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Electronic states of group-IV endohedral atoms in C_{28}

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We have systematically studied the interaction between the C_{28} fullerene molecule and the group-IVA endohedral atoms C, Si, Ge, and Sn, using state-of-the-art electronic structure and total-energy calculations based on density-functional theory. We find no covalent bonding between these atoms and the fullerene cage. The nature of the cage-atom interaction involves charge transfer from the endohedral atom to the cage which produces weak, mostly ionic binding. The degree of charge transfer increases with the atomic number of the endohedral atom. By comparing the electronic structure of the group-IVA endohedral cage compounds to Zr@C_{28} (a group-IVB endohedral), we find that the latter bonds strongly to the cage due to a covalent interaction between the Zr 4*d* states and the C_{28} states. We extrapolate the trends found for the group-IV endohedrals to suggest other possibly stable systems and to provide insight to the stability of the experimentally observed U@C_{28} complex.

I. INTRODUCTION

An interesting aspect of the recently discovered carbon fullerene molecules is their ability to trap a single atom at the center of the cage, producing molecular packages with potentially unusual properties. Early experiments in this area concentrated on C_{60} and larger fullerenes.[1] More recent work has shown that C_{28}, a smaller fullerene of tetrahedral symmetry, is also capable of trapping an internal, or endohedral, atom.[2] Specifically, U and the group-IVB elements Ti, Zr, and Hf appear to produce exceptionally stable packages when trapped in C_{28}.[2] From its atomic structure and tetrahedral symmetry, C_{28} is expected to behave as a tetravalent superatom.[2] The detailed nature of bonds that such an entity can form to other atoms, either endohedrally or externally placed, remains largely unexplored and little understood. The concept of a multiatom structure acting as a superatom has been invoked in two other cases, spherical semiconductor heterostructures,[3] and endohedral complexes of C_{60}.[4]

In this paper we examine the electronic structure of C_{28} and the ability of this molecule to entrap atoms of various sizes. We systematically study the bonding of the fullerene cage to endohedral atoms from group-IVA of the Periodic Table. With four valence electrons these atoms tend to prefer fourfold coordination and covalent bonding, and may be expected to show strong bonding to a tetravalent cage. In fact, we find little evidence for *covalent* bonding between the fullerene cage and the endohedral atoms C, Si, Ge, and Sn. Instead, the bonding is weak and essentially ionic in character, with electronic charge transferred from the endohedral atom to the cage. By contrast, the group-IVB endohedral Zr exhibits strong bonding to the cage.[2,5] By comparing the electronic structure of Zr@C_{28} to that of the group-IVA systems, we trace the strong bonding to a covalent interaction between the Zr 4*d* states and the cage orbitals. Extrapolating from our observations for the group-IVA endohedrals, we predict that large, hexavalent endohedral atoms with *s* and *p* valence electrons are likely to produce a complex with a large gap between occupied and unoccupied states, through ionic bonding. Such systems should be chemically stable. The experimentally observed stable complex U@C_{28},[2] on the other hand, should be qualitatively similar to the Zr@C_{28} case, where strong interaction between large-angular-momentum endohedral valence states and cage orbitals leads to covalent bonding.

The paper is organized as follows: Section II discusses the electronic states of C_{28}, Sec. III describes the structural properties of the cluster with different group-IVA endohedrals and their relative stability, Sec. IV examines the electronic properties of the group-IVA endohedrals, Sec. V makes comparison to other endohedral comlexes, Sec. VI considers possible distortions of the cage and exohedral complexes, and Sec. VII summarizes our results and draws conclusions from the comparisons.

II. ELECTRONIC STATES OF BARE C_{28}

The calculations reported in this work are based on the density-functional theory (DFT) in the local density approximation (LDA).[6] We use a Gaussian-orbital basis set for representing the electronic states of the fullerene cage and the endohedral atoms. We use an accurate numerical integration scheme in real space to evaluate the cluster total energies.[7] Atomic forces are calculated with the Hellmann-Feynman-Pulay approach.[8] The forces and energies are then used together in a conjugate-gradient scheme to relax the cluster structures. The structures of all the endohedral complexes were relaxed until the forces on various atoms vanished to 0.01 a.u.

