Electronic Structure of Sc@C$_{60}$: An *ab Initio* Theoretical Study

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We have studied the electronic structure of Sc@C$_{60}$ at the self-consistent-field Hartree–Fock (SCF-HF) level of theory employing a double-zeta (DZ) basis set. Binding energies have also been calculated employing a hybrid of HF and density functional theory (herein denoted as HF-BLYP). Several electronic states in C_{5v} and C_{3v} symmetry were considered. A double-minimum configuration is found for the open-shell $^4A_2$ electronic ground state in C_{5v} symmetry. The lowest energy minimum has Sc located 1.175 Å away from the center of the cage, approaching a C$_{60}$ pentagon along a C_5 axis. Bonding between the Sc atom and the cage occurs by donation of the 4s electrons to the lowest unoccupied orbital of C$_{60}$ and by 3d electron interaction with the antibonding orbital associated with the five double bonds radiating from the pentagon closest to Sc ($\sim$2.5 Å). The other local minimum has Sc located at the center of the cage and is predicted to be 1.2 eV higher in energy at the highest level of theory employed in this work (DZ/HF-BLYP). The energy barrier for moving Sc from the center of the cage to the lowest energy position is predicted to be 0.1 eV at the same level of theory.

Introduction

Since the discovery of buckminsterfullerene in 1985,[1,2] and especially after the macroscopic preparation of fullerenes in 1990,[3] many theoretical and experimental investigations have been carried out on these novel molecules.[4] Numerous metallo-fullerenes such as La@C$_{82}$,[5] La$_2$@C$_{80}$,[6] U@C$_{28}$,[7] Ca@C$_{60}$,[8] Sc$_3$@C$_{82}$,[9] and Sc$_2$@C$_{2n}$ ($2n$ = 74, 82, and 84)[10] have now been experimentally identified. Understanding the electronic structure of these endohedral molecules is important because custom-filling the empty fullerenes could lead to species with tailor-made properties. Many theoretical studies have been carried out on endohedral fullerenes,[11] but so far, the experimental evidence is that only elements with Pauling electronegativities smaller than $\sim$1.5 (that is in general elements on the left of the periodic table) are spontaneously trapped inside fullerenes in arc and laser vaporization experiments.[12]

The mechanism of endohedral fullerene formation remains unknown, and the nature of the metal–cage interaction has been studied only in a few cases. The large abundance of U@C$_{28}$ and the relative size of the U atom and the C$_{28}$ cage are consistent with covalent bonding between them.[7,12] On the other hand, the experimental evidence and theoretical calculations on Ca@C$_{60}$ both indicate that an ionic interaction exists between Ca and the carbon network.[8] Theoretical studies on La@C$_{82}$[13] have concluded that La donates its 6s electrons to the carbon cage. However, the most stable configuration has the La atom in a nearly +3 oxidation state,[13] a result consistent with the experimental ESR.[14] Another recent theoretical study[15] has confirmed the La^{3+}C$_{82}^{3-}$ picture, but these authors also found that, unlike La, Sc and Y form +2 endohedral complexes with C$_{82}$. The ultraviolet photoelectron spectrum (UPS) of La@C$_{82}$ has recently been measured[16] and found to be similar to that of C$_{82}$ except for three additional electrons accommodated in the lowest unoccupied molecular orbital (LUMO) and second LUMO of C$_{82}$. Evidently, different bonding situations characterize the few metallofullerenes so far studied. Needless to say, understanding the endohedral bonding mechanism will help elucidate the properties of these molecular systems.

Alkali-doped buckminsterfullerene (A$_3$C$_{60}$) has been shown to be a superconducting material with a relatively high T_c.[17] However, the alkali atoms are very reactive and produce a material that is hard to work with. It has been hypothesized that adequate endohedral substitution of C$_{60}$ could yield a compound with similar electronic characteristics, but with a much smaller reactivity due to the dopant isolation. Sc and La have long been favorite candidates for this purpose.

In this paper, we have chosen Sc@C$_{60}$ as a prototype endohedral fullerene with potentially interesting electronic properties. In particular, only Sc@C$_{82}$,[15] Sc$_3$@C$_{82}$,[18] and Sc@C$_{28}$[12] have previously been theoretically studied in the scandium–fullerene family. Because scandium has a 4s^{2}3d^1 atomic configuration, it could presumably donate its three valence electrons to the t$_{1u}$ LUMO of C$_{60}$. This is currently the conventional view of the analogous electron donation mechanism at play in A$_3$C$_{60}$. Furthermore, Sc@C$_{2n}$ (for $2n$ larger than 28) has been experimentally observed in laser-vaporized scandium–graphite experiments,[19] and Sc@C$_{60}$ was found to be predominant over its neighbors. Thus, macroscopic preparation of Sc@C$_{60}$ should not be ruled out.

