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Orientation Dependence in C_{60} Surface-Impact Collisions

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The effect of molecular orientation on collisions between C_{60}(buckminsterfullerene) and a solid surface was studied by carrying out simulations based on the Tersoff potential for the C−C interaction and modeling the surface by a structureless wall. Simulations were run with initial molecular kinetic energies of 100 and 300 eV, at impact angles relative to normal incidence of 10°, 20°, and 30°. The simple nature of the simulations permitted the examination of thousands of trajectories with random initial C_{60} orientations, in contrast to all previous studies, which have been highly limited in this respect. The data obtained included information about the redistribution of energy and angular momentum and about collisional fragmentation. The results are strongly dependent upon the initial molecular orientation and lead to wide distributions of the quantities studied. Since structured surfaces are expected to intensify the orientation dependence, it is concluded that one must use a substantial ensemble of trajectories to obtain meaningful average behavior. The ensemble averages are qualitatively similar to relevant experimental results and thereby support the conclusions advanced.

Introduction

Fullerenes have become popular as subjects for the study of surface-induced dissociation of hot polyatomic molecules, and a number of recent experimental investigations[1−6] have examined the collisions of energy-resolved fullerene ions with various solid surfaces. These experiments show that (1) the collisions are very inelastic, transferring large amounts of the incident kinetic energy into internal energy of a highly distorted structure; (2) for normal incidence at incident kinetic energies above about 150 eV per C_{60}^+ ion, many of the distorted ions eventually dissociate, with C_n^+ fragments detected for even n ranging from 58 to below 40 (as might be expected, collisions at grazing incidence cause nondissociative electron-transfer yielding neutral C_{60});[7,8] and (3) at energies at and above about 300 eV, a more immediate catastrophic fragmentation occurs, yielding a broad range of fragment sizes of both odd and even n.

In efforts complementary to the experimental studies, a number of investigators have sought to model the fragmentation and energy distribution using molecular dynamics simulations in which neutral C_{60} was caused to collide with a hydrogen-terminated[9,10] or bare[11] diamond(111) surface. Although these studies used rather different methods ranging from classical dynamics based on the now well-known Brenner potential[12] to tight-binding (TB) and density-functional quantum-mechanical approaches, they were consistent in their predictions of chemical reaction with surface hydrogen atoms. They also predicted significant conversion of initial kinetic energy into internal energy of the C_{60}, at lower incident energies without immediate rupture (termed resilience),[1] and at higher incident energies with more immediate fragmentation. Simulations of the collision of C_{60} with an Si(111) surface have also been reported recently (with the C_{60} bare, within a C_{240} cage, or surrounded by xenon).[13] These simulations predicted resilience and fragmentation at the same energy ranges as in collisions with diamond(111).

Recently Hsiao et al.[14] reported a study in which a number of semiempirical quantum-mechanical Hamiltonians were applied to collisions of C_{60} with a passive surface, which was described by a position-dependent potential acting on each atom of the incident molecule. Comparison among the semiempirical methods and with tight-binding calculations on the same system indicate that methods based on the neglect of differential diatomic overlap (NDDO) can satisfactorily reproduce the features of tight-binding calculations and have the additional advantage that they offer promise of providing a useful description of bond-breaking effects that cannot be treated well by TB methods. It is obvious that the use of the passive surface simplified the simulations and facilitated the exploration of semiempirical methods that are far more computationally intensive than TB or the use of classical potentials.

Both the simulations of Hsiao et al. and those of the earlier workers were severely limited in their exploration of the collision phase space. The early work of Mowrey et al.[9] was restricted to normal incidence. The impact point on the surface was chosen randomly for each of 50 trajectories at each incident energy, but there is no indication of a distribution of C_{60} orientations. Blaudeck et al.[10] studied only one impact angle (20° from normal) and considered three relatively symmetrical C_{60} orientations: pentagon toward surface, hexagon toward surface, and C−C bond toward surface. Galli and Mauri[11] studied only normal incidence at a single C_{60} orientation. Hsiao et al.[14] also examined a single C_{60} orientation, but with impact angle 20° from normal. These limitations are hardly surprising in view of the computational intensity arising, for some investigators, from the complexity of the solid surface and, for others, from the complexity of the quantum-mechanical methods.

