

# Metallic coverings of calcium on C<sub>60</sub>

X.G. Gong<sup>a</sup>, Vijay Kumar<sup>b,c,\*</sup>

<sup>a</sup> *Institute for Solid State Physics, Academia Sinica, 230031 Hefei, People's Republic of China*

<sup>b</sup> *Institute for Materials Research, Tohoku University, 2-1-1 Katahira Aoba-ku, Sendai 980-8577, Japan*

<sup>c</sup> *Dr. Vijay Kumar Foundation, 45 Bazaar Street, K.K. Nagar (West), Chennai 600 078, India*

Received 15 May 2000; in final form 18 August 2000

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## Abstract

We present results of the electronic structure and stability of calcium coverings on C<sub>60</sub> using a linear combination of atomic orbitals and the local density functional approximation. Calculations on Ca<sub>x</sub>C<sub>60</sub> with  $x = 12, 20$  and 32 show partial charge transfer from calcium atoms to C<sub>60</sub> and hybridization of the calcium and fullerene states. This leads to (i) a large binding energy of Ca on C<sub>60</sub> which decreases with an increasing coverage and (ii) formation of a metallic shell on C<sub>60</sub>. The large abundance of the Ca<sub>32</sub>C<sub>60</sub> complex is shown to be due to geometric factors in agreement with experiments. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Following the discovery of fullerenes and their solids [1], there has been much interest in developing novel materials from clusters [2,3]. Efforts have been made to prepare fullerenes with metal atoms either encapsulated [4,5] or added on the surface [6–8]. Experiments [6] on metal (M) coverings on C<sub>60</sub> and C<sub>70</sub> fullerenes showed large abundance of M<sub>32</sub>C<sub>60</sub> and M<sub>37</sub>C<sub>70</sub> complexes with M = Ca, Sr or Ba. The stability of these species was related to geometric packing as 32 (37) atoms of these divalent elements cover all the faces of C<sub>60</sub> (C<sub>70</sub>) in a nearly close packed manner. Therefore, it was also suggested to be a way of counting the number of rings in fullerenes. We present here results of a study of the electronic structure and stability of such coverings of calcium atoms on C<sub>60</sub>

and suggest that it could provide another novel way of producing metallic forms of materials due to the strong stability of the C<sub>60</sub> cage and the large adsorption energy of metal atoms.

Related to this problem of the interaction of metal atoms with C<sub>60</sub> are the studies of intercalation [9,10] of graphite as well as metal overlayers [11] on graphite surface which have been found to exhibit a rich variety of low-dimensional electronic, magnetic and transport properties. In both cases there is charge transfer from metal atoms to graphite layers. It has been shown [11] that for a low coverage of potassium on a graphite surface, the adatoms are found to be distributed far from each other in order to reduce Coulomb repulsion. The charge transfer was shown to be 0.28 $e$  and the binding energy, 0.89 eV for each K atom. These values reduce to 0.17 $e$  and 0.76 eV respectively for a (2 × 2) coverage of potassium. In this case the electronic states were found to be quite delocalized within the potassium overlayer. For fullerenes, adsorption occurs on a curved surface

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\* Corresponding author. Fax: +81-22-215-2052.

E-mail address: kumar@imr.edu (V. Kumar).

and this could lead to novel forms of metallic catalysts with 5-fold symmetry and high dispersion. Also, such carbon complexes with partially filled electronic shells of metal covering could have interesting electronic and magnetic properties.

Earlier studies [12] on the  $\text{Li}_{12}\text{C}_{60}$  cluster with Li atoms on the 12 pentagonal faces of  $\text{C}_{60}$  showed charge transfer from Li atoms to  $\text{C}_{60}$  such that its two ( $\text{T}_{1u}$  and  $\text{T}_{1g}$ ) lowest unoccupied molecular orbital (LUMO) states get completely filled leading to a closed shell configuration of this cluster with a gap of about 1.4 eV. For the divalent elements, the mass spectrum of  $\text{Ca}_x\text{C}_{60}$  shows [6] complexes with  $x = 32$  to be strongly abundant. There are also strong peaks at  $x = 35$  and 38 but no prominent peaks at  $x = 12$  and 20 which suggest that divalent metals behave differently from alkalis. Also coatings with Ti and V show [7,8] a different magic behaviour with  $\text{M}_{62}\text{C}_{60}$  being the most prominent species. Here we consider adsorption of 12, 20 and 32 calcium atoms on  $\text{C}_{60}$  and discuss the electronic structure, stability and bonding in these complexes.

## 2. Method of calculation and results

We have used a linear combination of atomic orbitals [13] to solve the Kohn–Sham equations self-consistently within the local density approximation. The binding energies have been calculated for  $\text{C}_{60}$ , icosahedral  $\text{Ca}_{12}$ , dodecahedral  $\text{Ca}_{20}$ , icosahedral  $\text{Ca}_{32}$  and  $\text{Ca}_x\text{C}_{60}$  complexes. For 12, 20 and 32 Ca atoms pentagonal, hexagonal and all the faces of  $\text{C}_{60}$  were covered respectively. Considering the calcium atoms alone, all the atoms lie on a nearly spherical surface which can be considered as a shell to be coated onto the  $\text{C}_{60}$  molecule. The radius of the shell has been varied to obtain the lowest energy configuration. However, to simplify the calculations, we fixed the bond lengths in  $\text{C}_{60}$  for optimizing the atomic structure of  $\text{Ca}_x\text{C}_{60}$ . A more detailed optimization was done for  $\text{Ca}_{12}\text{C}_{60}$ . This led to a small relaxation of the bond lengths for  $\text{C}_{60}$  and a gain of a few eV which is very small as compared with the total binding energy of  $\text{C}_{60}$ . This is expected not to affect the

conclusions reached in the present study in any significant way.