Computational Details

In this paper, the direct SCF method[20] as implemented in the TURBOMOLE package[21] was used throughout. Equilibrium geometries were obtained employing analytic energy gradient techniques and all open-shell electronic states were calculated at the restricted Hartree–Fock level (*i.e.*, as spin eigenfunctions). The basis set for carbon is a double-zeta (DZ) contraction of van Duijneveldt primitive set (7s3p/4s2p)[22] and is identical to the one employed in previous fullerene studies.[23,24] For scandium, the Wachters basis set[25] (14s9p5d/10s6p2d) was supplemented with Hay's diffuse 3d function[26] and two uncontracted 4p functions as recommended by Hood *et al.*[27] This combination of functions yields a contracted (10s8p4d) Gaussian basis for Sc. Local (LDA)[28] and gradient corrected Becke–Lee–Yang–Parr (BL-YP)[29,30] density functional calculations were carried out employing a code developed in our research group. The electron density obtained at the DZ/SCF level of theory is used to estimate both exchange and correlation energies in a hybrid scheme as discussed in refs 31 and 32. This hybrid method has been very successful in reproducing the experimental thermochemistry of several reactions.[31] All calculations were carried out on a HP-730 workstation at Rice University.

Results and Discussion

Three electronic states of Sc@C$_{60}$ were studied in this work. The theoretical results are presented in Table 1. The calculations

TABLE 1: SCF Hartree–Fock Predictions for the Relative Energies, Orbital Energies, Off-Center Displacement, and Charge of Sc in Different Electronic States of Sc@C$_{60}$ in C$_{5v}$ Symmetry

electronic state	ΔR (Å)	Sc charge	ΔE (eV)	orbital energy (hartrees)		percentage of Sc character	
				a_1	e_1	a_1	e_1
$^4A_2(a_1^1e_1^2)^a$	1.175	+2.40	0.0	−0.394	−0.191	96	0
$^2E_1(a_1^2e_1^1)$	1.480	+2.15	1.4	−0.205	−0.201	35	5
$^4E_2(a_1^0e_1^3)$	1.464	+2.22	2.2		−0.123		89
$^4A_2(a_1^1e_1^2)^b$	0.0	+2.54	0.5	−0.172	−0.264	0	99

^{a} Total energy is −3028.830 95 hartrees. ^{b} Sc is at the center of the cage.
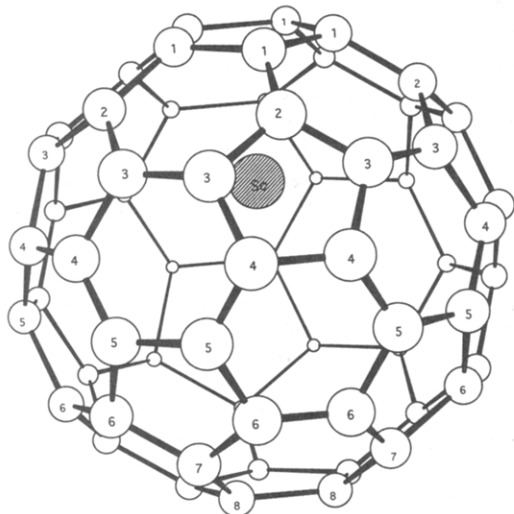
Figure 1. Equilibrium geometry of the $^4A_2$ state in C$_{5v}$ symmetry of Sc@C$_{60}$ as predicted by the SCF Hartree–Fock method employing a double-zeta basis.

were carried out in C$_{5v}$ symmetry which allows the Sc atom to move along the molecular C$_5$ axis (*i.e.*, to approach a pentagon). Of the three electronic states studied in this work, the $^4A_2$ is Jahn–Teller stable, whereas the other two, $^2E_1$ and $^4E_2$, are Jahn–Teller unstable. On the basis of our previous study of Ca@C$_{60}$,[8] we presume that in the present case the Jahn–Teller stabilization energy would also be small. The three electronic states have lowest energy equilibrium geometries with Sc positioned off center. At the DZ/SCF level of theory, we obtain that the $^2E_1$ and $^4E_2$ electronic states are higher in energy than the $^4A_2$ ground state by 1.4 and 2.2 eV, respectively. Remarkably, two local minima were found for the $^4A_2$ electronic state in C$_{5v}$ symmetry. The one with Sc displaced 1.175 Å off center is the lowest energy minimum, whereas the other minimum with Sc at the center of the cage is higher in energy by 0.5 eV (DZ/SCF).

