Freedom and Constraints of a Metal Atom Encapsulated in Fullerene Cages

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Ab initio molecular dynamics applied to fullerenes with La and Y inside reveals an unforeseen picture of these fascinating host-guest complexes and answers long-standing basic questions on the metal-cage interaction. Adsorption sites of the metal atom, nature, and time scale of its motion are identified. They depend on the cage structure in a simple way, applicable to any fullerenelike host with electron donors inside. Results for (La, Y)@C_{82} are consistent with experiment and suggest its potential as electronic molecular switch. Light is shed onto the strikingly poorer stability of (La, Y)@C_{80}. [S0031-9007(96)00739-9]

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Fullerenes are a beautiful example of hollow structures that give rise to endohedral host-guest complexes [1] with a wide range of potential applications as molecular and solid-state devices [2]. In particular, incorporation of metal atoms is expected to yield diverse physical properties, such as superconductivity, ferromagnetism, and nonlinear optical response. Only during the past few months are we witnessing the flourishing of interesting results from the experimental side, which seem to finally open up this new area of materials science. In fact, although the first metallofullerene with La encapsulated in the C_{60} cavity was discovered almost simultaneously with Buckminsterfullerene itself already more than ten years ago [3,4], several reasons have slowed progress down. Certainly one was the difficulty to synthesize metallofullerenes in macroscopic quantities and to cleanly characterize them. Very recently, however, the crystal structure of a metallofullerene (Y@C_{82}) was resolved [5], and furthermore organic synthesis has indicated new unconventional methods to open the carbon cages [6,7]. Another, and crucial, reason is that the understanding of their physical and chemical behavior is still limited. In fact, key long-standing questions that are indeed common to many host-guest complexes remain unanswered: "Are there general and simple rules for the metal-cage bonding, or has one to resort to quantum chemical calculations case by case? At room temperature, does the metal atom move inside the molecular cavities? If so, how and on which time scale? Why do certain selected high fullerenes, especially C_{82}, appear to be "stable" with metals encapsulated, while C_{60} itself does not?" Simple stability criteria invoking different electronic properties, such as the existence of a gap in one but not in the other, are not supported by current evidence: namely, both (La,Y)@C_{60} and (La,Y)@C_{82} are radicals, with the unpaired electron delocalized over the cage [2,8,9]. On the other hand, clarifying such issues on the basis of experimental grounds is not obvious. They are, however, ideal for theoretical investigation aided by realistic computer simulations that enable one to directly access the host-guest interaction.

In this Letter, we present *ab initio* molecular dynamics simulations of La and Y fullerenes, namely, the cases most extensively studied so far experimentally, for which our answers to the above questions can be directly compared to observation. Our results reveal how a given geometrical structure determines the metal chemisorption sites, and to what extent bonding constraints limit the freedom of the metal atom. In particular, a different dynamical behavior becomes manifest for the two key cases. In C_{60}, high symmetry and low barriers allow the guest to diffuse and make a round trip in ~1 psec. C_{82}, on the other hand, offers only few and *unforeseen* attractive nests to the metal atom. Trapped there, it moves with characteristic times of ~0.1 psec. Studying these two examples does not restrict our findings: the scheme emerging from our calculations for the chemistry and the characteristics of the atomic dynamics in fact applies to any carbon cage with electron donors encapsulated. With this well-defined picture in mind, we finally tackle the relative stability issue and speculate on possible realistic practical applications.

Experiment and theory for C_{82} agree that the metal atom, be it La or Y, is positioned off center, close to the carbon shell, and that it donates three valence electrons to the cage [8–11]. Nothing more can be inferred from experiment concerning the nature of the chemical bonding, however, and calculations so far cannot be considered exhaustive because they are static and limited to only a few structures. In particular, in (La,Y)@C_{82} the cage structure is generally assumed to be the same as the most probable one for empty C_{82} (of C_2 symmetry), and only one configuration has been considered with the metal atom on the C_2 axis [12]. Our calculations used density-functional-theory-based Car-Parrinello molecular dynamics (MD) [13,14] with local spin-polarized exchange and correlation functionals (LSD) [15]. Our investigation developed in four main steps: (i) An extended optimization for both La@C_{82} and Y@C_{82} using simulated annealing procedures, which revealed the presence of a few energetically preferred and previously unforeseen chemisorption sites and also demonstrated that the C_2 position, being ~0.55 eV higher than the global minimum, is unlikely to be of any relevance; (ii) a series of constant-temperature MD simulations of La@C_{82} at room temperature (using the Nosé-Hoover thermostat [16]) with different initial configurations; (iii) structural optimization for La@C_{60} and Y@C_{60}; and (iv) room-temperature MD simulations for La@C_{60}. The picture that emerges can now be briefly summarized.