It is the aim of the present study to investigate the effect of C_{60} orientation and impact angle on the collisions of the molecule with a model surface. Because the experiments with which simulations can be compared involve collisions of C_{60} ions rather than the neutral C_{60} that have been the subjects of

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all the calculations, neither the previous studies nor that to be reported here can expect complete agreement with experiment. What we are, however, able to show is that orientation and impact-angle effects can be expected to lead to fairly broad distributions of center-of-mass kinetic energy, angular momentum, and fragmentation patterns and that meaningful analyses require the use of a sufficiently large ensemble of trajectories. To accomplish our objective, we used a passive surface similar to that employed by Hsiao et al., describing the atom−atom interactions within the C_{60} molecule by the empirical classical potential introduced by Tersoff.[15] In view of the fact that the collisions cause energy redistributions that are large compared with ambient thermal energies, we concluded that we would learn little from simulations at different temperatures and confined our study to zero temperature. These choices made it practical to examine thousands of trajectories at each selected impact angle and incident energy. The remainder of this paper describes our work in more detail.

Simulations

Simulations were carried out with a classical molecular dynamics program written by one of the authors (F.E.H.), modified from a program by another of the authors (H.-P.C.) to insert a passive wall and permit the accumulation of statistical data from multiple trajectories. The C atoms interact with each other according to the Tersoff potential with its recommended parameters,[15] and each atom interacts with the wall according to the model potential used by Hsiao et al.:

$$V = V_0[1 - \tanh(\gamma z)] \tag{1}$$

where z is a Cartesian coordinate of the atom, $V_0 = 100$ hartree, and $\gamma = 1.0$ bohr^{-1}.

Trajectories were started with the C_{60} at large enough positive z that its interaction with the wall was negligible and with internal coordinates corresponding to the equilibrium structure predicted by the Tersoff potential (which is quite close to that observed experimentally). The initial orientation of the C_{60} with respect to the wall was set for each trajectory by applying a random rotation to a standard orientation. The atoms were assigned a uniform initial velocity consistent with the desired impact orientation and molecular kinetic energy.

The system was propagated in time by a sixth-order Gear predictor−corrector method[16] with time steps of $0.1t_0$, where our unit of time (related to mass in atomic mass units, energy in hartree, and length in bohr) is $t_0 = 1.033$ fs. Except as noted otherwise, trajectories were run for 10 000 steps (slightly over 1 ps). The adequacy of the simulation methods is confirmed by stability in the computed total energies to six figures over extended time periods.

For the purpose of defining molecular fragments, atoms were regarded as members of the same fragment if their separation was within the outer cutoff of the Tersoff C−C potential (2.1 Å). The fragmentation was analyzed on the basis of the atom positions at the ends of the trajectories.

Results and Discussion

Our standard ensemble consisted of 1000 trajectories with random C_{60} orientations at a specified impact angle and incident center-of-mass (CM) kinetic energy. We examined impact angles 10°, 20°, and 30° from normal incidence, at CM kinetic energies 100 and 300 eV.

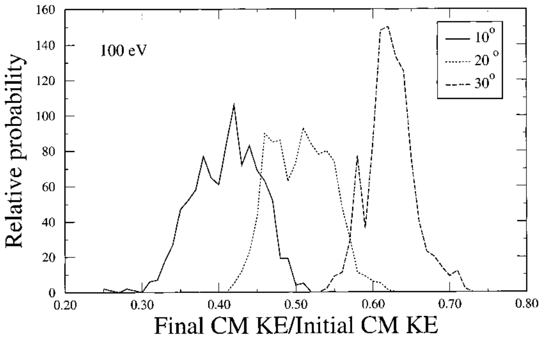

Figure 1. Distribution of the ratio of final to initial CM kinetic energy for 100 eV collisions with model surface, for ensembles of trajectories at random molecular orientations at the indicated impact angles relative to normal incidence.

