Large Scale Quantum Simulations: C_{60} Impacts on a Semiconducting Surface

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We present tight binding molecular dynamics simulations of C_{60} impacts on the reconstructed diamond(111) surface, carried out with an $O(N)$ method and with cells containing 1140 atoms. The results of our simulations are in very good agreement with experiments. Furthermore they provide a detailed characterization of the microscopic processes occurring during the collision and allow the identification of three impact regimes. Finally, the study of the reactivity between the cluster and the surface gives insight into the deposition mechanisms of C_{60} on semiconducting substrates.

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Since the discovery [1] of the unique stability of C_{60} molecules against surface induced fragmentation, the investigation of fullerene interactions with solid substrates has become an exciting field of research [2–9]. Collisions of C_{60} on several surfaces have been reported to induce no fragmentation of the impinging molecules, for initial kinetic energies E_k up to a few hundred eV [1]. This property is unprecedented in molecular-ion surface-induced phenomena and has earned C_{60} the name of *resilient* molecule.

Of particular interest is the case of C_{60} impacts on semiconducting surfaces which can form covalent bonds with the cluster. The study of these bonds is a challenging problem, from a fundamental point of view. Furthermore such an investigation is an essential prerequisite for the understanding of fullerene deposition on nonmetallic substrates. These deposition processes have recently been proposed [10] as a way of synthesizing thin films which would retain specific characteristics of the incident clusters.

In order to understand the physics of C_{60} collisions on solid substrates, it is crucial to reveal the processes occurring *at* the surface. Whereas these processes are difficult to probe experimentally [1], they can be investigated by computer simulations. Recently, simulations of C_{60} impacts on a hydrogenated diamond surface have been performed by using both classical potentials [6] and tight binding (TB) Hamiltonians [7]. The comparison between the results of the two studies and experiments [7,8] indicates that a quantum mechanical (QM) treatment is necessary in order to have an accurate description of the cluster-surface interactions.

Realistic simulations of C_{60} interactions with a surface require cells with at least several hundreds of atoms. Until recently QM computations for systems of this size have not been possible because of the computer time required by conventional algorithms, which grows as the cube of the number of atoms in the system (N). Indeed the only QM study reported to date [7] has been limited to small molecular dynamics (MD) cells. In the last two years, methods for electronic structure calculations and MD simulations have been introduced [11–13], which are based on algorithms whose computational workload grows linearly with the system size. These approaches [often referred to as $O(N)$ methods] have opened the way to QM-MD simulations of systems much larger than previously accessible and to the study of new problems.

In this Letter we present QM-MD simulations of C_{60} impacts on a semiconducting surface as a function of the molecule incident energy, carried out with an $O(N)$ method [12], and with MD cells containing 1140 atoms. Interatomic forces are described according to a TB Hamiltonian [14], derived from first principles (FP) calculations. We considered the (2×1) reconstructed diamond(111) surface. This surface can be expected to form bonds with the impinging C_{60}, since its uppermost layer contains threefold coordinated (3f) π bonded atoms; it therefore represents a good candidate for the study of covalent bonds between the fullerene and a semiconducting substrate. Our work constitutes the first QM study of such interactions and the first large scale TB-MD simulation based on an $O(N)$ methodology. The results of our calculations are in very good agreement with experiments carried out under the same impact conditions [1–5]. Furthermore they allow us to characterize the microscopic processes occurring during the collision and thus to identify three different impact-energy regimes.

