6124 J. Phys. Chem. 1993, 97, 6124–6126

ARTICLES

Numerical Simulation of He^+ and Li^+ Collisions with C_{60}

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Received: November 3, 1992; In Final Form: March 22, 1993

Classical molecular dynamics have been used to simulate He^+ and Li^+ collisions with C_{60} in free space and on an iron substrate. We observe the implantation of He^+ to form endohedral $He^+@C_{60}$ at various energies in the energy range 35–90 eV. Li^+ collisions with C_{60} do not form $Li^+@C_{60}$. Instead we found insertion and fragmentation to form $Li^+@C_{54}$ and $Li^+@C_{56}$ in the energy range 115–200 eV. The yield of any particular collision depends strongly not only on the incident energy but also on the incident angle and the point of impact and has a weak dependence on whether or not the C_{60} is on the substrate or in free space.

Since the recent discovery[1] of an efficient process for the synthesis of fullerenes, there has been a dramatic increase in interest in these compounds. Recent research efforts have focused on developing new fullerene-based materials. One method that has been investigated is the incorporation of dopants into the hollow cage structure of C_{60} through high-energy collisions.[2–7] Helium,[2–4] neon,[5] lithium, and sodium[6] have been successfully implanted into C_{60} using collision techniques. In this paper, we report on numerical simulations of high-energy collisions of He^+ and Li^+ with C_{60} in free space and on the surface of an Fe substrate. These calculations were undertaken with the intent to interpret and serve as a rough complementary guide to ongoing experiments by Zuhr and collaborators.[7] We believe that the results of the simulations provide at least qualitative insights into some of the fascinating possibilities in ion-implanting fullerenes.

Classical molecular dynamics (MD) is used to simulate the collision process. The interactions in the system were modeled by four different interaction potentials: the carbon–carbon in the C_{60} molecule, the ion–C_{60}, the C_{60}–substrate, and the ion–substrate image potential.

The carbon–carbon interactions were modeled by the Tersoff potential.[8] This potential has been used successfully by Ballone and Milani[9] to study the structure and stability of carbon clusters, C_n, $50 \leq n \leq 72$. We generated the equilibrium structure of C_{60} by using the conjugate gradient method to minimize the energy of a perfect 60 carbon atom truncated icosahedron with an initial diameter of 7.1 Å. The resulting structure has a radius of 3.68 Å with nearest-neighbor distances separated into two long pentagon edges $r_l = 1.50$ Å and one short hexagon edge $r_s = 1.45$ Å. NMR data[10] finds $r_l = 1.45 \pm 0.015$ Å and $r_s = 1.40 \pm 0.015$ Å which is 3.5% smaller than that predicted by the Tersoff model.

The ion–C_{60} interaction was approximated by considering each carbon atom independently. By combining the asymtotic limit for the ion interacting with a neutral carbon atom and the repuslive part of a Lennard-Jones potential for carbon and adjusting for the ionic radius, we constructed the carbon–ion interaction potential

$$V_{c\text{-}ion}(r) = 4\epsilon\left[\frac{1}{Z^2}\left(\frac{\sigma_{ci}}{r}\right)^{12} - \left(\frac{\sigma_{ci}}{r}\right)^{4}\right] \tag{1}$$

$$\epsilon = \frac{1}{8}\frac{\alpha e^2 Z^2}{\sigma^4} \qquad \alpha = {}^4/_3 \times 10^{-24}\ cm^3$$

$$\sigma_{ci} = (\sigma_c + \sigma_{ion})/2$$

where σ_c and σ_{ion} are the carbon and ionic diameters, and Z is the charge of the ion. We set $\sigma_c = 2.84$ Å,[11] $\sigma_{He^+} = 0.7935$ Å,[12] and $\sigma_{Li^+} = 1.36$ Å[13] and $Z = 1$. The short-range part is truly very rough. It reflects the overlap of the core of the incident ion with the carbon atom, at which point the exclusion principle demands a rapid increase in kinetic energy represented in the same way as in the case of two neutral atoms (the Lennard-Jones potential) by the $1/r^{12}$ term. A refinement of this short-range part of the interaction between the ion and the C_{60} complex could require much greater effort,[14] which might even require going beyond pairwise interactions.