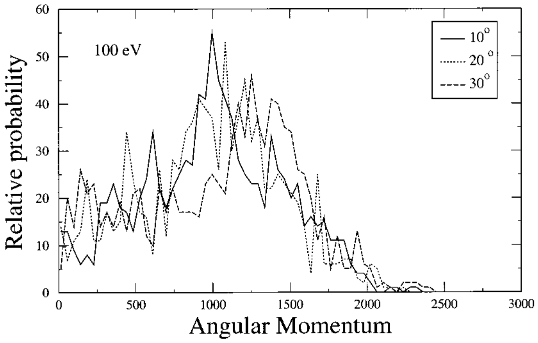

Figure 2. Distribution of the magnitude of the final angular momentum (in units of $\hbar$) about the CM, for 100 eV collisions with model surface, for ensembles of trajectories at random molecular orientations at the indicated impact angles relative to normal incidence.

100 eV. Collisions at this energy did not lead to fragmentation during the simulation time, nor was fragmentation observed in a small number of trajectories extended to 40 000 steps (∼4 ps). As shown pictorially by Mowrey et al.,[9] the collision distorts the C_{60}, but the incident kinetic energy does not become locally concentrated enough to break the molecule. C_{60} has with the Tersoff potential a binding energy of 6.75 eV/C atom or, if we ignore the difference between the two distinct C−C bonds in C_{60} (there are 45 of each), a bond strength of 4.50 eV. Both these energies are considerably larger than each atom's share of the incident kinetic energy (approximately 1.67 eV/C atom). These numbers may help to explain why the net result is a transfer of a portion of the incident energy into vibrational and rotational excitation. This observation is consistent with the experimental studies of C_{60} ions in the 100 eV collision range.

The details of the simulated energy transfer depend strongly upon the impact angle and the molecular orientation. Figure 1 shows the distribution of final CM kinetic energies for each of the impact angles investigated. At 10° from normal incidence, roughly 60% of the incident CM kinetic energy is transferred on average into internal energy. At impact angles 20° and 30° from normal, the average energy transfers are respectively about 10% and 20% less. It is significant, and not adequately revealed by previous investigations, that the amount of energy transferred is a sensitive function of the C_{60} orientation, even when (as here) the collision is with a structureless surface. The result is that the distributions of final CM kinetic energies are rather broad, encompassing as much as 20% of the incident energy.

A further indication of the complexity of the collision process is provided by an examination of the extent to which the energy transfer produces molecular rotation. In Figure 2 are plotted distributions of the magnitude of the final molecular angular momentum for each of the impact angles. We have chosen to report the angular momentum in units of $\hbar$, so the large numbers

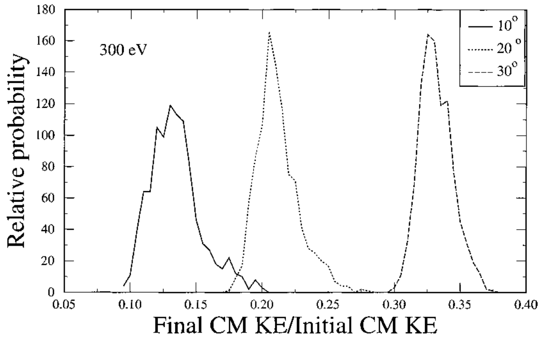

Figure 3. Distribution of the ratio of final to initial CM kinetic energy for 300 eV collisions with model surface, for ensembles of trajectories at random molecular orientations at the indicated impact angles relative to normal incidence.

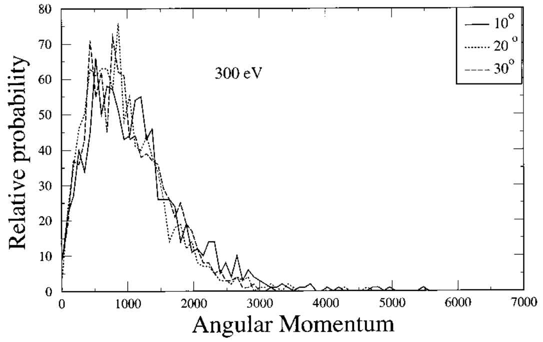

Figure 4. Distribution of the magnitude of the final angular momentum (in units of $\hbar$) about the CM, for 300 eV collisions with model surface, for ensembles of trajectories at random molecular orientations at the indicated impact angles relative to normal incidence.

are consistent with classical rotation. We see that the asymmetry associated with random C_{60} orientation leads to significant amounts of angular momentum with a wide distribution, even for nearly normal incidence.