In our calculations, we used the $O(N)$ method of Ref. [12]. This approach is based on an energy functional with implicit orthogonalization constraints and on a localized orbital (LO) formulation. We adopted the TB Hamiltonian ($\mathcal{H}$) proposed by Xu *et al.* [14,15]. The LOs were centered on atomic sites, extending up to second neighbors (in the notation of Ref. [12], $N_h = 2$) [16]. We simulated neutral C_{60} molecules colliding with a reconstructed C(111) surface at initial energies $E_k = 60$, 80, 120, 150, 180, 210, 240, 300, and 400 eV. Each of the nine runs lasted from 0.3 to 1 ps. The efficiency of the $O(N)$ algorithm allowed us to carry out all calculations on workstations. C_{60} impinged upon the surface at normal incidence, with a double bond between two hexagons facing a Pandey chain of the surface. The C(111) substrate was represented by a slab composed of 12 layers, each containing 90 C atoms. The dimensions of a layer were 22.72 × 21.86 Å in the x and y direction, respectively. The slab was terminated on each side by a reconstructed surface, and periodic boundary conditions were applied along x and y. Nine surface layers were allowed to move. According to the size of our MD cell and to the number of mobile layers, we estimate that the shock wave produced by a collision is echoed back to the impact region about 0.2 ps after the impact. This is the time interval during which we observe the formation of bonds between C_{60} and the surface. Therefore the characterization of the three impact energy regimes (ER's) proposed in the following is not affected by finite size effects.

Before starting the simulation of C_{60} collisions, we optimized the slab and the molecule geometries independently. Our results for the surface reconstruction [17] compare well both with those of a conventional [extended orbital (EO)] calculation using the same $\mathcal{H}$ [18], and with the findings of first principles (FP) computations [19]. The two characteristic bond lengths of C_{60} calculated within the LO formulation differed by 5% (single bond) and 2.5% (double bond) from those optimized with EO [17]. Also in this case the TB results [20] are in good agreement with those of FP calculations [21].

We now turn to the discussion of the different regimes of C_{60}-surface interactions which we observed in our simulations. For $E_k = 60$, 80, and 120 eV (low ER) the molecule does not form any bond with the surface [22]. The minimum distance between C_{60} atoms and the substrate D is approximately constant during the collision and very close to 2 Å, as seen in Fig. 1, where we show D as a function of the simulation time (t). The impact provokes large distortions in the fullerene cage: the cluster height is decreased from 7.0 to 3.9, 3.4 and 3.1 Å, for $E_k = 60$, 80, and 120 eV, respectively, and the flattened molecule adapts its shape to that of the reconstructed surface (see Fig. 2). For $E_k = 120$ eV, a few bonds of the molecule are broken during the collision, whereas no bond breaking is observed at lower energies. This can be seen in Fig. 3 which displays the number of differently coordinated sites of C_{60} as a function of t. In all of the three cases, after the impact the cluster

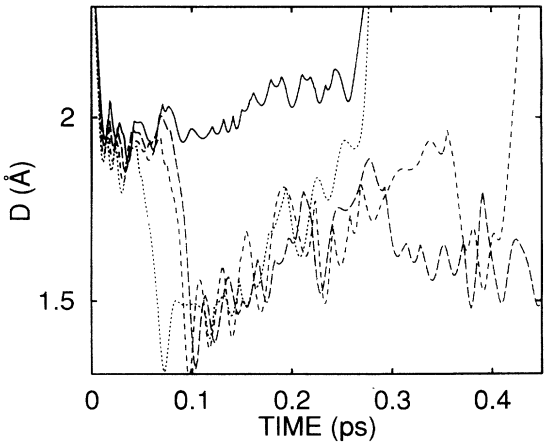

FIG. 1. Minimum distance (D) between C_{60} and the surface as a function of the simulation time: solid, long dashed, dashed, and dotted lines correspond to $E_k = 120$, 150, 180 and 210 eV, respectively.