The asymptotic part of the interaction at large r (i.e., $1/r^4$) is exact provided the polarizability α (in eq 1) reflects the C_{60} complex; we take this value of α from experiment.[15] The $1/r^4$ asymptotic form derives as follows: (a) Introducing the perturbation potential of the ion $V_\lambda(\mathbf{r}) = -\lambda Ze^2/r$ (where r is the distance from the ion to the center of a carbon atom and λ is a scaling coupling constant), the Hellman–Feynman theorem leads to the following pair interaction:

$$V_{c\text{-}ion}(r) = \frac{1}{\lambda}\int_0^1 [n_\lambda(\mathbf{r}')V_\lambda(\mathbf{r}-\mathbf{r}')\ d^3r']\ d\lambda \tag{2a}$$

where $n_\lambda(\mathbf{r}')$ is the induced density due to V_λ plus the point charge of the carbon nucleus. (b) Since we are in the asymptotic limit, $|\mathbf{r}'| < |\mathbf{r}|$ and

$$V_\lambda(\mathbf{r}-\mathbf{r}') = -\frac{\lambda Ze^2}{r} - \frac{\lambda Ze^2}{r^3}(\mathbf{r}\cdot\mathbf{r}') + \ldots \tag{2b}$$

which when used in eq 2a and integrated over d^3r' leads to

$$V_{c\text{-}ion}(r) = \int_0^1 Q_\lambda \frac{Ze^2}{r^2}\ d\lambda \tag{2c}$$

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0022-3654/93/2097-6124$04.00/0

where Q_λ is

$$Q_\lambda \equiv \int n_\lambda(\mathbf{r}')\hat{r}\cdot\mathbf{r}'\, d^3r' \tag{2d}$$

(c) Finally since in the asymptotic limit Q_λ is equal to the electric field $\lambda Ze^2/r^2$ multiplied by the polarizability α of the C_{60} complex, we get at once (using eq 2c) the $1/r^4$ term of eq 1.

MNDO[16] calculations for Li^+–C_{60} systems provide some interesting comparisons with our classical potentials. Both the MNDO and our calculations predict a minimum for the Li^+ inside the C_{60} cage at about 1.9 Å from the center of the six-membered ring. MNDO predicts energy barriers for passage through the six-member and five-member rings of 7.3 and 10.3 eV, respectively. We predict 5.9 and 17.6 eV, respectively. Since our asymtotic limits at large r are exact, this result suggests that we are overestimating the short-range repulsive interactions, particularly in collisions at the center of the five-member rings. The barrier for the six-member ring compares favorably.

The C_{60}-substrate interaction was approximated by also treating each carbon atom imdependently. The attractive part was derived from the work of Zaremba and Kohn[17] on the polarization force between a neutral atom and a metallic solid surface. The repulsive part was again based on the Lennard-Jones type of repulsion and is very crude. We used

$$V_{c\text{-}substrate}(x) = B[(\sigma_{cs}/x)^{12} - (\sigma_{cs}/x)^3] \tag{3}$$

$$B = (8.2)(0.529/\sigma_{cs})^3, \qquad \sigma_{cs} = 2.19\ \text{Å}$$

where x is the distance from the substrate and the substrate is assumed to be iron. Using the conjugate gradient method to minimize the energy of the C_{60}–substrate system, we found a bonding energy of ~0.84 eV.

The final contribution to the interaction potential for the incoming ion results from the image potential. Following the work of Lang and Kohn,[18] the ion–substrate interaction is approximated as

$$V_{is}(x) = -\frac{A}{x - x_0} \qquad \text{for } x > 2.5\ \text{Å}$$

with $A = 3.57$ eV and $x_0 = 0.8464$ Å, where x_0 is the correction to the classical image plane due to the details of the surface electron density[18] and the effect of exchange and correlations (see Rasolt and Perrot[19]).

At this point, it is appropriate to raise a significant caveat with respect to the potential model. There has been both experimental[20] and theoretical[21] work that suggests that on some metal surfaces, there may be a transfer of at most 1–2 electrons from the metal to the adsorbed C_{60}. This clearly would change the asymptotic part of the ion–C_{60} potential, as well as the substrate–C_{60} interaction. However, because of the high energies and short time scales of these collisions, the results of any collision are primarily determined by the short-range ion–C interaction. The other, longer-ranged portions of the potential will affect quantitative details such as the impact energy at which an ion–fullerene compound might be knocked off the substrate. In particular, our modeling of the substrate–C_{60} interaction without charge transfer at most underestimates the strength of the interaction. The only significant effect of this assumption is that the calculations might predict the product of the collisions would be knocked off the substrate when in fact they remain on the surface. This would be most significant for the Li^+ implants where all the Li^+–fullerene complexes are knocked off the substrate at the energies at which insertion occurs. Furthermore, only isolated C_{60} molecules on the substrate are considered. It is possible to have multilayer C_{60} films as well. The experiments of Ohno *et al.*[20] indicate that any charge transfer is largely confined to the first layer of buckyballs, which raises the spectre of yet another "substrate"–C_{60} potential for multilayer films. Given present uncertainties, we decided to keep these initial calculations simple and limited, and the calculations for collisions with the C_{60} on the substrate should be used with this understanding of the limitations of the C_{60}–substrate potential.