Also presented in Table 1 are the molecular energies of the valence orbitals and their percentage of Sc character. When analyzing these data, it is helpful to note that the I_h t$_{1u}$ LUMO of C$_{60}$ splits into a$_1$ + e$_1$ in C$_{5v}$ symmetry.

The DZ/SCF equilibrium geometry of the lowest energy state, off-center $^4A_2$, is shown in Figure 1. This a$_1^1$e$_1^2$ configuration has the Sc 4s^2 electrons donated to the e$_1$ LUMO of C$_{60}$, whereas the singly occupied a$_1$ valence orbital is a mixture of the Sc 3d orbital (96%) with a small component of C$_{60}$ orbitals. In this structure, Mulliken population analysis shows that the charge transfer from Sc to C$_{60}$ is +2.40 (DZ/SCF), corresponding to 1.99, 0.19, and 0.22 charge units with s, p, and d character, respectively. Therefore, the Sc 4s electrons are completely transferred to C$_{60}$. The 3d orbitals of Sc overlap the nearby carbon atoms, resulting in an interaction with the antibonding orbital associated with the five double bonds radiating from the pentagon closest to Sc (the five C$_1$–C$_2$ bonds in Figure 1). Thus, bonding between the Sc atom and C$_{60}$ occurs by donation of the

TABLE 2: Equilibrium Bond Lengths of the C$_5$, $^4A_2$ Ground State of Sc@C$_{60}$ As Predicted by the SCF Hartree–Fock Method Employing a Double-Zeta Basis^a

| carbon pair (i,j)	bond length (Å)	deviation from C$_{60}$ (Å)	$R[C(i)–Sc]$ (Å)
1–1	1.449	−0.002	2.487
1–2	1.416	+0.046	
2–3	1.438	−0.013	2.796
3–3	1.396	+0.028	3.097
4–3	1.447	−0.004	
4–4	1.454	+0.003	3.529
4–5	1.374	+0.006	
5–5	1.458	+0.007	3.901
6–5	1.440	−0.011	
6–6	1.378	+0.010	4.257
7–6	1.451	+0.000	4.456
7–8	1.370	+0.002	
8–8	1.451	+0.000	4.463
R(Sc–center)			1.175

^{a} See Figure 1 for atom labels.

4s electrons to the LUMO of C$_{60}$ and by the Sc 3d electron interaction with the cage orbitals. Mulliken population analysis indicates that the charge in Sc@C$_{60}$ is not uniformly distributed over the fullerene cage. The carbon atoms charges decrease with the Sc–C distance from −0.12 (closest) to −0.01 (furthest). The center of negative charge is relatively close to the Sc atom resulting in a small dipole moment (0.077 au) obtained for Sc@C$_{60}$ at the DZ/SCF level of theory. As shown in Table 1, the charge transfer from Sc to C$_{60}$ is +2.40 and +2.54, for the two minima found along the $^4A_2$ potential energy surface.

The $^4A_2$ electronic state was also studied in C$_{3v}$ symmetry, which allows the Sc atom to move along a C$_3$ molecular axis. In other words, the possibility that Sc could approach a cage hexagon was also explored. We found that, at the DZ/SCF level of theory, the lowest energy structure for this configuration has Sc displaced 1.518 Å off center and is 1.1 eV higher in energy than the C$_{5v}$ lowest minimum. In this C$_{3v}$ structure, bonding between Sc and the cage occurs via 4s electron donation and 3d electron interaction with the antibonding orbitals associated with the three double bonds in the hexagon closest to Sc. The bonding mechanism is similar in both the C$_{5v}$ and C$_{3v}$ structures. The main difference is just the number of double bonds that the Sc atom approachs in each case (*i.e.*, five versus three).