We first determined the minimum energy structure of C_{28} using our computational approach. This cluster is assumed to have tetrahedral symmetry.[2] The 28 atoms are arrayed in 12 pentagons and 4 hexagons on the cluster surface, and each atom is threefold coordinated. The surface contains only three distinct bond lengths, the hexagon bond r_h (also making up one side of the pentagons), the apex pentagon bond r_a, and a basal pentagon bond r_p (see Fig. 1). Our relaxation of the C_{28} structure yields $r_h = 1.428$ Å, $r_a = 1.446$ Å, and $r_p = 1.510$ Å, in good agreement with other recent calculations.[2,5]

The electronic structure of C_{28} is an open shell in a DFT/LDA paramagnetic calculation (spin states equally occupied). The highest occupied molecular orbital (HOMO) state is a t_2 (threefold degenerate, aside from spin) level which can accommodate six electrons, but contains only four electrons in the DFT/LDA ground state. An unoccupied a_1 (onefold degenerate, aside from spin) state lies only 0.25 eV above the HOMO. Recent spin-polarized calculations[5] have shown that the C_{28} cluster ground state is a quintet ($S = 2$) spin state, formed by raising one of the t_2 electrons to the a_1 level, and placing all the electrons in the spin-up state. The spin-polarized quintet configuration lowers the total energy by 0.38 eV.[5] The next unoccupied electronic level is a twofold degenerate state of e symmetry, about 2.5 eV above the HOMO. The energy diagram of the valence states of C_{28} is shown in the bottom panel of Fig. 2.

The electronic structure of C_{28} suggests the possibility of tetravalent chemical bonding. In analogy to the free carbon atom, C_{28} has four electrons shared between a p-like state (the t_2 level) and an s-like state (the a_1 level). Hybrid orbitals constructed from linear combinations of these states could be used as a basis for covalent bonds to an endohedral atom. In a more ionic picture, the C_{28} cluster can accomodate four additional electrons to completely fill the states near the HOMO level and leave a large gap between those states and the lowest unoccupied states. In this picture, an endohedral atom that can donate four valence electrons to the cage should be an ideal candidate for closing the electronic shells.

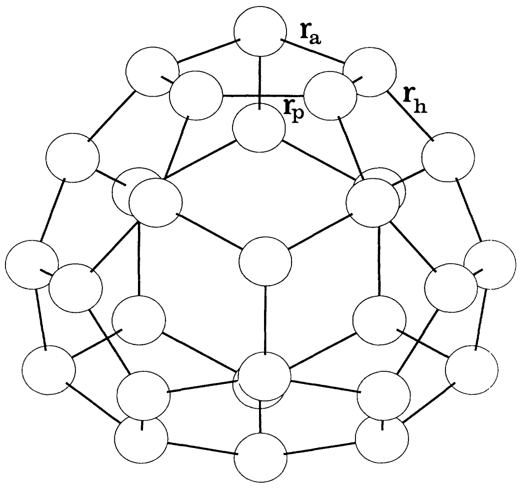

FIG. 1. The structure of the C_{28} cage. The three independent bond lengths described in the text are identified as r_h, r_a, and r_p.

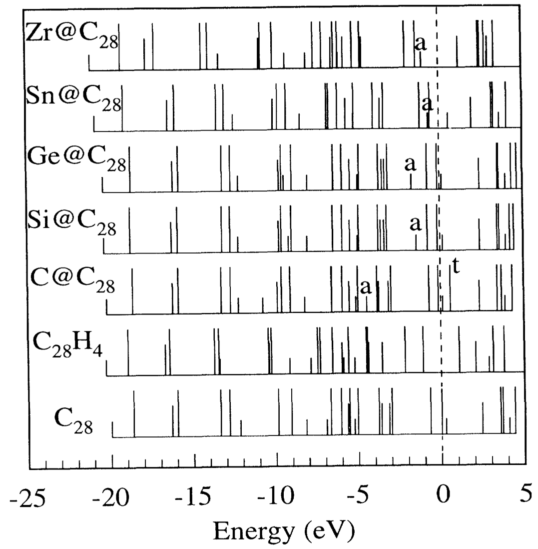

FIG. 2. The electronic states of C_{28}, $C_{28}H_4$, and the various endohedral complexes. The zero of energy in each case is the energy of the Fermi level (indicated by a dashed vertical line). In the cases where a gap exists between HOMO and LUMO states, the position of the Fermi level is taken to be the middle of the gap. The relative height of individual states represents the degeneracy, d, of the levels (d = 1, 2, or 3). Accidental degeneracies exist at several places, which cannot be discerned on the scale of this figure. The different diagrams are shifted vertically for clarity. The a_1 level associated with the s state of the endohedral atoms and the t_2 level associated with the p state of the C endohedral are identified by the letters a and t, respectively, directly above them.