300 eV. At this energy, the situation is more complex because the collisions lead to fragmentation. The incident CM kinetic energy, 5.0 eV/C atom, is now comparable with the C_{60} binding energy per atom and larger than the average bond energy. Figure 3 presents the final CM kinetic energy distributions for the three impact angles studied. In qualitative agreement with experimental investigations, we see a transfer of most of the incident CM kinetic energy, ranging on average from about 85% at 10° to somewhat over 65% at 30°. Again we note that the distributions have significant width (between 7% and 10% of the incident energy). In Figure 4 we show the angular momentum distributions for these trajectory ensembles. The distributions are broad and less dependent on impact angle than at 100 eV, presumably an effect of the more violent collision.

We observed fragmentation for all incident orientations at all three impact angles but obtained specific results that were highly orientation-dependent. The distribution of fragment sizes is shown in Figure 5. Note that individual collisions at different C_{60} orientations produce different sets of fragmentation products, so that the entire distribution cannot be determined from a small number of trajectories. This fact is signaled to an alert reader by the occurrence of small numbers of fragments of many sizes larger than 30; at 300 eV, most of the collisions produce one larger cluster (usually between 20 and 40 atoms) and an average of about eight or nine smaller fragments. These fragmentation patterns are qualitatively similar to those observed experimentally for C_{60} ions.

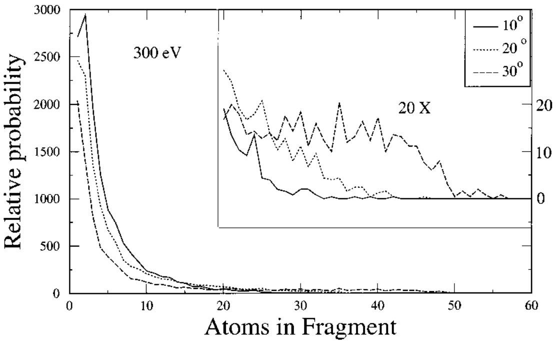

Figure 5. Distribution of fragment sizes after 300 eV collisions with model surface, for ensembles of trajectories at random molecular orientations at the indicated impact angles relative to normal incidence.

TABLE 1: Energy and Angular Momentum Distributions of Clusters Formed by Simulated Collisional Fragmentation of C_{60}[a]

n	N	$\langle V\rangle$, eV	$\langle E\rangle$,[b] eV	σ_E, eV	$\langle L\rangle$	σ_L
2	237	−2.41	−1.88	0.49	63	35
3	132	−3.06	−2.34	0.49	126	65
4	94	−3.35	−2.67	0.38	181	91
5	52	−3.67	−2.97	0.35	215	125
6	47	−3.80	−3.02	0.41	323	158
7	26	−3.93	−3.16	0.41	331	149
8	24	−4.01	−3.21	0.35	339	143
>16	91	−4.39	−3.54	0.19		

[a] For details, see text. The number of C atoms in the fragment is n, the number of fragments this size in the sample is N, the mean potential energy per atom is $\langle V\rangle$, the mean total internal energy per atom is $\langle E\rangle$, its standard deviation is σ_E, and the mean magnitude of the fragment angular momentum (in units of $\hbar$) is $\langle L\rangle$, with standard deviation σ_L. [b] With the potential used, $\langle E\rangle$ for zero-temperature C_{60} is −6.75 eV/atom.

The fragmentation process typically begins immediately after the collision, usually initially yielding a few small clusters and one or two larger clusters. During a subsequent period lasting a fraction of 1 ps, many of the larger clusters further fragment; thereafter, little additional fragmentation was observed. We confirmed this observation by extending a few trajectories to 40 000 steps (~4 ps) and by the further analysis reported below.

To more completely understand the energy-transfer process, we ran an ensemble of 100 trajectories at impact angle 20° and incident CM kinetic energy 300 eV, extending the simulation for 20 000 steps (~2 ps, twice the number used in our standard procedure). For these trajectories we conducted a more complete analysis of the fragments and their energetics. Within statistical limits, the fragmentation patterns were similar to those of our main studies, indicating that significant fragmentation did not take place during the second picosecond of the trajectory.

