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Tantalum-fullerene clusters: A first-principles study of static properties and dynamical behavior

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The static structural properties and the relative stability of fullerene molecules decorated with one, two, and three Ta atoms at different exohedral sites are investigated via first-principles calculations. We find that the most stable clusters are likely to be those in which a Ta atom is at a site of high electron density, such as the hexagon-hexagon double bond of the fullerene molecule, and if the Ta atoms cluster together on the surface of the cage. Dynamical simulations of the $C_{60}Ta_3$ system are performed via Car-Parrinello molecular dynamics, and they show that the Ta atoms on the surface of the fullerene are affected by a rather high mobility, similar to the surface diffusion of a physisorbed species. Though a Ta dimer is formed at relatively low temperatures, the $C_{60}Ta_3$ cluster is dynamically stable up to a temperature of ~ 1000 K, ruling out purely thermal heating as a major factor responsible for any fragmentation process at least on time scales of a few picoseconds.

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I. INTRODUCTION

Fullerene molecules, particularly in their doped and functionalized forms, have aroused much experimental and theoretical interest in recent years. Detailed investigations on doped fullerene molecules with dopant atoms in substitutional, endohedral, and exohedral sites of the fullerene cage have been carried out in several experiments. Particularly interesting are the recent experiments of the group of Martin, in which fullerene molecules have been coated with alkali-metal atoms,[1] alkaline-earth metal atoms,[2] and transition-metal atoms.[3] The behavior and properties of each of these systems is quite different. In particular, while fullerene molecules remain stable when coated with alkali or alkaline-earth metal atoms, in transition metal—fullerene clusters, the transition-metal atoms are found to interact strongly with the fullerene cage. In fact, the latter transform into metal-carbide or metallocarbohedrene clusters when exposed to high laser intensities.[3]

The most unusual and unexpected behavior, however, has been observed in photofragmentation studies of C_{60} coated with Ta atoms.[3] Photofragmentation experiments generally involve molecular excitation, induced by an incident photon, which then promotes subsequent molecular fragmentation. For both $C_{60}Ta$ and $C_{60}Ta_2$, photofragmentation proceeds by the successive emission of C_2 dimers[4] (in the case of $C_{60}Ta$, however, Ta is first expelled before the subsequent C_2 release). On the other hand, in the case of $C_{60}Ta_m$ $(m \geqslant 3)$, the photofragmentation proceeds by successive C_3 emissions. The loss of a C_3 unit from the C_{60} molecule might presumably result in the disruption of the fullerene structure,[3] since fullerenes contain only an even number of carbon atoms.[5] However, the structure of the cluster after C_3 emission is not known from the experiments, and it is possible that the cage actually remains intact via some as-yet-unknown mechanism.

In fact, it is well known that the fullerene cage is not easy to destroy. The C_{60} structure in particular is very stable having a binding energy per atom only about 0.7 eV less than that of graphite.[6] The C_{60} cage is also very stiff, with a bulk modulus of ~ 717 GPa (Ref. 7)—this is about 1.6 times that of diamond. Similarly, C_{60} molecules in the solid phase collapse only when compressed to pressures above 22 GPa.[8] Finally, solid C_{60} has been reported to polymerize upon irradiation with visible or uv light, with the molecules linking together to form a covalently bonded structure.[9] The fragmentation of the fullerene cage is therefore quite fascinating, and several recent experiments have sought to better understand the underlying mechanism. Yet, the details of the process still elude accurate experimental determination and can only be tentatively guessed at, *a posteriori*, from the experimental outcome.

The main experimental techniques used for fragmentation studies[6] are photofragmentation; collision of charged C_{60} ions with gas-phase molecules or with surfaces on which they are used as impinging projectiles; and electron irradiation. Thermal fragmentation can also occur, provided the temperature is sufficiently high, but the importance of electronic excitations in this process remains to be seen.

Photofragmentation usually tends to be a relatively gentle process, resulting in a contraction of the fullerene structure by the emission of successive C_2 units, thereby shrinking the size of the fullerene without destroying the cage.[10] The fullerene mass drops till it finally bursts because of the high strain energy.[6] Collision-induced fragmentation studies involving gas phase molecules[11,12] also find that fragmentation proceeds via the loss of an even number of carbon atoms. C_{60} ions impinging on surfaces are strongly deformed and exhibit an impressive resilience of the bonding network, provided that the incident ion energy is less than ~ 250 eV in the case of Si surfaces,[13] and ~ 200 eV in the case of graphite[14] or diamond[15] surfaces. In the case of the latter, when the incident ion energy is greater than 200 eV, the C_{60}^+ ions fragment with a loss of C_2 units. Finally, heavy ion irradiation of C_{60} breaks it up into individual carbon atoms.[16] We note that several experiments on femtosecond excitation of fullerenes suggest that the long-time relaxation is dominated by dimer emission,[17] as in most of the processes described above. However, no clear answers about the short-

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time nonthermal relaxation are available from the experiments. A recent theoretical study shows that the first stages of the nonequilibrium dynamics may be dominated by a breathing phonon mode followed by the cold ejection of single carbon atoms,[18] causing the destruction of the fullerene structure.

Thus, in general, it would appear that fullerenes fragment by losing C_2 units, because this allows them to retain a stable closed cage structure.[19] Nonfullerene isomers, on the other hand, dissociate predominantly by C_3 loss,[20,21] which is thermodynamically favored over C_2 loss, if the cohesive energy of C_{n-3} and C_{n-2} is not very different. We note also that, while scenarios for the absorption of C_2 by C_{60} have been identified in molecular dynamics (MD) simulations,[22] no route has been found for the absorption of a C_3 cluster, which is consistent, once again, with the requirements of Euler's theorem.

To the best of our knowledge, the only experiments in which carbon-trimer emission from C_{60} has been observed are those by Martin *et al.*[3] discussed earlier, and ion-mobility experiments on Nb-coated C_{60} clusters by Jarrold *et al.*[23] The latter show that for collision-induced excitation and dissociation of $C_{60}Nb_m$ clusters, with $m \geqslant 3$, one of the dissociation channels involves C_3 emission. It is significant that in the experiments due to Jarrold *et al.*, the experimental technique and conditions are entirely different from those in the experiments due to Martin *et al.*, and still yield the same results. Infact, in the photofragmentation experiments by Martin *et al.*, C_3 emission is observed even when the cluster is ionized with a low-intensity (excimer) pulse (with energy between 4 eV and 6.4 eV), so it is not clear what role—if any—this "gentle" laser pulse plays in the fragmentation process.[24]

Further, the results on C_3 emission are unique to experiments on C_{60} coated with Ta and Nb atoms. Now, even though these elements are separated by an entire period in the periodic table, the atomic radii of Ta and Nb are very similar, ~ 1.47 Å, and they are known to possess very similar chemical behavior.[25] Furthermore, Ta and Nb replace one another isomorphously in several compounds without inducing any change of form or physical properties, with the exception of the density.[25] Hence, the observed similarity in the fragmentation behavior of C_{60} coated with either of these two elements is not surprising. What is surprising, however, is the fact that no other dopants lead to such a fragmentation of C_{60}. Hence, the question arises: what is the special role of Ta or Nb in this process?

In the light of these experimental results and in order to unravel some of the puzzles raised by them, we attempt, in this work, to understand the nature of the C_{60}-Ta interaction via a first-principles study of C_{60}-Ta clusters. Working within the framework of density-functional theory (DFT), we first analyze statically the structure and the stability of a single C_{60} molecule coated with either one or two Ta atoms at different exohedral sites. To complement this investigation, we also analyze the structure and stability of a few significant isomers of $C_{60}Ta_3$.

Finally, we study the finite-temperature dynamical behavior of the $C_{60}Ta_3$ cluster by performing a Car-Parrinello molecular dynamics (CPMD) simulation[26] and investigate the role of purely thermal processes in possible pathways for carbon-trimer emission and cluster fragmentation.