III. GROUP-IVA ENDOHEDRALS IN C_{28}: STRUCTURE AND STABILITY

To investigate the details of endohedral bonding in C_{28} we systematically studied the bonding of the group-IVA atoms, from C to Sn. In each case, the endohedral atom was placed at the centrosymmetric position inside the cage, and the cage atoms were allowed to relax to the minimum energy maintaining the overall tetrahedral symmetry of the complex. Regarding the equilibrium position of an endohedral atom in C_{28}, it was previously found that an off-center relaxation for the Ti endohedral

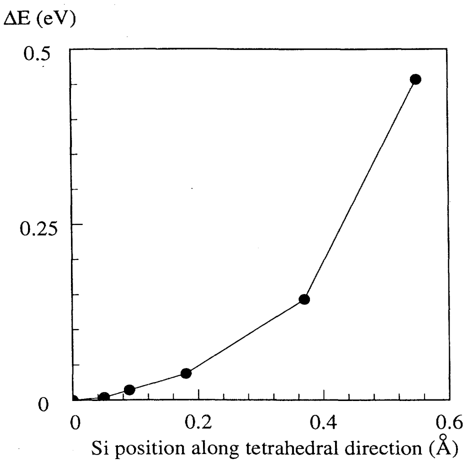

FIG. 3. The energy of the Si@C_{28} system versus the off-center displacement of the Si endohedral atom along one of the four equivalent tetrahedral axes of the cage.

along one of the four equivalent tetrahedral axes (toward the carbon atoms at the apex of the pentagons) is energetically favorable.[9] Zr, on the other hand, was found to be stable at the cage center.[5] To test for possible off-center relaxation of the group-IVA endohedrals, we investigated the off-center relaxation of the Si endohedral along one of the tetrahedral axes. The Si endohedral was moved off center in steps of 0.1 Å, out to about 0.6 Å, keeping the positions of the cage atoms fixed. As shown in Fig. 3, the central position is found to be stable for Si. We expect that the other group-IVA endohedrals will behave in the same way. Table I compares the lengths of the three independent bonds on the C_{28} cage, and also the distance from the endohedral atom to the apex tetrahedral atom of the cage, for the various endohedral complexes. The bond lengths on the cage are seen to depend only very weakly on the endohedral atom, with a tendency toward expansion of the cage as the size of the endohedral atom increases.

The binding energies of the endohedral atoms in the cage are given in Table II. The binding energy is defined as the energy difference between the empty C_{28} cage in the quintet spin state plus an isolated triplet ($S = 1$) spin M atom and the M@C_{28} system. Table II indicates the weak binding of the group-IVA endohedrals in C_{28}. C and Sn are both slightly unbound and Si and Ge have binding energies of only about 1 eV. Note that this binding is very small compared to the total binding energy of the cage, which comes from the 42 covalent C–C bonds. In the case of Si, the extra binding amounts to 0.045 eV per cage atom, compared to the total LDA binding energy of 8.05 eV/atom for the bare cage. For comparison, the LDA binding energy for C_{60} is 8.54 eV/atom. In contrast to the group-IVA endohedrals, Zr is bound by about 12.6 eV inside the C_{28} cage.[5] This corresponds to an additional 0.45 eV/cage atom in Zr@C_{28}, making the thermodynamic stability of this system competitive with that of C_{60}.

TABLE I. Structure of the C_{28}, $C_{28}H_4$, and endohedral complexes M@C_{28}, where M is a group-IV element. We use r_h for the hexagon bond, r_a is a bond to the apex atom of the pentagon, r_p a bond between base atoms in the pentagons, and r_c the distance from the center of the cluster to the tetrahedral apex atoms (in the endohedral complexes this is the endohedral-cage "bond" length). All lengths are in Å. The last column gives the separation between HOMO and LUMO states, in eV.

	r_h	r_a	r_p	r_c	HOMO-LUMO gap
C_{28}	1.428	1.446	1.510	2.46	0.00
$C_{28}H_4$	1.412	1.525	1.507	2.66	2.18
C@C_{28}	1.438	1.466	1.504	2.52	0.26
Si@C_{28}	1.450	1.464	1.515	2.52	0.30
Ge@C_{28}	1.454	1.462	1.528	2.51	0.26
Sn@C_{28}	1.460	1.467	1.504	2.57	1.10
Zr@C_{28}	1.456	1.460	1.499	2.53	2.21

TABLE II. Binding energy (E_B), charge transfer (ΔQ), atomic level energies (ϵ_s and ϵ_p) of the valence states, and energy of the cage a_1 state (ϵ_{a_1}) relative to the HOMO level, for the different group-IVA endohedral complexes. All energies are in eV.