Stripped of its three electrons, the metal ion is attracted by the electron-rich regions. These correspond to the double bonds at the fusion of two hexagons in the pyracylene configuration [see Fig. 1(a)], which provides an optimal environment for the guest ion by allowing it to be efficiently coordinated to the maximum number (five) of double bonds. In C_{60}, there are 60 such equivalent sites (owing to the 30 double bonds and the Jahn-Teller splitting). In C_{82}, there are several such sites, which, however, differ in the arrangement of the rings surrounding the pyracylene unit [Figs. 1(b)–1(d)]. Configuration 1(b) is C_{60}-like and has the same curvature radius as in C_{60} (3.3 Å), which is smaller than in 1(c) and 1(d) (3.8 and 3.7 Å). Steric and electronic factors thus cooperate to energetically favor the configuration in 1(b). The presence of the positive ionic charge polarizes the electron density around it (see Fig. 2), thus strengthening the chemical bonding and locally modifying the cage [17]. The curvature radius decreases less in C_{60} (0.1 Å) than in C_{82} (0.2–0.3 Å), showing that the latter adapts better to the chemisorption. Thus, the binding energy of the C_{82} metallofullerene turns out to be higher by ~0.65 eV, consistent with its higher stability. Several of the static properties are shared by the configurations in Figs. 1(b)–1(d) in C_{82} [18], and are also in common with C_{60}. In particular, the (La,Y)-carbon first coordination is six, which agrees with available extended x-ray absorption fine-structure (EXAFS) data [19]; the spin density is delocalized on the cage, as observed in EPR experiments [2,20], and the (adiabatic) ionization potentials and electron affinities have very similar values (IP = 6.1–6.3 eV, EA = 3.3 eV), as do the dipole moments (DM = 3–4 D).

The MD runs at room temperature, however, show the limitations of the static picture and reveal a new scenario. In fact, the metal atom cannot be regarded as localized at a specific site, and the type of motion it undergoes is dramatically different in the two fullerenes.

In C_{60}, the dynamical path from one minimum to the next goes through a very flat region of the potential energy surface, the equivalent sites being close and separated by energy barriers lower than kT. The encaged atom diffuses and completes a "round trip" inside the molecule [see Fig. 3(a)] in only ~1.1 psec. As a consequence of its bonding constraints, at each instant it tends to keep a first coordination as close to six as possible, and its displacement is mostly tangential (at a distance of 1.2 ± 0.1 Å from the cage center). The calculated vibrational spectrum [21] exhibits fingerprints of the presence of La because all the modes involving La are at much lower frequencies than those of the carbons. In particular, those involving the coupling of La and the cage have an average

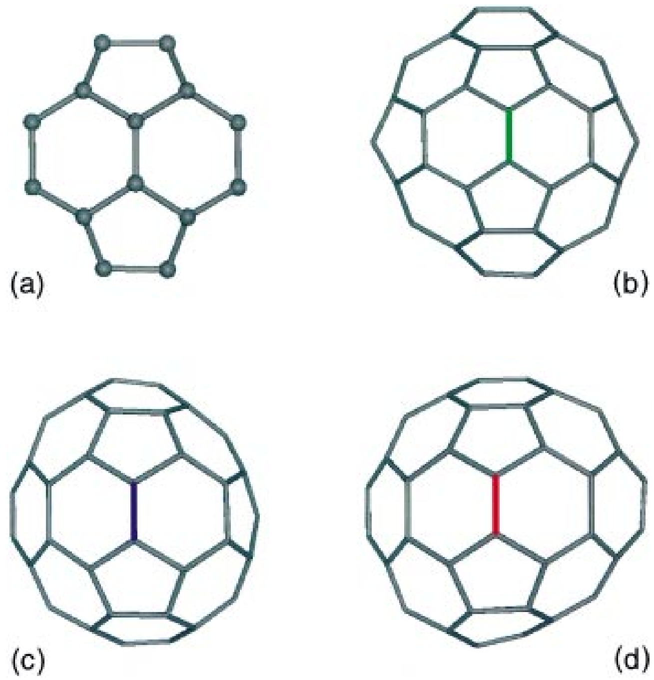

FIG. 1(color). Ring structures in fullerenes: pyracylene, (a) isolated and (b)–(d) with first surrounding rings; (b) shows as it is in C_{60}. In C_{82}, there are two configurations of the (b) type, eight of the (c) type, and four of the (d) type.