II. COMPUTATIONAL DETAILS

We adopt a DFT approach,[27] including the generalized gradient corrections to the local-spin density approximation[28] due to Becke[29] and Lee, Yang and Parr[30] for the exchange and correlation terms, respectively. Valence electrons are treated explicitly and their wave functions are expanded in a plane-wave basis set with an energy cutoff of 40 Ry, while core-valence interactions are described by Troullier-Martins norm-conserving pseudopotentials.[31,32] For Ta, the pseudopotential was constructed[33] using the ground-state electronic configuration $5d^3\ 6s^{1.96}\ 6p^{0.1}$. The cutoff core radii for $5d$, $6s$, and $6p$ states were set to 1.421 Å, 1.823 Å, and 0.799 Å, respectively. The Ta pseudopotential was tested for both convergence and transferability on the Ta_2 dimer, bulk Ta, and bulk TaC. The computed bond length for the dimer, 2.18 Å, compares well with the experimental value of 2.15 Å.[34] For bulk Ta and bulk TaC, good convergence for the total energy was achieved with an $8\times8\times8$ mesh of Monkhorst-Pack[35] **k** points. For Ta, the zero-pressure lattice constant was found to be 3.321 Å [experiment: 3.307 Å (Ref. 36)]; the bulk modulus 185.5 GPa [experiment: 193.7 GPa (Ref. 37)] and the bulk modulus derivative 4.204. For TaC, the zero-pressure lattice constant was found to be 4.507 Å (experiment:[36] 4.454 Å), the bulk modulus 295.4 GPa (experiment:[38] ≈ 286 GPa), and the bulk modulus derivative 4.0. The good agreement of our theoretical values with experiment provides support for the reliability of these pseudopotentials.

Each cluster is placed in a cubic simulation cell whose side has a length of 14.29 Å. In order to avoid spurious interactions with the images of the system in neighboring simulation cells, induced by the use of periodic boundary conditions, we adopted an isolated cell approach following the scheme of Barnett and Landmann.[39] The large size of the cell, more than twice the diameter of the C_{60} molecule, ensures enough space, both to accommodate the large Ta atoms and to achieve a good minimization of the finite-size effects.

A. Static calculations (optimization)

For C_{60}, we chose the experimentally determined structure[40] as the starting configuration. We note that throughout this paper, the convention followed for numbering the carbon atoms in the C_{60} cage is to number them pentagon by pentagon. The Ta atoms are placed at different sites on the cage—the center of a pentagonal face (p), center of a hexagonal face (h), center of a pentagon-hexagon bond $(p\text{-}h)$, center of a hexagon-hexagon bond $(h\text{-}h)$—in each case, at a distance of ~ 1.9–2.0 Å from the nearest Carbon atoms of the fullerene cage. For $C_{60}Ta$, four high-symmetry isomers, with the Ta atoms placed at the sites discussed above, were studied. For $C_{60}Ta_2$ clusters, a large number of high-symmetry isomers is possible, which differ also in the distance between the two Ta atoms on the cage. This is true also for the $C_{60}Ta_3$ cluster. For instance, the Ta atoms could

TABLE I. Optimized bond lengths for C_{60} and isomers of $C_{60}Ta$, with the smallest and largest values obtained indicated. Also given are the binding energies (b.e.) of the Ta atom to C_{60} in each isomer. All distances are in Å, and energies in eV. The various isomers of $C_{60}Ta$ referred to have the Ta atom at the following sites: Is(1)—hexagon-hexagon $(h\text{-}h)$ bond center; Is(2)—pentagon-hexagon $(p\text{-}h)$ bond center; Is(3)—center of a hexagonal face (h); Is(4)—center of a pentagonal face (p).

	C_{60}	Is(1)	Is(2)	Is(3)	Is(4)
C—C bond length	1.47	1.465–1.511	1.458–1.542	1.427–1.509	1.453–1.483
C═C bond length	1.41	1.403–1.418	1.409–1.452	1.403–1.474	1.409–1.442
C-Ta bond length		2.178	2.344–2.364	2.390–2.586	2.540–2.561
b. e. of Ta to C_{60}		1.097	0.28	0.176	0.073

be clustered together at various sites on the same hexagonal or pentagonal face, or on neighboring faces; dispersed on next-nearest-neighbor or further faces; placed on opposite sides of the cage; or just randomly distributed over the cage.

For each isomer studied, the geometry of the cluster is fully relaxed, and the structure is optimized,[41] until the minimum energy configuration is attained. The accuracy achieved is $<5\times10^{-4}$ a.u. for the largest component of the ionic forces, and one order of magnitude smaller for their average value. All the geometry optimizations are performed by the direct inversion in iterative subspace technique.[42]

B. Dynamics

Starting again from the experimentally determined structure[40] for C_{60}, three Ta atoms are initially placed at the centers of hexagonal faces, which are approximately equidistant from each other on the cage, the Ta atom—nearest C atom distance being set to 2.13 Å. [Fig. 4(a)]. A MD integration time step of 0.097 fs, and a fictitious electron mass of 900 a.u., ensured a good control of both the adiabaticity and the conserved variables throughout the simulation.

a. Dynamical simulation 1: 6.76 ps, final temperature of 360 K. The geometry of the neutral $C_{60}Ta_3$ cluster was first optimized, till the maximum component of the force acting on an atom is $\sim10^{-1}$ a.u., and the electrons were quenched onto the Born-Oppenheimer surface. Then a CPMD on this (N,V,T) ensemble was performed.[41] The system was allowed to evolve freely for a total simulation time of $\sim$1.45 ps. Then, it was heated to about 330 K in $\sim$0.4 ps and reequilibrated at this new target temperature for $\sim$0.96 ps. The heating process was repeated, raising the temperature to 360 K; at this temperature, the system was equilibrated again for $\sim$2.84 ps. In order to make contact with the experiments[3] the system was positively charged and quenched, and the free evolution of this charged cluster was then studied for another 1.15 ps.

We note that in this case, the total simulation time is rather long on a typical quantum simulation scale, and the final temperature attained is relatively low and close to standard room temperature.

b. Simulation 2: 4.13 ps, final temperature of 1,000 K. The geometry of the positively charged $C_{60}Ta_3$ cluster is first optimized as described above (maximum force component $\sim5*10^{-3}$ a.u.). The first CPMD run lasted $\sim$0.21 ps. The system was then heated to 300 K, equilibrated for $\sim$2.0 ps, and subsequently heated further to attain the target value $T=1000$ K in $\sim$1.92 ps.

We note that in this case, the total simulation time was shorter than in the former case, while the final temperature attained was much higher.

III. RESULTS AND DISCUSSION

A. Optimization

a. C_{60} molecule. The relaxed structure of the C_{60} molecule as obtained by our approach is in excellent agreement with both experiments and previous first-principles calculations.[43,44] The C-C bond lengths are found to be 1.47 Å for the single bond and 1.41 Å for the double bond, while the reported experimental values[40] are 1.458(6) Å and 1.401(10) Å, respectively. The computed binding energy per atom is 8.17 eV [to compare, earlier calculations yield a value of $\approx$7.24–8.5 eV,[45] while the experimental value is $\approx$6.94–6.98 eV (Ref. 46)]. The highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap for the C_{60} molecule is found to be 1.647 eV, in rather good agreement with previous first-principles calculations[47] and with experiments (1.9–2.5 eV from photoemission and inverse photoemission,[48] and 1.55 eV from photoabsorption[49] measurements). The icosahedral symmetry of C_{60} implies a high level of electronic degeneracy,[6] which is well reproduced in our calculations. In particular, the HOMO is fivefold degenerate and the LUMO and LUMO $+1$ are each threefold degenerate.

b. $C_{60}Ta$ clusters. The bond lengths and binding energies of the Ta to C_{60} in four low-energy isomers of $C_{60}Ta$ are summarized in Table I. The isomers are shown in Fig. 1, with the total energies of the isomers relative to the stablest isomer, given in the caption. For C_{60} with one Ta atom, the most stable isomer (i.e., the one with the lowest total energy) is found to be the one in which the Ta atom is at the center of a hexagon-hexagon $(h\text{-}h)$ bond. [Isomer Is(1) in Fig. 1(a) and Table I]. This is not surprising as the $h\text{-}h$ (double) bond centers are known to be the regions on the fullerene structure at which the electronic charge density distribution reaches its maximum value.[50] The binding energy of the Ta atom to the C_{60} cage is 1.1 eV, and represents the largest binding found in the $C_{60}Ta$ isomers. This rather tight binding is also reflected in the relatively short Ta-C bond distance, namely,