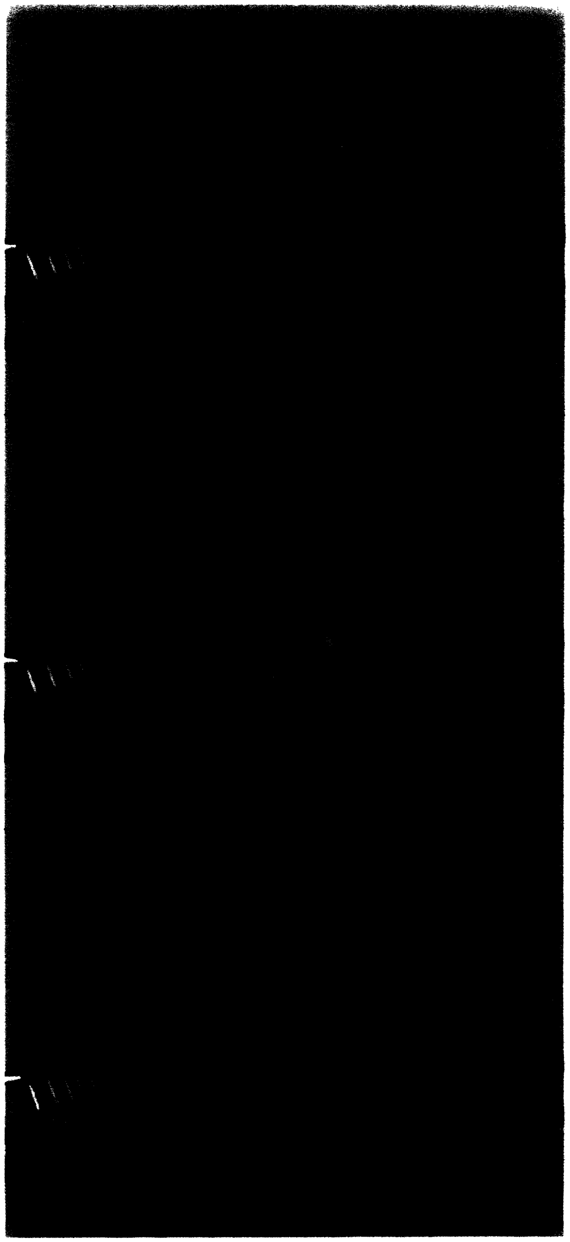

FIG. 2. Snapshots of the uppermost five layers of the slab and of C_{60} for different E_k and at given simulation times (t): $E_k = 120$ eV and $t = 0.14$ ps (upper panel); $E_k = 150$ eV and $t = 1.00$ ps (middle panel); $E_k = 300$ eV and $t = 0.33$ ps (lower panel). (See text.) Red and green spheres denote 3f and 4f atoms of the slab, and black spheres indicate C_{60} atoms.

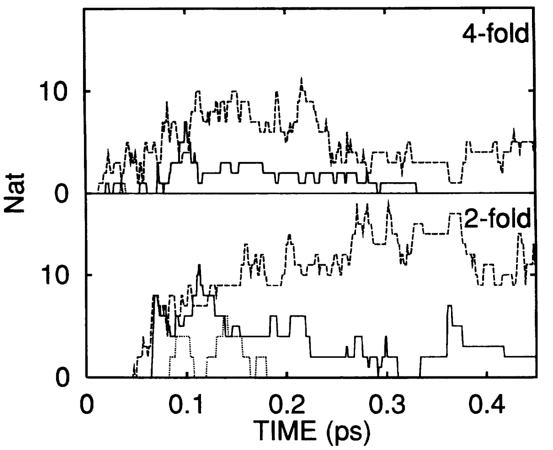

FIG. 3. 2f and 4f C_{60} atoms (N_{at}) as a function of the simulation time for selected E_k: dotted, solid, and dashed lines correspond to $E_k = 120$, 180 and 300 eV, respectively.

leaves the surface without any defect in the original cage. The kinetic energies of the center of mass (E_{cm}) of the outgoing molecule is displayed in Fig. 4. In this ER, E_{cm} shows a clear dependence upon E_k. In particular E_{cm} is proportional to E_k for incident energies up to 80 eV, i.e., in the energy interval in which no bonds of the cluster are broken.

For $120 < E_k < 240$ eV (medium ER), the molecule does not only suffer large distortions upon impact on the surface, but also forms bonds with the substrate. During the collision, some bonds of the C_{60} cage are broken, resulting in the formation of twofold coordinated (2f) sites. The presence of defects in the C_{60} structure causes the molecule to react with the surface, at variance with what happens in the low ER. Indeed, after some oscillations around 2 Å, D suddenly decreases to a value of about 1.5 Å (see Fig. 1). Not surprisingly, the surface atoms involved in the bonding belong to the topmost layer, which contains 3f sites. In this ER, the number of bonds between C_{60} and the surface depends weakly on E_k and, during the collision, is approximately 2. For $E_k = 150$ eV, we find that these bonds are stable after the impact and that the cluster is adsorbed on the surface (see Fig. 2). We note that Busman, Lill, and Hertel [2] suggested that intact C_{60} can be absorbed on a graphite substrate [2,5], after collisions at 140 eV; indeed at this energy a clear decrease in scattering intensities is observed experimentally. At $E_k = 180$ and 210 eV, the C_{60}-surface bonds break after the collision, and the molecule leaves the substrate with $E_{cm} = 8$ and 15 eV, respectively. These findings compare well with those of Ref. [2], where the measured E_{cm} of fullerene ions scattered from graphite (10–20 eV) is found to be nearly independent of the impact energy, for E_k larger than 140 eV. In this medium ER, the topology of the molecule remains cagelike, although defects are present in the original structure (see Figs. 2 and 3).