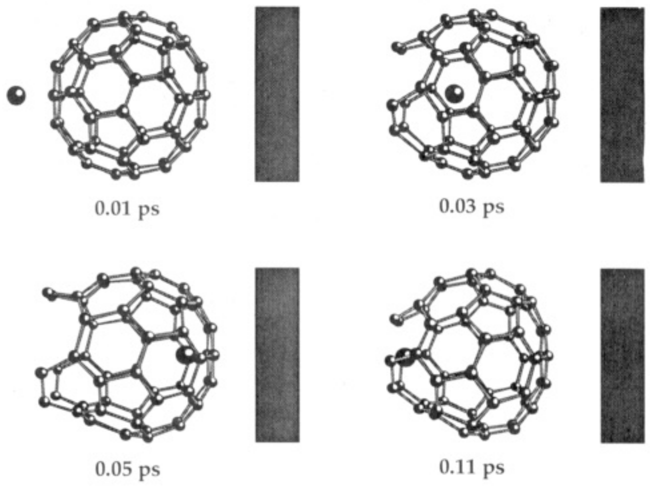
The C_{60} was aligned with the axis of either the five-member or six-member ring normal to the substrate. Ions were collided with the bucky ball at the center of the ring with angles of 0°, 15°, and 30° relative to the ring axis. Collisions for the same geometry with C_{60} in free space were also simulated. Our intent was to determine an implantation path that would result in the insertion of the ion into the fullerene cage while causing the minimum damage. Naturally the center of the six-member ring offered the best possibility. The five-member ring was tested as well.

Molecular dynamics runs of 1–5 ps were carried out for each collision with time steps of 10^{-5} ps. In all cases, the C_{60} was initially at rest. While the presence of the substrate did effect the final configuration of the ion implanted fullerene in some collisions, the substrate interaction was most important in determining whether or not the fullerene ion complex remained on the substrate after the collision. While this is essential information for designing and interpreting ion implantation experiments, it is a question that we can only point to as important and give a rough idea of impact energy effects with and without a substrate.

For He^+ collisions with C_{60}, it was found that the ion could be inserted into the C_{60} cage without damaging the structure. This occurred through the six-member ring at normal incidence between 35 and 45 eV and at 15° incidence between 45 and 90 eV. We should add a word of caution. When the incident beam exceeds approximately 53 eV (i.e., the ionization energy of $He^+ \rightarrow He^{2+}$), eq 1 is no longer applicable. We need to take our results for insertions at energies above 53 eV with additional caution. The $He^+@C_{60}$ molecules[22] remained on the substrate in all cases. For the collisions considered at 30° incidence the He^+ was reflected from the C_{60}.

At 35 eV and normal incidence on the six-member ring, the He^+ ion's initial collision imparts sufficient energy to spread the carbon atoms apart while reflecting the ion back at low enough energy that it is trapped near the surface of the C_{60}. On the next oscillation, the He^+ passes through the spread apart carbon ring into the C_{60} cage. By the time it reflects off the back ring of the C_{60} and returns to the entrance point, the six-member ring has closed and the ion is trapped. At 40 eV and above the incoming He^+ has enough energy to push the six-member ring apart and directly enter the cage. Up to 45 eV, the process that keeps it inside the cage is the same as at 35 eV. At 50 eV, the energy of the He^+ is sufficiently great that it reflects off the back six-member ring and then back out the way it entered before the six member ring can close up sufficiently. Changing to 15° incidence prevents the He^+ from reflecting directly out through the six-member ring it pushed through to enter. Instead it rattles around in the cage and for the collisions considered it could be trapped for ion energies between 50 and 90 eV in free space and between 45 and 80 eV when on the substrate. The results of any particular 15° incidence collision depends not only on the angle relative to the six-member ring axis but also on the orientation of the ion collision path relative to the hexagonal face. For the 30° incidence collisions considered, the He^+ did not penetrate the six-member ring and no He^+ fullerene complexes were formed. To look at the dynamics of the events, we made computer animations of them. Figure 1 shows a few frames for a 45-eV He^+ collision at normal incidence on a six-member ring of the C_{60} molecule on an Fe substrate.