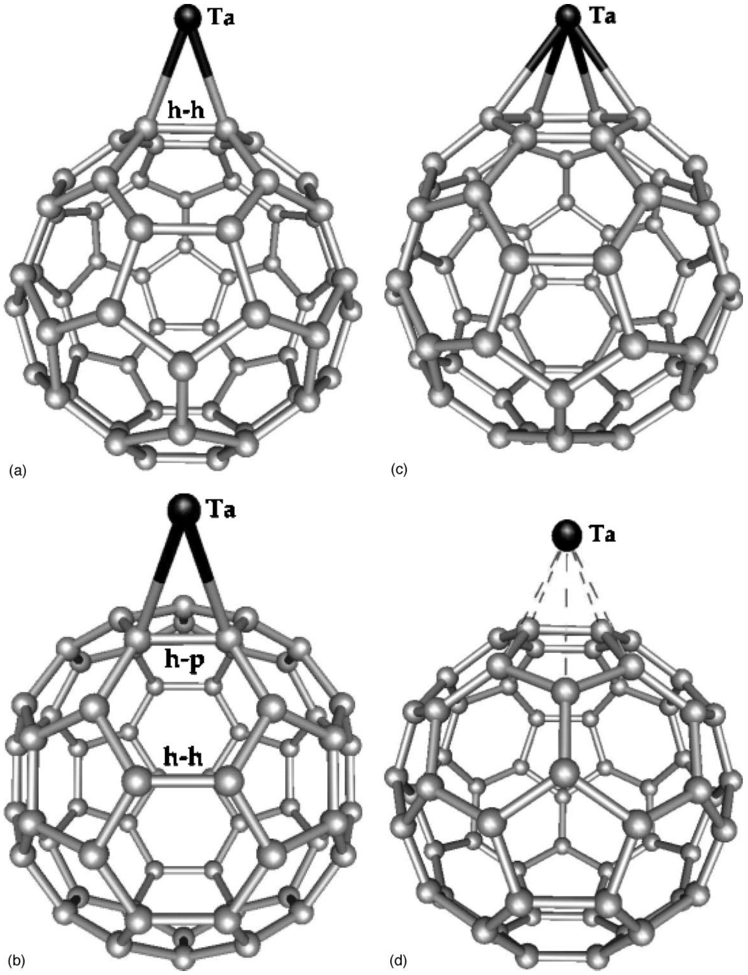

FIG. 1. Four high-symmetry isomers of $C_{60}Ta$. The labeling of the isomers referred to is explained in Table I. The total energies of the optimized structures, relative to that of the stablest isomer, Is(1), shown in (a), are as follows: (b) [Is(2)], 0.82 eV; (c) [Is(3)], 0.92 eV; (d) [Is(4)], 1.02 eV. For Is(1), the Ta-nearest carbon distance is 2.178 Å.

2.178 Å. It is interesting to note that this bonding of the Ta atom with the C atoms across the *h*-*h* bond, leads to the elongation of the *h*-*h* bond, from its double bond value of 1.41 Å to 1.56 Å. Our results on $C_{60}Ta$ clusters support the conjecture of Jarrold *et al.*[23] for $C_{60}Nb$ clusters that the most likely C_{60}-Nb bonding geometry is an $\eta-2$ bridge over the *h*-*h* double bond of C_{60}. In their models of the structure of a Nb complex (the complex being ethylene, naphthalene, or C_{60}-fragments containing upto 20 carbon atoms), optimization at the Hartree-Fock level gave a distance of 2.00 Å between the Nb atom and the center of the double bond.[23]

The energy difference between the most stable structure and the next stable configuration [isomer Is(2) of Fig. 1(b) and Table I] is about 0.82 eV. On the other hand, the maximum energy difference between the three (less stable) isomers is only ~ 0.21 eV. The Ta-C distances for these isomers also differ considerably from that in Is(1), and are rather large, going up to 2.59 Å for the less stable structures. These distances are to be compared with typical Ta-C bond lengths in the bulk,[36] or in neutral or charged Ta_mC_n clusters,[51,52] which are 2.00 Å, at most.

c. $C_{60}Ta_2$ clusters. For clusters containing two Ta atoms, the bond lengths and binding energies of the Ta to C_{60} are summarized in Tables II parts (a) and (b)]. Interestingly, the most stable isomer is found to be the one in which the two Ta atoms are located on the same hexagon, on adjacent *h*-*h* double bonds, Isomer Is(1) of Fig. 2(a) and Table II. We note however, that unlike in the case of the most stable isomer of $C_{60}Ta$, our optimization of isomer Is(1) of $C_{60}Ta_2$ yielded positions of the Ta atoms slightly displaced from the centers of the C-C double bonds. Thus, for one Ta atom, the Ta-C distances are 2.178 Å and 2.385 Å, while for the other Ta atom, the Ta-C distances are 2.134 Å and 2.5 Å. The Ta-Ta distance (dimer bond-length) is 2.381 Å. The binding energy of the Ta atoms to the C_{60} molecule, 3.405 eV, is the largest in the case of this isomer. A $C_{60}Ta_2$ isomer with the Ta atoms at *h*-*h* bonds, but on opposite sides of the fullerene cage [isomer Is(2) in Fig. 2(b) and Table II] was found to be much less stable, by about 0.96 eV, than isomer Is(1). These results are in some consonance with the ion-mobility measurements of Jarrold *et al.*, which indicated that the structure of $C_{60}Nb_2$ is that of a Nb_2 dimer bridging two *h*-*h* bonds of a single hexagon on the C_{60} cage, rather than trans-Nb atoms (i.e., Nb atoms at *h*-*h* bonds, but on opposite sides of the cage), at variance with the bonding schemes in some Pd and Pt complexes.[23,53,54] All the other isomers investigated (Fig. 2)

TABLE II. Optimized bond lengths for some isomers of $C_{60}Ta_2$, with the smallest and largest values obtained indicated. Also given are the binding energies (b.e.) of the Ta atoms to C_{60} in each isomer. All distances are in Å, and energies in eV. The isomers referred to have the two Ta atoms at the following sites: Is(1)—on the same hexagon of the C_{60} cage, at adjacent hexagon-hexagon (*h*-*h*) bond centers, C(2)-C(11) and C(10)-C(12); Is(2)—on symmetrically opposite sides of the cage, at *h*-*h* bond centers, C(20)-C(22) and C(34)-C(36); Is(3)—at *h*-*h* bond centers, C(48)-C(51) and C(32)-C(53), which are separated by a pentagon; Is(4)—at *h*-*h* bond centers, C(48)-C(51) and C(34)-C(36), which are separated by two hexagons and a pentagon; Is(5)—at centers of symmetrically opposite pentagonal faces, C(1)-C(2)-C(3)-C(4)-C(5) and C(56)-C(57)-C(58)-C(59)-C(60); Is(6)—at pentagon-hexagon (*p*-*h*) bond centers, C(4)-C(5) and C(6)-C(7), of two adjacent hexagons; Is(7)—at a *h*-*h* bond center, C(1)-C(2) and a *p*-*h* bond center, C(48)-C(51); Is(8)—at *p*-*h* bond centers, C(6)-C(7) and C(54-C(55); Is(9)—at *p*-*h* bond centers, C(4)-C(5) and C(58)-C(59) on symmetrically opposite pentagons; Is(10)—at centers of opposite hexagonal faces, C(1)-C(2)-C(11)-C(12)-C(10)-C(6) and C(47)-C(48)-C(51)-C(52)-C(56)-C(60).