For each of the 798 clusters produced from the above-described ensemble and containing more than one C atom, we calculated from the final atomic positions and velocities its CM kinetic energy, potential energy, total energy, and angular momentum about its CM. We then computed its binding energy per C atom as (CM kinetic energy-total energy)/(cluster size). For clusters of sizes 2−8, our sample contained a population we deemed large enough to generate meaningful statistics, and in Table 1 we give mean values of the potential energy per atom, and mean values and standard deviations for the binding energy per atom and the cluster angular momenta. The table also includes a similar analysis for all clusters of size greater than 16 atoms (taken together as a group). Less complete statistical information is presented in Table 2 for clusters of intermediate size. In addition, for each trajectory of the ensemble

TABLE 2: Energy Distributions of Intermediate Sized Clusters Formed by Simulated Collisional Fragmentation of C_{60}[a]

n	*N*	⟨*V*⟩, eV	range of *E*, eV	⟨*E*⟩,[b] eV
9	19	−4.00	−(2.58−3.65)	−3.16
10	13	−4.04	−(2.88−3.51)	−3.21
11	11	−4.15	−(3.07−3.67)	−3.37
12	18	−4.08	−(2.83−3.59)	−3.35
13	10	−4.10	−(3.18−3.70)	−3.40
14	11	−4.30	−(3.07−4.19)	−3.54
15	7	−4.15	−(3.16−3.67)	−3.35
16	6	−4.21	−(3.29−3.75)	−3.48

[a] For details, see text. The numbers of fragments of these sizes are too small to support analyses of variance. The number of C atoms in the fragment is *n*, the number of fragments this size in the sample is *N*, the mean potential energy per atom is ⟨*V*⟩, range of *E* is that of the total internal energy per atom, and ⟨*E*⟩ is its average value. [b] With the potential used, ⟨*E*⟩ for zero-temperature C_{60} is −6.75 eV/atom.

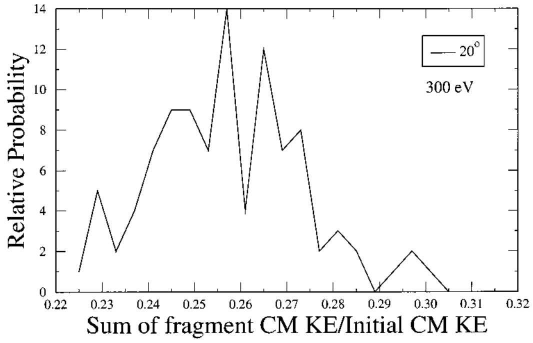

Figure 6. Distribution of the ratio of the sum of the final fragment CM kinetic energies to the initial CM kinetic energy after 300 eV collisions with model surface, for an ensemble of trajectories at random molecular orientations at an impact angle of 20° relative to normal incidence.

we calculated the sum of its fragments' CM kinetic energies, the distribution of which is shown in Figure 6. This distribution is shifted to higher energy than that in Figure 3, indicating that only a portion of the CM kinetic energy transfer was to internal energy of the fragments. The discrepancy, of course, is due to the fact that the fragments are not all moving in the same direction.

The additional data show, as expected, that the fragments are generally in states fairly far from those of minimum potential energy but that on average they are fairly securely bound. The binding energy per atom increases to some extent with cluster size, but this is to be expected from the fact that larger clusters will have a higher ratio of bonds to atoms. All the collisions have destroyed the energetically favorable structure of the original C_{60} molecule. We also see, from Figure 6, that a significant fraction of the initial CM kinetic energy remains as CM kinetic energy of the fragments, reducing the amount of energy available for further fragmentation. One additional observation, not reflected in the tables, is that two of the 798 clusters (both diatomic) had negative binding energies and therefore will dissociate after the elapse of sufficient time. Very few of the polyatomic clusters had extremely small net binding energy.

Conclusions

A classical simulation of C_{60} surface-impact collisions is capable of reproducing the broad outline of comparable experimental data even if the surface is modeled by a structureless wall. However, even though the wall has no atomic structure, the detailed results depend strongly upon the C_{60} orientation as well as the controllable experimental parameters. We argue that this orientation dependence can be expected to persist, and perhaps intensify, if comparable simulations were carried out for more realistic surfaces. We therefore conclude that meaningful results for simulations of the collisions of large molecules with surfaces necessarily require the examination of a large ensemble of trajectories, a condition that has not been met in simulations previously reported.

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