Normal incidence collisions of He^+ with the center of a five-member ring produced no He^+ fullerene complex. Up to 80 eV the He^+ reflected leaving the C_{60} intact. By 100 eV the He^+



0.01 ps 0.03 ps

0.05 ps 0.11 ps

Figure 1. The 45-eV He^+ collision at normal incidence with the six-member ring of a C_{60} molecule on an Fe substrate at 0.01, 0.03, 0.05, and 0.11 ps. The He^+ ion is indicated by the larger ball and the position of the substrate by the solid bar. The He^+ is trapped in the endohedral cavity of the C_{60}.

reflected, but the collision knocked off 10 carbon atoms. Higher energies only produced greater damage to the C_{60}.

In a number of experiments,[2–4] 8-keV C_{60}^+ is collided with a gas of helium atoms and $[He@C_{60}]^+$ is found. While the details of the interaction between C_{60} and He is different depending on which is ionized, the overall kinetics should be similar. Translating this experiment into a frame of reference where the C_{60} is stationary and the helium is moving corresponds approximately to 45 eV He. Our simulations for He^+ collisions with C_{60} in free space show direct insertion for normal incidence through the six-member ring at this energy. Other longer time scale processes for insertion are also possible. These are discussed later for the $Li^+@C_{60}$ system.

The Li^+ collisions with C_{60} did not result in any $Li^+@C_{60}$ molecules. We did find $Li^+@C_{54}$ for normally incident Li^+ on the six-member ring with energies in the 115–150-eV range and $Li^+@C_{54}$ as well as $Li^+@C_{56}$ for ions incident on the six-member ring at 15° incidence with energies between 170 and 200 eV. Again, core excitations need to be accounted for at these higher energies. Furthermore, it was found that the collision energies were sufficiently high that the $Li^+@C_n$ did not remain on the substrate. The $Li^+@C_{54}$ were formed by knocking off the atoms in the six-member ring through which it entered the molecule. The six carbon atoms were ejected as three C_2 molecules formed from the carbons connected by the shorter hexagon bonds. The $Li^+@C_{56}$ were formed by knocking two C_2 pairs (which were also formed from carbons with the shorter bonds) from the six-member ring on which the ion was incident. For the 30° incidence collisions considered the Li^+ was reflected and no Li^+ fullerene complex was formed. Similarly for normal incidence collisions with the five-member rings no Li^+ fullerene complex was formed.

At 115 eV, the lowest energy for formation of $Li^+@C_{54}$, the insertion process is similar to the 35-eV insertion of He^+ in that the incident ion is first trapped close to the surface before entering the cage. The initial collision imparts sufficient energy to the six members of the ring of knock them off while reflecting the ion back at very low velocity. When it oscillates back toward the C_{54} it has sufficient energy to enter the structure before it relaxes.

Experiments by Wan, Christian, and Anderson[6] in which Li^+ ions were collided with C_{60} vapor at 600 K showed a 6-eV barrier to formation of $Li^+@C_{60}$. In our simulations, when the C_{60} was equilibrated to 600 K in 10 ps runs with time steps of 10^{-4} ps and then collided with Li^+ ions in 5-ps runs with 10^{-5}-ps steps, there were no insertions. This suggests more complex longer time processes are responsible. Such processes would most likely occur on too long a time scale for molecular dynamics simulations to be feasible. The 6 eV experimental value for the barrier compares well with our calculated 5.9-eV barrier for the six-member ring.

Finally, the comparison with MNDO calculations suggests our ion–carbon potentials may overestimate the strength of the short-range interactions. As a result, our calculations for the implantation thresholds may be too high. The Li^+ collisions with C_{60} predicted that carbon atoms are fragmented in multiples of C_2. This type of fragmentation of C_{60} is consistent with experiment.[2–7]

Our calculations are for sufficiently short times that they essentially treat only mechanisms that can result in direct implantation during collisions. These mechanisms would be most important in ion implantation of solid targets such as C_{60} on substrates where multiple collisions are less likely.

Acknowledgment. We would like to acknowledge R. Zuhr for discussing his experiments with us. We would also like to acknowledge M. T. Robinson, E. W. Plummer, R. H. Compton, and R. E. Haufler for helpful conversations. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. M.K. was partially supported by Oak Ridge Associated Universities.

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