	E_B	ΔQ	ϵ_s	ϵ_p	ϵ_{a_1}
C@C_{28}	-0.09	0.69	-13.606	-5.361	-4.33
Si@C_{28}	1.26	1.91	-11.287	-4.582	-1.29
Ge@C_{28}	0.85	1.91	-12.006	-4.479	-1.56
Sn@C_{28}	-0.35	2.82	-10.379	-4.272	-0.03

IV. GROUP-IVA ENDOHEDRALS IN C_{28}: ELECTRONIC STATES

To understand the bonding of endohedral atoms in C_{28}, it is useful to study the trends in the electronic structure of the complexes formed with group-IVA endohedral atoms. In Fig. 2 we compare the electronic levels of the empty C_{28} cage with those of the endohedral complexes. In the empty cage, only four electrons occupy the HOMO level, which has a total degeneracy of six (including spin). In each of the endohedral systems, the HOMO level is fully occupied, opening a small gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) state, see Table I. A striking feature in Fig. 2 is the fact that the energy levels associated with the empty cage are largely unchanged for all the endohedral complexes. This indicates that most of the electronic states of the cage are inert with respect to interactions with endohedral orbitals. The differences in the eigenvalue spectra shown in Fig. 2 can be traced to the interaction between the valence s level of the endohedral atom with the cage states of a_1 symmetry lying 7.1 eV below the HOMO. In each system, these states form symmetric-antisymmetric combinations with energies different from those of the free atom valence s state and the empty cage a_1 state. The symmetric state is shifted down in energy and the antisymmetric state is shifted up. For all the endohedrals except C, a Mulliken analysis of the charge in these two states indicates that the higher-lying state has predominant endohedral character, while the lower state has more charge located on the cage. Since both the symmetric and antisymmetric combinations are fully occupied, no net covalent bonding results from this interaction. It is interesting to trace the position of the antisymmetric level in the various endohedral complexes. In the case of C@C_{28}, this level is 4.33 eV below the HOMO level. For the Si, Ge, and Sn endohedrals, this level remains below the HOMO, by -1.29 eV, -1.56 eV, and -0.03 eV, respectively. In the case of Sn, however, some additional mixing occurs with the a_1 LUMO state, pushing that level somewhat higher in energy, and giving it some Sn $5s$, character. The trend in the position of the a_1 level associated with the endohedral atoms closely parallels the trend in the corresponding free atomic energy levels (calculated within LDA), as shown in Table II. The sequence of the free-atom valence s states has the ordering $C(2s) < Ge(4s) < Si(3s) < Sn\ (5s)$. Note, in particular, that the energy ordering of Si and Ge s levels is inverted with respect to atomic number ordering both in the free atoms as well as in the endohedral complexes.

A similar trend can be identified for the endohedral valence p levels. In the case of C@C_{28}, for example, a state of t_2 symmetry lies just above the a_1 LUMO level of the cage (see Fig. 2). This state has predominantly endohedral $2p$ character, although it also has a significant admixture of cage orbitals; its position near the HOMO is a consequence of the near degeneracy of the endohedral C $2p$ levels with the HOMO level of the cage. The hybrid character of the state above the HOMO implies that there are states lower in the valence band that have some endohedral $2p$ character. The corresponding valence p states of the other endohedral atoms lie well above the HOMO level of the empty cage, as can be inferred from close inspection of Fig. 2, and do not mix significantly with cage states.