(a)

	C_{60}	Is(1)	Is(2)	Is(3)	Is(4)	Is(5)
C—C	1.47	1.455–1.526	1.464–1.511	1.456–1.511	1.455–1.513	1.465–1.483
C═C	1.41	1.397–1.542	1.404–1.589	1.390–1.555	1.402–1.564	1.409–1.435
C-Ta		2.134–2.50	2.168–2.178	2.170–2.186	2.175–2.190	2.546–2.597
b. e. of Ta to C_{60}		3.405	2.444	2.027	1.963	1.842

(b)

	Is(6)	Is(7)	Is(8)	Is(9)	Is(10)
C—C	1.449–1.574	1.447–1.552	1.436–1.626	1.450–1.634	1.460–1.492
C═C	1.402–1.494	1.403–1.437	1.404–1.473	1.400–1.472	1.410–1.444
C-Ta	2.140–2.441	2.175–2.735	2.161–2.349	2.147–2.813	2.567–2.614
b. e. of Ta to C_{60}	1.164	0.992	0.875	0.704	0.116

are characterized by stabilities close to the stability of isomer Is(2), or below.

The trends observed for the $C_{60}Ta_2$ isomers are rather similar to the case of clusters containing only one Ta atom. Generally, the isomers in which one or more Ta atoms are located at *h*-*h* (double) bonds display a greater stability than the isomers in which one or more Ta atoms are located at *p*-*h* (single) bonds. Even less stable are those isomers for which the Ta atoms are placed at the centers of hexagonal faces, or pentagonal faces. The decrease in stability of an isomer seems to go hand in hand with the Ta atoms being positioned at sites of lower electron density, and consequently being less strongly bound to the cage. This is evident from both, the decrease in the binding energies of the Ta atoms to the cage, and the increase in the Ta-C bond distances in the isomer. The Ta-C bond lengths in the least stable isomers reach a maximum value of ~2.6 Å.

d. $C_{60}Ta_3$ clusters. We extended our analysis to a few significant isomers of $C_{60}Ta_3$. The results obtained from optimization (Fig. 3) confirmed that the trends observed in the $C_{60}Ta$ and $C_{60}Ta_2$ isomers are maintained as far as the stabilities, the binding energy of the Ta atoms to the cage, and the Ta-C bond lengths in the cluster, are concerned. Thus, the most stable isomer [isomer Is(1) in Fig. 3(a)] is the one in which all three Ta atoms are on the same hexagon. However, while one Ta atom is approximately at a *h*-*h* double bond center, [d:Ta(3)-C(1) = 2.404 Å and d:Ta(3)-C(6) = 2.243 Å], the other two Ta atoms are considerably shifted during the optimization from the adjacent *h*-*h* bonds, to almost apical positions over the carbon atoms [thus, d:Ta(2)-C(12) = 2.256 Å and d:Ta(1)-C(2) = 2.176 Å while d:Ta(2)-C(10) = 2.534 Å, d:Ta(2)-C(11) = 2.676 Å, d:Ta(1)-C(11) = 2.535 Å, d:Ta(1)-C(1) = 2.704 Å]. At this stage, we are not completely certain that this isomer is indeed the most stable, or whether there might exist a more stable isomer with all the three Ta atoms centerd exactly at *h*-*h* bonds of the same hexagon. However, we were not able to obtain such an isomer with our optimization. In our stablest isomer, Is(1), the Ta trimer has the following bond lengths: d:Ta(1)-Ta(2) = 2.472 Å; d:Ta(1)-Ta(3) = 2.456 Å, and d:Ta(2)-Ta(3) = 2.493 Å. The binding energy of the Ta atoms to C_{60} is ≈7.27 eV. The second isomer we studied, in which the Ta atoms are clustered together less closely (with two Ta atoms on *h*-*h* bonds of the same hexagon, and one Ta atom on an adjacent hexagon) has Ta-C distances varying between 2.13–2.63 Å, while the binding energy of the Ta atoms to the cage is ~4.36 eV. In the case of the third isomer of $C_{60}Ta_3$, with the Ta atoms placed far apart, we were unable to even converge the structure below a force of 10^{-3} a.u.; at this level of convergence, the energy is much larger than that for the other two (fully converged) isomers. Once again, our results are in some consonance with the experiments of Jarrold *et al.*,[23] which indicated that, in $C_{60}Nb_3$, the Nb atoms are clustered closely together on the cage surface, (though they also conjectured that all the Nb atoms are positioned at *h*-*h* bonds of the same hexagon), rather than distributed randomly on it.

We remark that the strong C_{60}-Ta interaction observed in the experiments[3,23] does not seem to be reflected in unusually strong C_{60}-Ta bonds in the $C_{60}Ta_n$ ($n = 1,3$) clusters; in fact, our optimized bond lengths are even slightly longer than those found in typical Ta-C compounds and clusters.

B. Dynamics

a. General observations. Dynamical simulations were performed on both, the neutral and the charged clusters, in order to heat the systems and investigate the role of temperature in a possible C_3 emission reaction pathway. This study is important, as temperature effects can play a crucial role in causing strong chemical transformations. For instance, C_{60} can be fragmented by heating to temperatures of ≈ 5000 K.[55,56] Further, recent experiments[57,58] show that the transformation of fullerite into nanostructured carbon can be induced by laser pulses below the absorption gap. We note also, that in the experiments by Martin *et al.* and Jarrold *et al.*, though the experimental techniques are entirely different, temperature seems to be playing an important role. Thus, in the photofragmentation mass-spectrometric experiments, the ionizing laser pulse also heats the cluster. This is borne out by the fact that at higher laser intensities, there is an increasing degree of cluster fragmentation,[3] which may be attributed to the greater heat deposited in the clusters by the pulse. In the ion-mobility experiments, on the other hand, the excitation is promoted by a collisional mechanism, which also leads to an increase in ionic temperature.

It is well known that the C_{60} fullerene can accept up to 12 electrons, and accomodate them as spin-up spin-down couples into the lowest two unfilled states, each of which is triply degenerate. Thus, one would not expect a profound difference in the dynamics of $C_{60}Ta_3$ and $C_{60}Ta_3^+$. Indeed, this is our inference from the simulations. When the neutral cluster, after heating and equilibrating at $T=360$ K, is charged, there is no discernible difference in the dynamics of the charged molecule for the rest of the simulation time of ~ 1.15 ps. Similarly, in the second simulation in which the system was charged from the beginning, the dynamics becomes slightly different only at the higher temperatures attained within a shorter total simulation time. However, at this stage, it is not certain that the difference is indeed to be ascribed entirely to the higher heating rate, and not to the charge of the system.

The main difference between the two simulations seems to arise from the differences in their durations and in the final temperatures attained within this time. The first simulation may be thought of as mimicking the slow relaxation processes of the system. The second simulation, on the other hand, mimics a faster relaxation of the system, as the cluster was not allowed to equilibrate for a long time at each temperature plateau, before undergoing the subsequent temperature increase. Since no detailed information about the time scales and temperatures is available from the experiments, both these simulations were necessary.

b. Mobility of Ta atoms. The heating of the cluster excites several vibrational phonon modes, clearly visible in the trajectory generated by the dynamics. Perhaps the most surprising result that we obtained is that a high mobility affects the