In Table 2, we present all the symmetry-independent bond lengths of the $^4A_2$ electronic ground state in C$_{5v}$ symmetry (see Figure 1). The deviations from the C$_{60}$ bond lengths as well as all Sc–C distances are also included in Table 2. The shortest Sc–C bond lengths are those to carbons 1 and 2 in Figure 1, 2.487 and 2.796 Å, respectively. These distances are close to the average 2.49 Å Sc–C bond length reported for Sc(C$_5$H$_5$)$_3$[33] and consistent with a strong bonding picture between Sc and the cage. A similar C$_{5v}$ calculation at the DZ/SCF level of theory for Sc–cyclopentadiene gives a Sc–C equilibrium bond length of 2.575 Å. In this case, however, a different bonding mechanism for the closed-shell ground state yields Mulliken population charges of +0.26 (Sc), −0.24 (C), and +0.19 (H). It is worth noting that Sc donates both s (+0.32) and d (+0.42) electrons to the cyclopentadienyl ring, whereas there is back-donation (−0.48) from p electrons.

Roughly two-thirds of the C–C bond lengths in Sc@C$_{60}$ are nearly unchanged by the presence of the metal atom inside the cage. Bonding between Sc and the carbon cage only affects the bond lengths of a small section of the carbon network, most noticeably the C$_1$–C$_2$ double bonds which stretch by 0.046 Å. This result suggests that in large fullerenes multiple, noninteracting Sc atoms could simultaneously bond to different sections of the carbon cage without necessarily forming a cluster (Sc$_2$ or Sc$_3$) inside the cage.

Figure 2 shows an energy curve for the $^4A_2$ state along the C$_5$ molecular axis as a function of the distance to the center of the
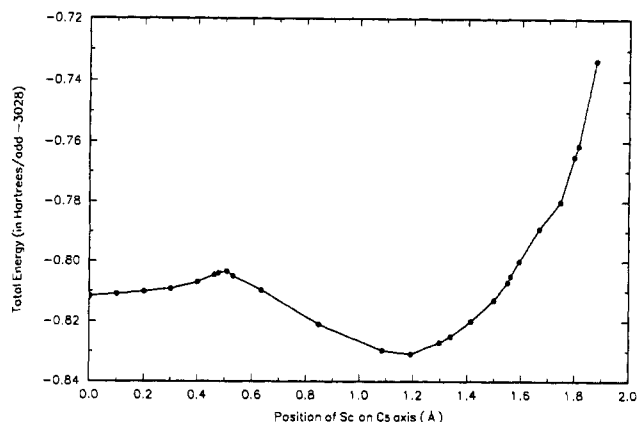
Figure 2. Double-minimum energy profile (DZ/SCF) of the $^4A_2$ state of Sc@C$_{60}$ when moving the Sc along the C_5 axis. The center position of Sc corresponds to 0.

cage. Each energy point was obtained by setting the Sc–center of the cage distance (R) to a fixed value and simultaneously allowing the rest of the carbon cage to relax. As mentioned above, two shallow minima were found. The energy separation between them is predicted to be 0.5, 2.0, and 1.2 eV at the DZ/SCF, HF-LDA, and HF-BLYP levels of theory, respectively. At the DZ/SCF level of theory, the barriers between these two minima were found to be 0.6 and 0.1 eV, from right to left and vice versa, respectively (see Figure 2). At the DZ/HF-BLYP level, these barriers become 1.2 and 0.1 eV, respectively. This result indicates that Sc can freely move inside C$_{60}$ at room temperature.

Finally, we present the calculated binding energy of Sc@C$_{60}$. The DZ/SCF method predicts that the molecule is unbound by 1.1 eV. However, inclusion of exchange-correlation effects based on density functional theory reverts this result to −2.0 (HF-LDA) and −0.6 eV (HF-BLYP). Thus, at these levels of theory, Sc@C$_{60}$ is predicted to be lower in energy than Sc + C$_{60}$.

Conclusion

It appears from our theoretical calculations that the electronic structure of Sc@C$_{60}$ is quite interesting. A double-minimum configuration is found for the quartet electronic ground state. The barrier between these minima is fairly small, and in both cases the net charge transfer is roughly ∼2.5 electrons. In the lowest energy state, the 4s electrons are completely donated to the cage and the 3d electron establishes a covalent interaction with the nearby (∼2.5 Å) carbon atoms. Based on these considerations, it is evident that Sc@C60 and alkali-doped C$_{60}$ will have different electronic structures. However, we cannot rule out that if Sc@C$_{60}$ is isolated in macroscopic quantities, it might have peculiar conducting properties. Given its open-shell electronic structure, Sc@C$_{60}$ should easily react with molecular oxygen when exposed to air.

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