The placement of the endohedral valence p states above the HOMO level of the cage represents a transfer of valence charge from the endohedral atom to the cage. This charge transfer can be computed by using the Wigner-Seitz method to partition space into regions nearest the various atoms in the M@C_{28} system, and then integrating the total valence charge in the region nearest the endohedral atom. We verified that the boundaries of the Wigner-Seitz (WS) zones constructed for these endohedral systems fall in regions of very small charge density, so that this method of partitioning the charge is physically meaningful. In computing the charge transfer to be associated with the various endohedrals, we subtract the electronic charge ($0.66e$) that resided in the central WS zone of the empty cage from the total integrated charge in the WS zone of the endohedral. The remainder is the total charge attributed to the endohedral atom, and the difference between this and the total valence charge of the neutral free atom (i.e., four electrons in the case of group-IVA atoms) is the charge transferred to the cage. The trend in charge transfer in the various endohedral complexes shown in Table II indicates that the charge transfer is a strong function of the atomic number of the endohedral atom. The carbon endohedral transfers only a fraction of an electron to the cage, while Sn transfers the majority of its valence electrons to the cage.

The computed charge transfer shown in Table II is consistent with the energy level spectra discussed above. For the C, Si, and Ge endohedrals, the levels with endohedral valence s character lie below the HOMO. These endohedrals can thus transfer at most their two valence p electrons to the cage. In the case of the carbon endohedral, the effective charge transfer is significantly less than two electrons because of the mixing of the endohedral $2p$ levels with lower-energy valence states of C_{28}. In each endohedral cluster, the charge transfer results in the opening of small HOMO-LUMO gaps of about 0.26–0.30 eV (see Table I). Since the HOMO and LUMO levels of the cage are not involved in interactions with the endohedral orbitals, these gaps are essentially unchanged from the empty cage. For the Sn atom, there is some endohedral $5s$ character in the LUMO state, corresponding to an additional transfer of charge beyond the two $5p$ electrons to the cage. Moreover, the mixing raises the energy of the LUMO, opening a larger gap of about 1.10 eV in this system.

V. COMPARISON TO GROUP-IVB AND OTHER ENDOHEDRALS

It is interesting to compare the electronic structure of the group-IVB endohedral Zr with that of the group-IVA atoms. In the top panel of Fig. 2 we show the energy level spectrum for Zr@C_{28}, using the relaxed atomic geometry for the cluster found in Ref. 5. Again for this system, most of the empty-cage orbitals are unaffected by interactions with the Zr valence orbitals. The $5s$ and $4d$ valence levels of the free Zr atom lie well above the HOMO level of the empty cage. In the case of the Zr $5s$ state, the strong mixing with cage orbitals seen for the valence s level of the group-IVA endohedrals is essentially absent. In effect, the Zr $5s$ electrons are simply donated to the cage. The Zr $4d$ states, on the other hand, mix strongly with the cage orbitals. In contrast to the group-IVA endohedrals, however, in Zr@C_{28} the antisymmetric combinations lie well above the HOMO level and are *unoccupied*, so that the net result is strong bonding between the endohedral Zr and the cage. As a further result of this bonding, the a_1 level is filled, giving rise to a large gap of about 2.2 eV to the lowest unfilled state. This analysis may also explain the stability of the U@C_{28} complex:[2] The presence of high-angular momentum valence electrons in U (valence states $5f^3 6d^1 7s^2$) may enhance significantly the bonding of this atom to the C_{28} cage, as in the case of Zr discussed above. It is noteworthy that one of the preferred oxidation states of U is 4^+, as in Zr.

By extrapolating the charge transfer picture developed above for the group-IVA endohedrals to hexavalent endohedral atoms (for example, group-VI elements), one might expect that the endohedral atoms will retain two electrons in the s level and transfer four p electrons to the cage states. This would be particularly favorable for the heavier group-VI atoms (Se and Te) which have higher-lying valence p levels. If this were the case, both the t_2 and the a_1 states near the Fermi level of the empty cage would be completely filled in the endohedral complex, leaving a rather large gap of about 2.5 eV to the lowest unfilled state. While the overall binding of the group-VI complexes due to this charge transfer may not be large, the large gaps should make these complexes chemically very stable, and thus they may be readily found experimentally.