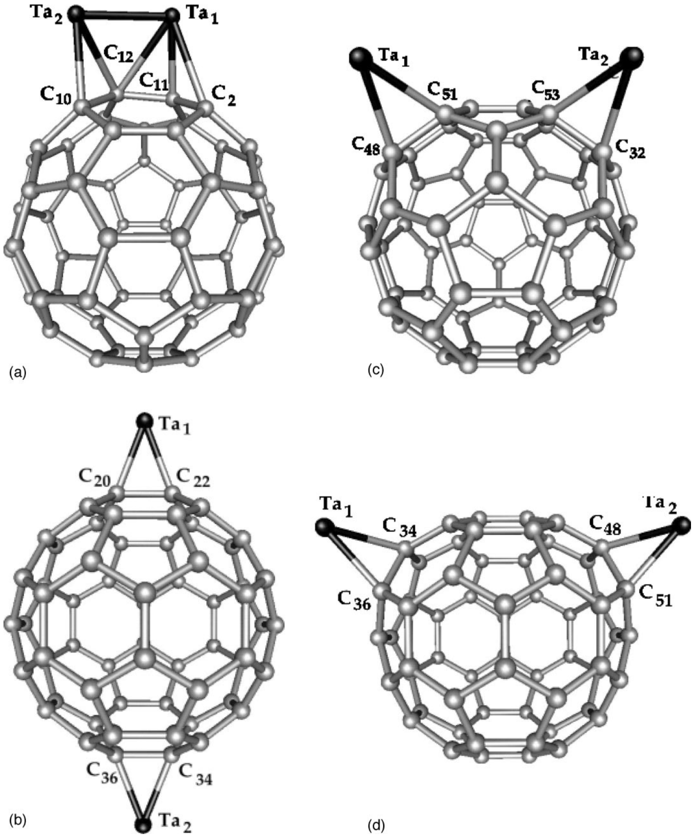

FIG. 2. Various isomers of $C_{60}Ta_2$. The labeling of the isomers referred to is explained in Table II. The total energies of the optimized structures, relative to that of the stablest isomer, Is(1), shown in (a), are as follows: (b) [Is(2)], 0.96 eV; (c) [Is(3)], 1.38 eV; (d) [Is(4)], 1.44 eV; (e) [Is(5)], 1.56 eV; (f) [Is(6)], 2.24 eV; (g) [Is(7)], 2.41 eV; (h) [Is(8)], 2.53 eV; (i) [Is(9)], 2.70 eV; (j) [Is(10)], 3.29 eV. For Is(1), d:Ta(1)-C(11) $= 2.134$ Å; d:Ta(1)-C(2) $= 2.5$ Å; d:Ta(2)-C(10) $= 2.179$ Å; d:Ta(2)-C(12) $= 2.385$ Å. The Ta-dimer bond length is 2.381 Å.

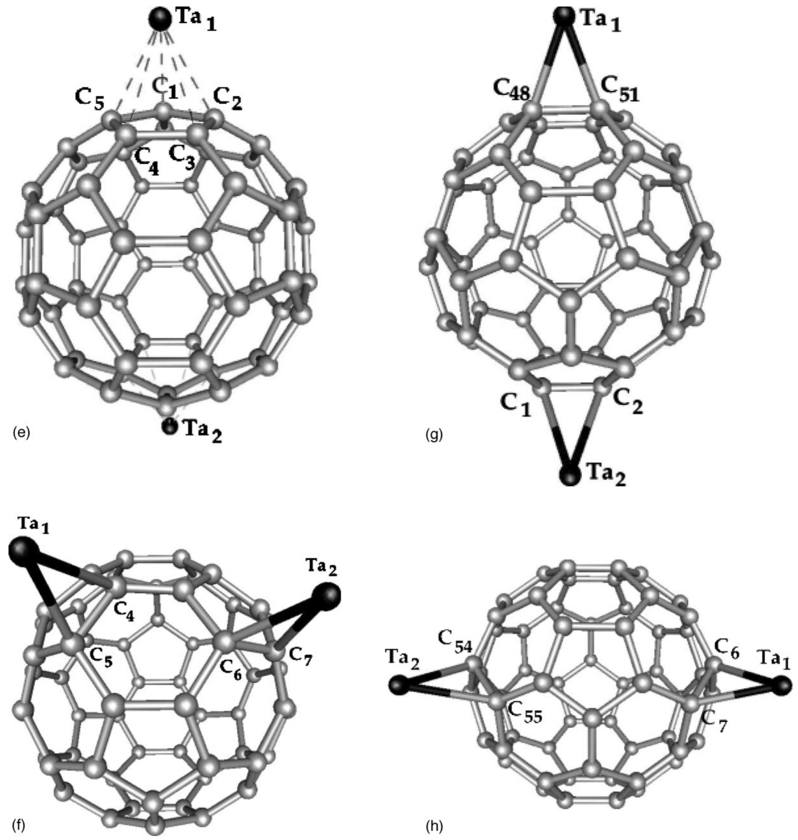

FIG. 2. (*Continued*).

Ta atoms accommodated on the C_{60} surface, similar to the diffusion of a physisorbed species on a surface. We note, however, that this mobility was quite unexpected, as it has not been reported in any previous *theoretical* study on exohedrally doped fullerenes, and dopant atoms have been generally believed to be strongly bound and fixed at their equilibrium positions on the fullerene cage.

However, our observations support recent *experimental* studies by Broyer *et al.*,[59,60] on C_{60} doped with a single alkali-metal atom (K or Rb). From measurements of the average dipole moment and the polarizability of the cluster, Broyer *et al.* deduced that the alkali atom moves randomly all over the C_{60} cage at room temperature.

Of course, our simulation conditions differ from those in the experiments due to Broyer *et al.*, as the presence of three Ta atoms in our study makes their motion on the C_{60} surface more complex. Thus, the motion of the Ta atoms is not completely random, but rather, is driven by a strong metal atom–metal atom attraction. Indeed, despite the initially large separations between the Ta atoms on the cage, a Ta dimer is quickly formed by the rapid movement of one of the Ta atoms towards the other [Fig. 4(b)]. This movement is accomplished by a fast bond making and breaking between the mobile Ta atom and the carbon atoms on the C_{60} cage. The process may be thought of as a *walk* of one Ta atom toward the other on the surface of the fullerene, resulting in a Ta-C bond-switching mechanism. The Ta dimer when formed is, in turn, also highly mobile on the fullerene cage, as it migrates towards the third Ta atom.

c. Simulation 1: C-C bond elongation, dimer formation and other details. In Simulation 1, Ta(1) and Ta(3) are both initially immobile at their respective sites, i.e., a p-h bond and a h-h bond. However, Ta(2) is rather mobile and in fact, at $T \sim 330$ K, Ta(2) switches from spot to spot *racing* towards Ta(1), which continues to stay bonded at a fixed position on the fullerene.

At this stage, we observed another quite unexpected occurrence. When the mobile Ta atom reaches the hexagon to which the fixed Ta atom is bonded, as it crosses a C-C (single) bond of that hexagon to move forward further, the C-C bond is stretched by *over 60%* of its equilibrium value [Fig. 4(c)]. This fleeting splitting of just one carbon-carbon bond of the fullerene network thus seems to be due to the excitation of a highly localized vibration. This could, in principle, have led to a destabilization of the cage. However, the vibration dies out quickly and the fullerene cage retains its stablity [Fig. 4(d)]. The two Ta atoms, Ta(1) and Ta(2), form a dimer.

We are thus confronted by a rather peculiar phenomenon: while one Ta atom remains chemically bound to its original site, thus indicating a stable chemisorption, the second one switches its original bond from site to site, behaving more like a physisorbed species. The interplay between the two metal atoms, one *moving* and one *waiting*, determines the dimerization.

Once the Ta dimer is formed, it is tightly bound, with a bond length which, however, varies by more than 50%. [Figs. 4(c)–4(g) and Fig. 5(a)]. At this stage, Ta(3) starts

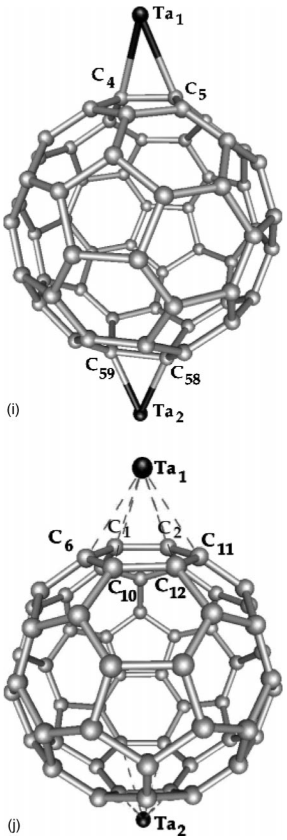

FIG. 2. (*Continued*).