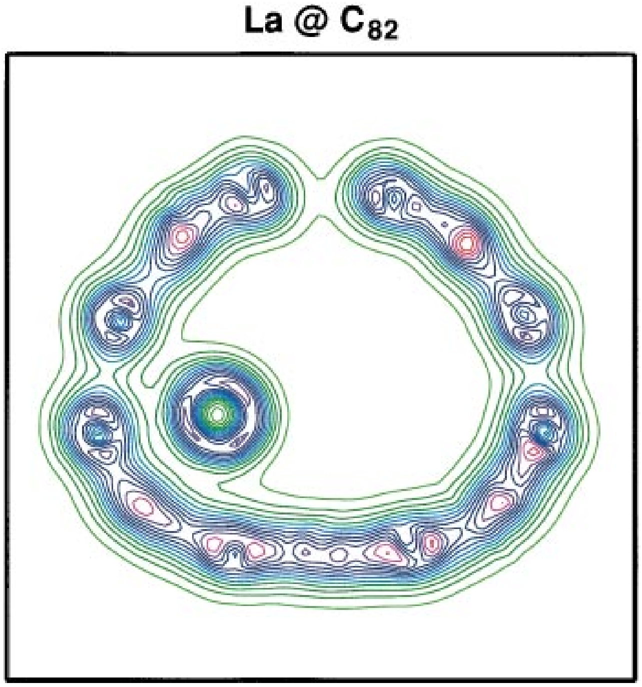

FIG. 2(color). La@C_{82} 2D projection of the electron density on a plane through the molecular axis. This refers to the configuration in Fig. 1(b). In all cases, the metal position is off center, as experimentally observed in Ref. [5]. The 1s core electrons of the carbon atoms are not considered, nor is the La core up to the $n = 4$ shell.

frequency of $\sim 150\ \mathrm{cm}^{-1}$, i.e., $\sim 100\ \mathrm{cm}^{-1}$ below the lowest frequency of C_{60}.

In C_{82}, only a few configurations provide an attractive nest for the metal atom (see Fig. 1). Indeed, there are only two types of possible situations in which the metal atom can be trapped at room temperature, illustrated in Figs. 3(b) and 3(d): The latter is centered around the configuration shown in Fig. 1(d), while in the former the minimum energy position corresponds to that in Fig. 1(b) and is ~ 0.15 eV lower. In our MD runs (2 psec), we have observed no transition from one to the other. There is an important difference in the dynamics of lanthanum in the two situations, which can be understood on geometrical grounds. In fact in Fig. 3(d), the pyracylene ring conformation is spatially "isolated," and this helps confine the ion in the potential well. In the complex vibrational spectrum [21], we recognized the harmonic oscillation of La about the minimum position, at $\sim 80\ \mathrm{cm}^{-1}$. In Fig. 3(b), in contrast, three pyracylene configurations [of the types (b) and (c) in Fig. 1] are fused together, and the minima are separated by energy barriers lower than kT. The ion is thus freer in this case, and delocalized over a wider region. Figure 3(c) shows how the distances of La from the center of the three closest "double bonds" vary during the simulation. Residence times are of the order of 0.1 psec. The motion is highly anharmonic and characterized by frequencies down to $50\ \mathrm{cm}^{-1}$. Vibrations of the carbons coupled to La in both cases [3(b) and 3(d)] are in the range of $160-180\ \mathrm{cm}^{-1}$, i.e., well separated (by at least $40\ \mathrm{cm}^{-1}$) from the rest of the spectrum. These features are in good agreement with recently measured IR and Raman spectra [22]. A better distinction of the two situations would be obtained by comparing the far-IR responses. On the other hand, the time scale of the ion motion is such that it can easily escape EPR observation. There are two measurements available at the moment, however, the interpretation of which is consistent with our results. 2D-EPR [23] in solution cannot distinguish between two different scenarios, namely, whether La is rigidly attached to the cage or undergoes very fast motion; ESR at different temperatures [24] suggests isomerization at 200 K and spatially limited La motion.