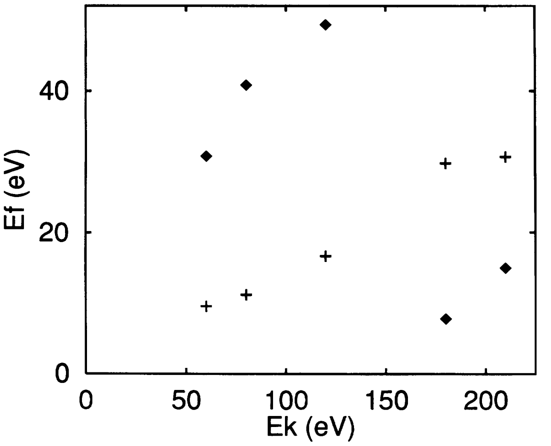

FIG. 4. Final energies (E_f) of C_{60} bouncing on the surface as a function of E_k: diamonds and crosses indicate the kinetic energy of the center of mass and the internal energy of the molecule, respectively.

Upon impact at $E_k \geq 240$ eV (high ER), we observe the formation of several bonds between C_{60} and the surface. Their average number increases with the incident energy, varying from about six to 16. Shortly after the collision, many bonds break within the molecule, and the cage structure is strongly modified (see Fig. 4); a disordered structure is formed and adsorbed on the substrate. After the 300 and 400 eV collisions, some of the C_{60} atoms form 2f chain structures (see Fig. 2); the formation of such chains was observed also in MD studies of fullerene melting [23].

Whenever C_{60} left the surface, we did not observe any fragmentation of the molecule. However, a rupture may be expected to occur some time after a collision if the internal energy (E_{in}) of the bouncing molecule (see Fig. 4) exceeds its stability threshold. MD investigations of fullerene melting [23] have shown that C_{60} becomes unstable when its internal kinetic energy (E_{in}) is between 30 and 40 eV.

In the low and medium ER the topology of the reconstructed surface is unaffected by the collision, although a considerable fraction of E_{in} is transferred from the molecule to the surface (e.g., as much as 50% for $E_k = 180$ and 210 eV). In the medium ER only the 3f atoms of the topmost layer bond to C_{60} atoms (see Fig. 2). In the high ER the fourfold coordinated (4f) surface atoms (belonging to the second layer) are also involved in bonding to the molecule. However, they remain 4f since their bonds with the third layer atoms are broken. This bond breaking induces a local surface dereconstruction from a π bonded chain geometry towards a (1×1) ideal arrangement (see Fig. 2).

We found that the presence of defects in the C_{60} molecule enhances its reactivity with the substrate. This is expected to play an important role in deposition processes of the fullerene on semiconducting surfaces. In particular, the variety of scanning tunneling microscopy images produced by covalently bonded C_{60} on, e.g., Si(111) [9], might correspond to molecules with different types of defects.

In summary, we have identified three impact energy regimes of C_{60} collisions on C(111). For $E_{\mathrm{in}} \leq 120$ eV, the molecule bounces off the surface without ever forming bonds and recovers its original shape after severe distortions. In a second regime, C_{60} forms covalent bonds with the surface. The cluster can be either adsorbed on or leave the substrate, with defects in its original structure. In the third regime ($E_k \geq 240$ eV) the molecule breaks after the impact, and pieces of the broken cage form stable bonds with the substrate, which can induce a local surface dereconstruction. When the molecule bounces off the surface, the kinetic energy of its center of mass shows a clear dependence on its incident energy in the low ER; on the contrary, E_{cm} depends weakly on E_{in} in the medium ER, in agreement with experiment. Finally, we have shown that QM simulations for systems containing thousands of atoms, so far not possible with conventional methods, are now feasible by using $O(N)$ approaches. In the simulations reported in this work, the gain in computer time with respect to conventional $O(N^3)$ methods is estimated to be of the order of 1000.