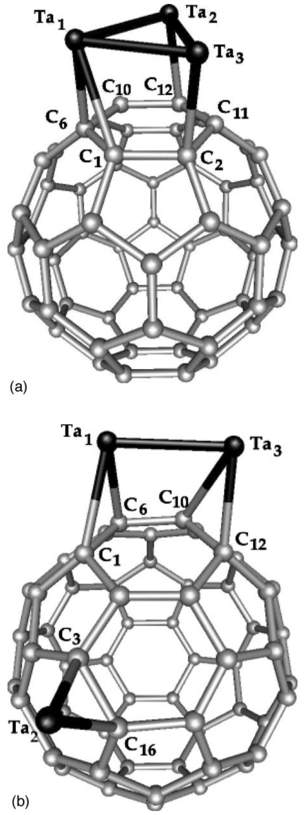

FIG. 3. Two isomers of $C_{60}Ta_3$. The isomers referred to are: (a) [Is(1)]: all three Ta atoms on the same hexagon, with one bridging a *h-h* double bond site, C(1)-C(2), and the other two shifted to almost apical positions over the carbon atoms, C(12) and C(10). (b) [Is(2)]: two Ta atoms on the same hexagon, and the third Ta atom on an adjacent hexagon, all bridging *h-h* double bond sites. The total energy of the optimized structure of Is(2), relative to the stablest isomer, Is(1), is 2.91 eV. For Is(1), d:[Ta(1)-C(1)) $=2.404$ Å and d:(Ta(1)-C(6)) $=2.243$ Å; d:Ta(2)-C(12) $=2.256$ Å, and d:Ta(3)-C(2) $=2.176$ Å while d:Ta(2)-C(10) $=2.534$ Å, d:Ta(2)-C(11) $=2.676$ Å, d:Ta(3)-C(11) $=2.535$ Å, d:Ta(3)-C(1) $=2.704$ Å. The Ta trimer in this isomer has the following bond lengths: d:Ta(3)-Ta(2) $=2.472$ Å; d:Ta(1)-Ta(3) $=2.456$ Å, and d:Ta(2)-Ta(1) $=2.493$ Å.

moving slightly, crossing from the original *h-h* bond to another *h-h* bond of the same hexagon, a position which brings it marginally closer to the Ta dimer. However, throughout almost the entire simulation, the third Ta atom remains relatively immobile on the fullerene surface, indicating again a true chemisorption character. It is the Ta dimer which acquires a high mobility, moving towards Ta(3), switching its bonds from site to site on the C_{60} surface, even detaching temporarily from the cage, but eventually reattaching to it in a stable binding configuration. This is not an artifact of the finite cell size, since the dimer actually begins to move back towards the fullerene cage, well before it reaches the simulation-cell boundary.

Though the Ta dimer moves towards Ta(3), its approach stops about a pentagon away and it settles down on a hexagon before forming any chemical bond with the dimer. Each Ta atom of the dimer comfortably bridges a *h-h* bond across the hexagon. This seems to be a position of at least local equilibrium for the system, as neither the monomer nor the dimer could be displaced within our simulation time, even when the temperature was raised from 330 K to 360 K. [Fig. 4(e)]. We infer that the *h-h* sites act as strong attractors for the metal atoms, either isolated or bound together, and on these sites, the chemisorption is strong enough to inhibit any thermally induced migration.

Upon charging ($Q=+1$) this configuration, the system experiences a kick, which perturbs the equilibrium attained by the neutral cluster, so that the Ta dimer begins to move away from the monomer. [Fig. 4(f)]. The dimer detaches from the cage and drifts away without reverting back to a bound configuration. [Fig. 4(g)]. Hence, the simulation was stopped, since it was clear that, at ~360 K, the electron loss had the effect only of destabilizing the metal-cage interaction and splitting the Ta dimer from the cage. Thus, we conclude that, around room temperature, an electronic excitation large enough to knock out (one) electron and ionize the cluster does not give rise to any sign of fragmentation and is therefore unlikely to be responsible for it.

d. Simulation 2: Some details. In Simulation 2, also, although initially all the Ta atoms move rapidly, with Ta(3) even crossing two hexagons and a pentagon, Ta(3) settles down to a *h-h* bond in a time of ~1.56 ps. Again, we conlude that, in the ground state, the *h-h* sites act as a sort of *chemical attractor* for the metal atoms. Indeed, Ta(3) spends the rest of the (simulation) time bound to this site until a temperature of ~1000 K is attained. The Ta dimer, [Fig.

5(a)], formed as a consequence of the mutual approach of Ta(1) and Ta(2), is affected by a rather large surface mobility, as in the previous simulation. However, during this dynamics, where higher temperatures are reached without allowing the system to equilibrate for a long time at each temperature plateau, we found that the Ta dimer does eventually form a chemical bond with the third Ta atom [Fig. 5(b)]. A triangular trimer is formed on the cage [Fig. 5(c)], but it detaches from the surface at ~1000 K [Fig. 5(d)]. This temperature corresponds to an energy of about 86.17 meV (~1.9 kcal/mol), which is much lower than the dissociation energy of Ta-C bonds. The fact that the Ta trimer detaches from the