Let us now remark on the relative stability of the C_{82} and the C_{60}-based metallofullerenes. Concerning the isolated molecules, the binding energy is certainly higher for (La,Y)@C_{82}, whereas the higher entropy in (La,Y)@C_{60} acts as a stabilizing factor. However, in the processes leading to the synthesis of the metallofullerene, an important role is played by intermolecular interactions,

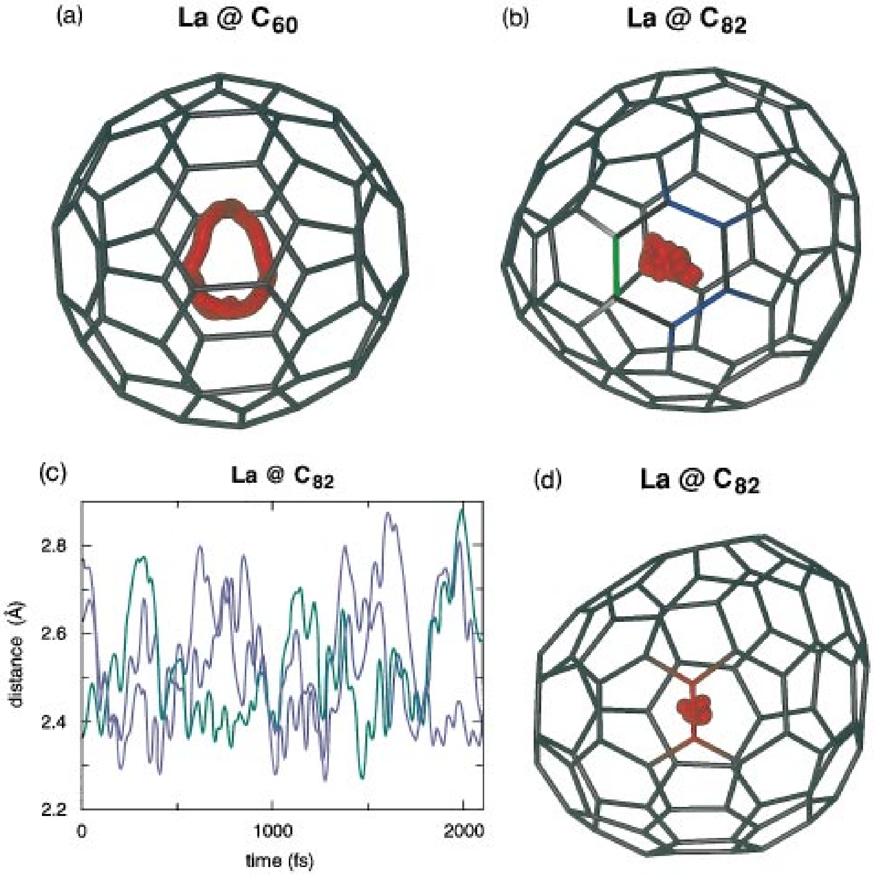

FIG. 3(color). The dynamical trajectory of La, inside C_{60} (a) and inside C_{82}, where it can be trapped in two different configurations [(b) and (d)]. (c) Variation of the distance of La from the centers of the three closest "double bonds" in (b) as a function of time. The atom moves fast, driving with it the local distortion of the cage structure and the deformation of the cage electron cloud.

in the solid state as well as in polar solvents. The deformation of the electronic cloud following the metal atom is strong in (La,Y)@C_{82} and remains spatially localized (dipole moments of the order of 4 D), whereas in (La,Y)@C_{60} it averages to zero on the time scale of a picosecond. This fact, in particular, tends to better stabilize the (La,Y)@C_{82} aggregates.

The C_{60}-based system is certainly interesting, being isoelectronic to the superconducting fullerides [9,25,26], with the three excess electrons occupying molecular states, and in view of its dynamical properties studied here. With the recent discovery of new chemical methods for opening the C_{60} cage [6,7], its synthesis has now become a realistic expectation. The C_{82}-based system, and most likely also other higher fullerenes of low symmetry, are more appealing for the fabrication of molecular devices, such as an electronic switch [27]. In fact, we have shown that, among the different optimal configurations for (La,Y)@C_{82}, the energetically degenerate ones are geometrically well separated, whereas the nondegenerate ones [Figs. 3(b) and 3(d)] have sufficiently different properties and are unlikely to be occupied simultaneously at room temperature. The barrier between them can be tuned either by applying an external electric field or by suitable doping, be it exohedral or substitutional.

In summary, Car-Parrinello LSD-based molecular dynamics has allowed us to acquire detailed information about “what happens in the cavity of a metallofullerene and why.” The insight we have gained here is not restricted to the particular systems we simulated, but can easily be extended to any fullerene, and eventually to carbon tubes, with electron donors incorporated as individual atoms or small aggregates. In fact, as we have seen, the key factors responsible for the preferred positions of the guest atom and for the type of motion it undergoes can be easily rationalized on the basis of the geometrical characteristics of the carbon cage and of its basic electronic properties [25,28,29]. This understanding should now help in designing endohedrally doped materials with specific characteristics. We have described two such examples.

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