VI. DISTORTED ENDOHEDRAL AND EXOHEDRAL COMPLEXES

The absence of covalent bonding in the group-IVA systems can be understood on general grounds by considering the bonding geometry of the carbon atoms on the cage. The group-IVA endohedral atoms favor fourfold coordination and sp^3-type bonding, which suggests that bonds to the four tetrahedral apex atoms of the cage should be favored. If the cage does not relax, however, the angle between the interior covalent bond and the surface C-C bonds would be less than 90^0. This is far from the tetrahedral bond angle preferred by sp^3-bonded carbon atoms and would induce large strain in the cage. It might be argued that relaxing the cage to place the apex atoms closer to the endohedral atom would alleviate this strain and enhance the prospects for bonding. Our calculations do not support this possibility, since in the relaxed cage geometry the apex atoms are puckered slightly outward, rather than inward, compared to the empty cage geometry (see Table I). However, it could also be possible that a covalently bonded structure, though stable, is separated by a large energy barrier from the structures we have considered, thereby making it unlikely that our conjugate gradient algorithm would find it. Such a structure exists, for example, for the Si_{29} cluster.[10] To test this possibility for carbon, we scaled the bond lengths of the Si_{29} structure to make the distance from the four apex atoms to the center of the cage equal to an ideal C–C single bond (1.54 Å). This C_{29} structure is 13 eV higher in energy than the $C@C_{28}$ structure discussed above. Furthermore, this strained structure relaxes back to the previously discussed endohedral structure without encountering an energy barrier.[11] We conclude that covalent, sp^3 bonding is energetically and structurally unfavorable in $M@C_{28}$ due to the stiffness of the cage.

To further demonstrate the stiffness of the C_{28} cage toward formation of simple sp bonds with endohedral atoms, and to elucidate the circumstances under which covalent bonding is favorable, we have performed complete geometrical optimizations on the exohedral $C_{28}H_4$ cluster. We find that the four hydrogen atoms readily form strong covalent bonds with the four apex carbon atoms along the tetrahedral axes of the cage, with bond lengths of $r_{C-H}=1.12$ Å. In contrast to all of the endohedral systems, the electronic states at the Fermi level are shifted significantly. The partially occupied t_2 and a_1 levels of the bare cage bond with the hydrogenic s levels and are shifted downward by 1.0 and 4.1 eV, respectively. The highest occupied t_1 cage state is shifted upward due to the relaxed geometry and becomes the HOMO. The DFT/LDA binding energy per hydrogen atom is 4.3 eV, which means that the C–H bonds in $C_{28}H_4$ are approximately 0.7 eV weaker than those found in methane.[12] Since the DFT/LDA atomization energy for H_2 is 2.45 eV per hydrogen atom,[12] we expect that $C_{28}H_4$ would form exothermically if the unsaturated clusters are produced in a background gas of molecular hydrogen. As shown in Table I, the mean radius of the carbon cage is only slightly perturbed for the hydrogenated molecule. However, in contrast to the group-IVA endohedral systems, the structure of the hydrogenated cage is altered significantly. The four tetrahedral apex atoms relax radially outward by 0.20 Å, the twelve adjacent atoms relax radially inward by 0.04 Å, and the remaining twelve atoms relax very little. Although the bonding observed in $Zr@C_{28}$ and $C_{28}H_4$ is different from an *electronic* point of view, the two systems are similar from a geometrical point of view. As in the case of the $C_{28}H_4$, the endohedral Zr atom also induces an outward relaxation of the four apex atoms (by 0.08 Å) but tends to keep the average radius of the molecule constant (see Table I). Furthermore, in both systems there exists a sizable gap between HOMO-LUMO states, in excess of 2 eV (see Table I).

VII. SUMMARY AND CONCLUSIONS

In summary, our systematic study indicates that the bonding of group-IVA endohedral atoms in the C_{28} fullerene is essentially ionic in character, deriving from the transfer of electrons from the endohedral atom to the fullerene cage. A detailed comparison to the isoelectronic group-IVB atom Zr indicates that the presence of high-angular momentum valence states in the endohedral atom greatly enhances the energetic stability of of the $Zr@C_{28}$ complex. Analysis of the electronic state spectrum suggests that group-VI endohedral complexes (for example, $Se@C_{28}$ and $Te@C_{28}$) may be chemically more inert than their group-IVA counterparts. This could have a large impact on the kinetics of endohedral fullerene formation, and could lead to enhanced production of C_{28} clusters with group-VIA atoms in the center. The experimentally observed $U@C_{28}$ complex is more akin to the $Zr@C_{28}$ case, where the presence of high-angular momentum valence states in the atom enhances the energetic stability through strong covalent bonding. This may explain the spectacular abundance of $U@C_{28}$ in experiments.[2] Our study of the hydrogenated cage and the group-IVA endohedrals suggest that the C_{28} molecule will favorably bond to systems that promote an outward puckering of the four apex atoms.

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