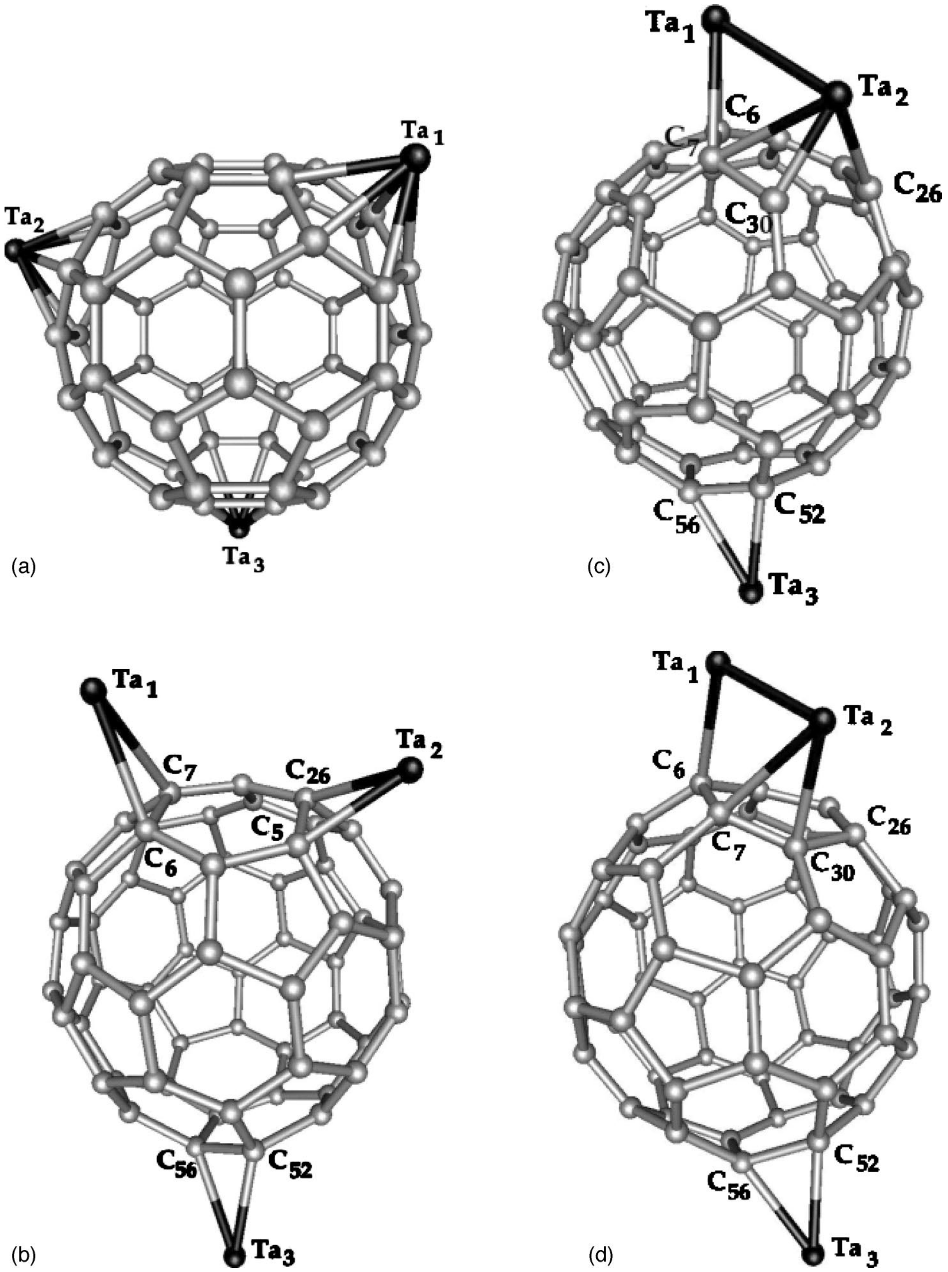

FIG. 4. Snapshots of $C_{60}Ta_3$ during the dynamical Simulation 1. (a) The starting configuration: The three Ta atoms, Ta(1), Ta(2), and Ta(3) are randomly dispersed on hexagonal faces on the cage, each at a distance of 2.13 Å from the nearest carbon atom. (b) $T=300$ K, $t=1.62$ ps: Ta(2) moves towards Ta(1), which is at the C(6)-C(7) bond. Ta(3) is at site C(52)-C(56). (c) $T=330$ K, $t=1.94$ ps: Elongation of the C(26)-C(30) (*p-h* single) bond, to the value 2.1 Å. This happens when Ta(2) crosses the *p-h* bond as it moves towards Ta(1) which is on the same hexagon, and dimerizes with it. Ta(3) continues at the site C(52)-C(56). (d) $T=330$ K, $t=1.98$ ps: Restoration of the C(26)-C(30) bond almost to equilibrium value (actually, 1.44 Å). Ta(3) continues at the site C(52)-C(56). (e) $T=360$ K, $t=5.66$ ps: The Ta_2 dimer has moved closer to Ta(3), which has also moved marginally to the site C(53)-C(32), on the same hexagon as before. However, the dimer and monomer do not get close enough to form a chemical bond. (f) $T=360$ K, $t=6.39$ ps: The $C_{60}Ta_3$ cluster is now charged. The Ta_2 dimer moves away from the Ta monomer, along the surface of the C_{60} cage. (g) $T=360$ K, $t=6.57$ ps: The Ta_2 dimer detaches from the surface of the C_{60} cage. The Ta monomer continues at the site C(53)-C(32).

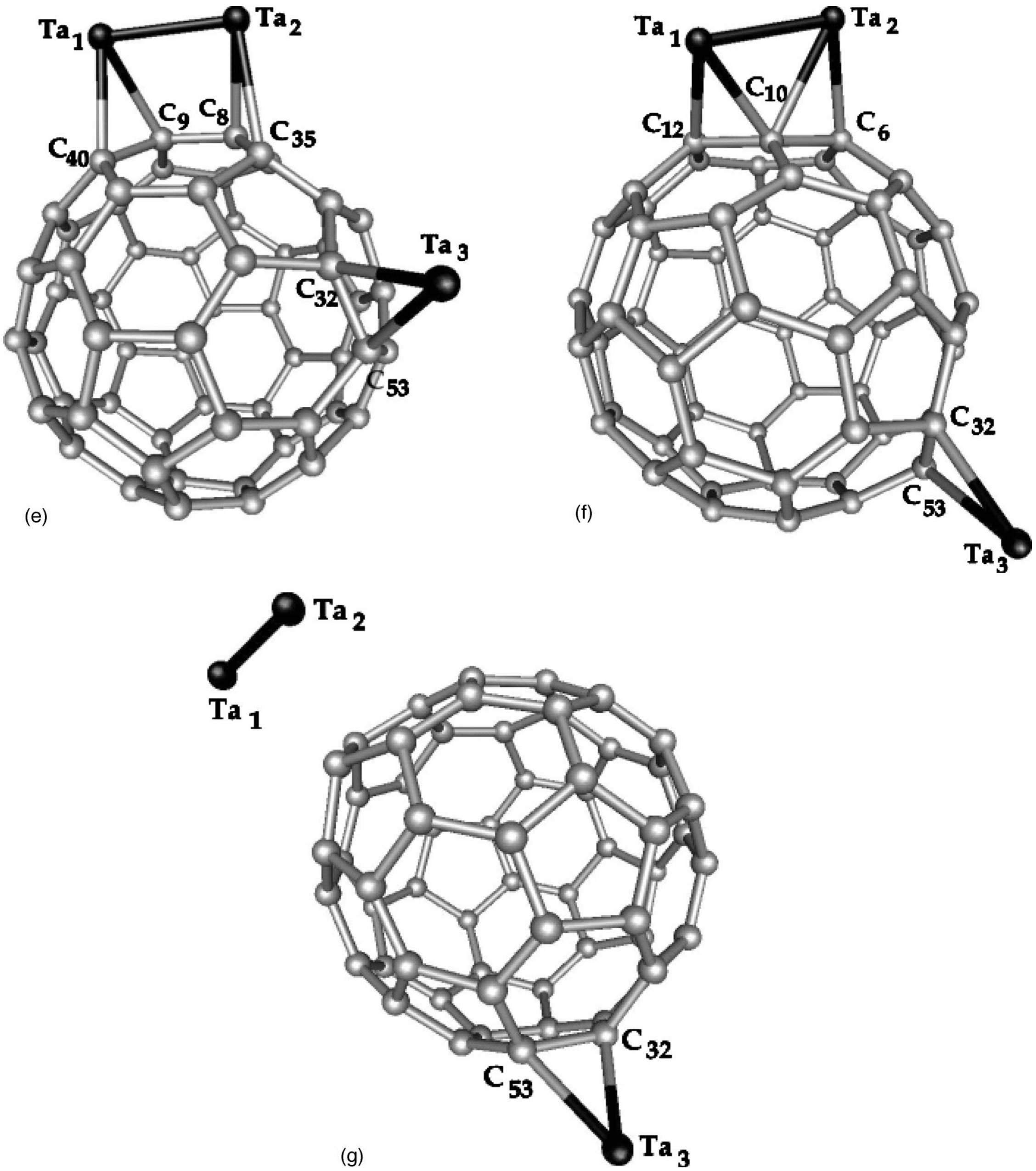

FIG. 4. (*Continued*).

C_{60} at 1000 K is a clear sign of physisorption of the metal cluster rather than the breaking down of true chemical bonds. Thus, it can be inferred that the formation of Ta clusters considerably weakens the interaction of the individual metal atoms with the fullerene. As a matter of fact, the trimer drifts away, and in the process the triangle opens up due to the vibrations of the Ta_3 molecule.

We continued the dynamics, heating the cluster to ~1400 K; however, the Ta atoms continued to drift away from C_{60} and did not show any sign of reattaching to the cage to form a bound Ta-fullerene structure.

e. Inferences. On the basis of our dynamical results described above, we can make several inferences about the possible pathways for the C_3 emission reaction.

Two such pathways have in fact been suggested in the literature. The first pathway proposed originally by Martin *et al.*, as explained earlier, is that in the process of emitting C_3 units, the fullerene cage breaks up. The cluster left behind would have only an odd number of carbon atoms; and such an odd-numbered cluster could not survive as a stable fullerene. In our simulations, the only sign of cage instability was the brief but significant enlargement of a C-C single bond. However the bond rapidly reverted to its original value. This implies that if this is the right pathway, dynamical and thermal effects, even for ionized clusters, are not responsible for the fragmentation process, at least on the pico second time scale.

