if the expansion is carried out over the appropriate time period represented in Fig. 1. That is, the primary effect found here of using excited compressible particles is *to determine the amount and rate of transfer of energy from internal to center-of-mass motion.* This is seen to depend on the excitation density[16] and repulsion between neighbors via the anharmonicity.

The dependence of the yield on excitation density is different from that predicted by the shock-wave mechanism for prompt sputtering in the cylindrical geometry,[3] although it was recently suggested that the model can be amended.[3] It is also different from the dependence predicted by the "hydrodynamic" model[20] and the "thermal spike" models.[1,4] For the intermolecular spacings and internal well depths appropriate for a condensed solid sample of *true* oxygen, energetic dissociation would be required[7] before electronic sputtering would occur, as predicted.[2,4,13] Therefore, for low-temperature solid O_2, the prompt sputtering process studied here is dominated by late, sublimationlike sputtering in the region of energy density covered experimentally.[2,13] On the other hand for a solid consisting of large organic molecules, the molecular dimensions are much greater than the separation between their boundaries, and therefore the excitation of low vibrational states in the *large number of modes* available can also be effective in producing ejection.[5] The rapid transfer of internal energy into center-of-mass motion is due to the significant interaction between neighbors, here a result of the large anharmonicity produced by highly exciting the molecules. This effect can also be produced by repulsive dissociation of organic molecules.[21,22] The strong interaction and rapid energy transfer also quenches the vibrational excitation level[4] of the initially excited molecules. Therefore, the process studied here for a very simple molecular system should be favorable for the prompt sputtering of intact, thermally labile biomolecules. It is also of interest as a problem in continuum mechanics.

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