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[15] We used a cutoff radius of 2.30 Å for the hopping parameters of $\mathcal{H}$ and for the two body repulsive potential, and $U = 8$ eV for the Hubbard-like term (see Ref. [14]). In simulations performed with $U = 0$ we observed unphysical charge transfers.

[16] At each MD step $\mathcal{H}$ was diagonalized iteratively with a conjugate gradient procedure, by performing 15 iterations per ionic move and by extrapolating linearly the input wave function from the two previous ionic steps. The time steps used for the integration of the equations of motion varied from 15 to 6 a.u. according to E_k.

[17] We find that the average bond distance in the surface chains is 1.44 Å and that the change in bond length between the second and third layer is 6%; the corresponding values reported in Ref. [18] are 1.48 Å and 6%, whereas those of Ref. [19] are 1.44 Å and 8%. However, our calculation seems to overestimate the dimerization of the surface chains (4% versus 0.2% in Ref. [18] and 1.4% in Ref. [19]). The differences between the LO and the EO formulations can be systematically reduced by using LOs which extend up to third neighbors ($N_h = 3$). For example in the case of C_{60} with $N_h = 3$ the errors are 1.1% (single bond) and 0.7% (double bond). We believe that calculations with $N_h = 2$ are sufficiently accurate for the purpose of the present investigation.

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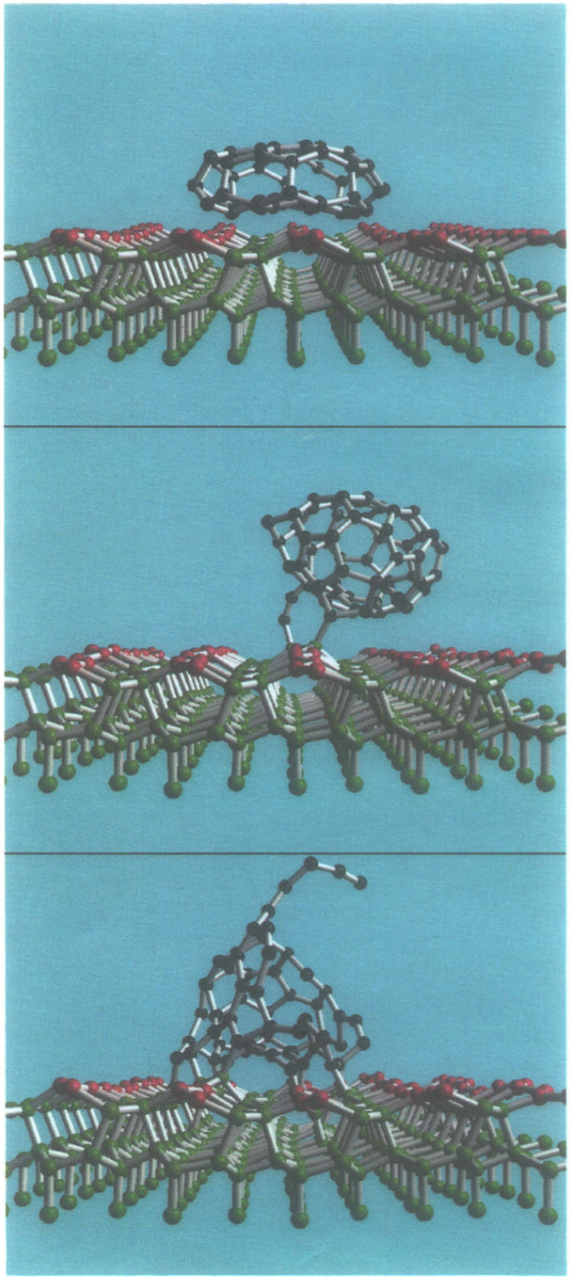

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