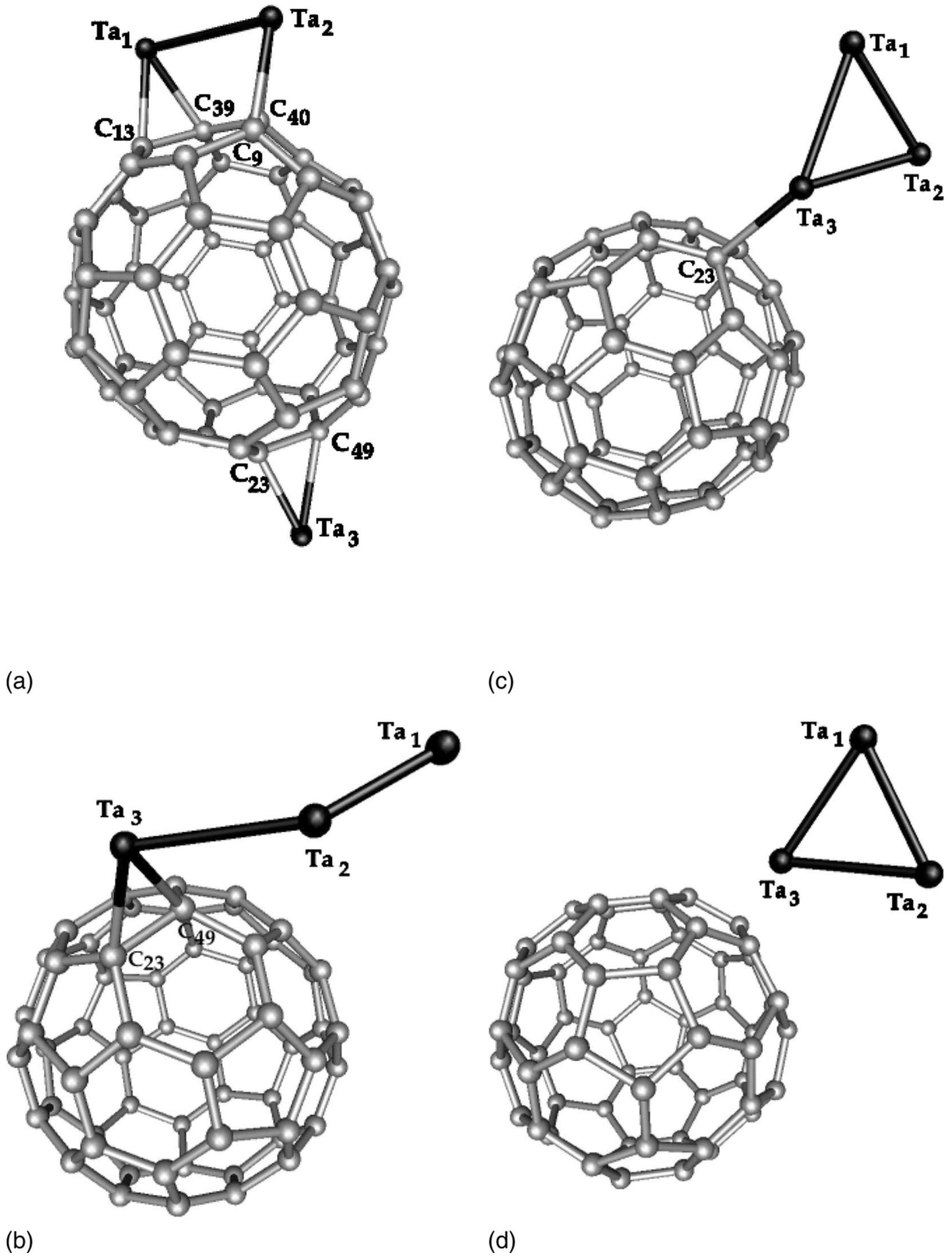

FIG. 5. Snapshots of $C_{60}Ta_3$ during the dynamical Simulation 2. The starting configuration is the same as in (a), but the cluster is charged from the start. (a) $T=300$ K, $t=1.69$ ps: Ta_2 dimer is formed on the C_{60} surface. The third Ta atom, Ta(3), is at site C(23)-C(49). (b) $T=850$ K, $t=3.99$ ps: Ta_3 trimer is formed due to the movement of the dimer towards Ta(3), which is still bonded at C(23)-C(49). (c) $T=950$ K, $t=4.13$ ps: Ta_3 trimer ring is formed. (d) $T=1000$ K, $t=4.16$ ps: Ta_3 ring leaves the C_{60} cluster surface.

The second pathway associated with the C_3 emission, suggested originally by Jarrold *et al.*,[23] is that the fullerene cage does not in fact break up. Instead, the channel of C_3 emission allows the fullerene cage to remain intact by incorporating one Nb atom into the cage network. The other two Nb atoms remain on the cage surface even after it has shrunk. Interestingly, the behavior of the Ta atoms on the surface of the fullerene cage in our simulation appears to be consistent with this scenario: as mentioned earlier, a Ta dimer is rapidly formed, which operates as a highly mobile and almost independent unit, while the third Ta atom stays strongly bonded almost at a fixed position on the cage.

Despite these inferences, an unambiguous C_3 emission reaction from the $C_{60}Ta_3$ cluster clearly did not occur in our simulations. An important reason for this could be that the time scale for C_3 emission is just too long, for instance, nanoseconds or even milliseconds, to be reproduced in the simulations.

This time scale limitation of MD simulations is in fact well known in many contexts. For instance, problems due to high barriers are often encountered in high-pressure studies of phase transitions.[61] Less often discussed are the problems arising due to low-entropic pathways between two minima.[62] Nature has infinite patience and the time scales of events in experiments are often very long. However, such long ''waiting periods'' are not possible in simulations. To overcome this problem, other methods are explored in simulations. For instance, the system may be heated to a high temperature in the hope that the event may occur quickly. However, the channels available at low temperature on a long time scale (akin to a low but narrow pass between two valleys) are not necessarily the same as those that are important at high temperature on a short time scale (akin to a high but broad pass between the two valleys).[62] Our simulations have shown that there are in fact no channels available for C_3 emission at temperatures above 1000 K, on a picosecond time scale (as the Ta atoms simply detach from the fullerene cage above this temperature, thus *hindering* this reaction channel). This result is significant, as it implies that the C_3 emission reaction cannot be driven by a straightforward thermal heating process—at least on the picosecond time scale. In contrast, pure C_{60} can be fragmented by a purely heating process, at temperatures of ≈ 5000 K.[55,56]

An avenue that may be worth exploring to a greater degree is the role of electronic excitations on the dynamics. For instance, recent *ab initio* simulations[63] of solid fullerite indicate that nonthermal fragmentation of the individual C_{60} cages occurs for sufficiently high electronic excitation. However, we emphasise that even in C_{60}, the effect of electronic excitations on the fragmentation behavior is far from being understood. Thus, recent tight-binding MD simulations on pure C_{60} (Ref. 55) indicate that there is no noticeable effect on the disruption of the cage apart from a marginal lowering of the fragmentation temperature by about 10% from ~ 5500 K. An *ab initio* MD study of the stability of C_{60},[56] on the other hand, showed that the fragmentation temperature is lowered by almost 50%, from 10 000 K.

IV. CONCLUSIONS

In this work, we have studied the C_{60}-Ta interaction in C_{60}-fullerene clusters doped exohedrally with Ta atoms. The motivation for this study was provided by the unusual results of the photofragmentation experiments of Martin *et al.*,[3] which measured carbon-trimer emission from C_{60} molecules doped exohedrally with three or more Ta atoms. To this end, we have investigated, via first-principles calculations, the structures and energetics of fullerene molecules doped with a number of Ta atoms varying between one and three. The most stable isomers are the ones in which one of the Ta atoms is at a site of high electron density, such as the h-h double bond. The picture offered by our static calculations is corroborated by the analysis of our dynamical simulations. Furthermore, in consonance with the ion-mobility measurements of Jarrold *et al.*[23] on $C_{60}Nb_m$ clusters, we also find that clustering of Ta atoms on the surface enhances the isomer's stability.

Finite temperature dynamics on $C_{60}Ta_3$ have shown that at least two Ta atoms are extremely mobile on the surface of the C_{60} cage, and are not strongly bound to it, behaving indeed like a surface-physisorbed species. However, interestingly, in our study, we find that the third Ta atom remains strongly bound to the cage, moving only very slightly throughout the simulations even upto a temperature of 1000 K, hence representing a true chemisorbed species. This behavior of the Ta atoms, in which two of them operate as a unit almost independent of the third, appears to be consistent with the picture envisaged by Jarrold *et al.* Except for a fleeting localized vibration which causes a very large increase of one C-C (single) bond length, the fullerene cage does not disrupt or destabilize even upon heating up to 1000 K, at least on the time scales of our study.

In summary, our Car-Parrinello dynamical simulations have revealed several novel insights into the C_{60} Ta_3 system. The large mobility of the Ta atoms on the surface of the C_{60} cage at finite temperatures (reported here for the first time to the best of our knowledge), and the Ta-Ta attraction, lead to clustering of the Ta atoms and finally to their detachment from the fullerene surface at relatively low temperatures (of ≈ 1000 K). This detachment at relatively low temperatures thus *precludes* the possibility of a straightforward thermal heating process driving the C_3 emission in any possible reaction pathway on the picosecond time scale.

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