The calculated binding energies and equilibrium bond lengths for different clusters are given in Table 1. For the isolated  $\text{C}_{60}$  molecule the structure was optimized by taking the experimental ratio (0.972) of single and double bond lengths. The equilibrium structure obtained by minimizing the total energy has a double bond length of 2.71 a.u. as compared with the experimental value of 2.65 a.u. and a highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap of 1.71 eV which is very close to 1.74 eV obtained from other density functional calculations [14]. The binding energy is 8.01 eV/atom which is comparable to the result of 8.3 eV/atom obtained in [15] and 8.53 eV/atom in [14]. The ionization potential and affinity level are calculated to be 7.09 and 3.6 eV respectively. This is again in good agreement with the experimental values [16–18] of 7.61 and  $2.65 \pm 0.05$  eV respectively.

Calcium shells with 12, 20 and 32 atoms were relaxed keeping the overall icosahedral symmetry. The resulting bond lengths and binding energies are also given in Table 1. In the case of  $\text{Ca}_{12}$  and  $\text{Ca}_{20}$  the Ca–Ca bond length is 6.44 and 6.51 a.u. respectively. However, for  $\text{Ca}_{32}$  the values are 6.13 and 6.74 a.u. The bond length is smaller than the value (6.96 a.u.) in bulk calcium. Divalent metal clusters exhibit non-metal–metal transitions as a function of size [19]. The binding energies in these clusters suggest that the bonding is more metallic in nature than van der Waals type. However, it is worth noting that the binding energy of these Ca clusters does not increase monotonically with an increase in the number of atoms. In particular for  $\text{Ca}_{20}$  the total binding energy is less than the value for  $\text{Ca}_{12}$ . This is not surprising since in the dodecahedral  $\text{Ca}_{20}$  cluster each atom has only three nearest neighbours as compared to five in the icosahedral  $\text{Ca}_{12}$  so that the total number of bonds are the same in the two clusters. This also leads to nearly the same total binding energy in the two cases. However, there is a substantial decrease in the binding energy/atom for  $\text{Ca}_{20}$  which is only 0.84 eV compared with the experimental bulk value of 1.84 and 1.49 eV/atom for  $\text{Ca}_{12}$ . From the Mulliken population analysis we find that the

Table 1

Binding energies ( $E_b$ ), nearest neighbour bond lengths ( $d_0$ ), HOMO–LUMO gap ( $E_g$ ) and occupation numbers of different orbitals for the icosahedral  $\text{Ca}_{12}$ , dodecahedral  $\text{Ca}_{20}$  and icosahedral  $\text{Ca}_{32}$  shells as well as  $\text{C}_{60}$  and  $\text{Ca}_x\text{C}_{60}$  complexes<sup>a</sup>

Cluster	$E_b$ (eV)	$d_0$ (a.u.)	$E_g$ (eV)	Occ. no.
$\text{Ca}_{12}$	17.9 (0.9)	6.44	0.8	Ca: 3p 5.99 3d 0.57 4s 1.44
$\text{Ca}_{20}$	16.8 (13.6)	6.51	0.3	Ca: 3p 6.00 3d 0.48 4s 1.52
$\text{Ca}_{32}$	50.1 (47.5)	6.13, 6.74	0.08	Ca: 3p 6.00 3d 0.66 4s 1.34
$\text{C}_{60}$	480.5	2.71	1.71	C: 2s 1.14 2p 2.86
$\text{Ca}_{12}\text{C}_{60}$	549.2	4.63 (C–Ca) 7.26 (Ca–Ca)	0.0	Ca: 3p 5.95 3d 0.75 4s 0.40 C: 2s 1.11 2p 3.07
$\text{Ca}_{20}\text{C}_{60}$	590.5	4.41 (C–Ca) 6.99 (Ca–Ca)	0.0	Ca: 3p 5.96 3d 0.71 4s 0.71 C: 2s 1.11 2p 3.09
$\text{Ca}_{32}\text{C}_{60}$	618.5	4.93 (C–Ca) 6.82, 7.50 (Ca–Ca)	0.0	Ca: 3p 5.95 3d 0.77 4s 0.88 C: 2s 1.11 2p 3.10

<sup>a</sup> Values of binding energies within brackets correspond to the bond lengths of calcium atoms in the fullerene complexes.

wave function in  $\text{Ca}_{20}$  cluster is more atomic-like as it is seen from the larger 4s character (Table 1) which results due to fewer neighbours. This also leads to a slight increase in the Ca–Ca bond length. In the case of  $\text{Ca}_{32}$ , 12 (20) atoms have coordination 5 (6) and the binding energy is 1.57 eV/atom which is slightly more than the value for  $\text{Ca}_{12}$  and is consistent with an increase in the coordination number of atoms.

We now discuss results for the fullerene complexes. In the case of  $\text{Ca}_{12}\text{C}_{60}$ , Ca atoms were placed on the pentagonal faces, in  $\text{Ca}_{20}\text{C}_{60}$  on all the hexagonal faces, and in  $\text{Ca}_{32}\text{C}_{60}$  on all the 32 faces of  $\text{C}_{60}$ . All these complexes have icosahedral symmetry similar to an isolated  $\text{C}_{60}$  molecule. In Table 1, we have given some of the calculated

properties of calcium coverings on  $\text{C}_{60}$ . From the Mulliken population analysis we find a large charge transfer of about 11 electrons from the calcium shell of  $\text{Ca}_{12}\text{C}_{60}$  to the fullerene while for  $\text{Ca}_{20}\text{C}_{60}$  and  $\text{Ca}_{32}\text{C}_{60}$  the charge transfer is nearly 12 electrons. The adsorption energy is 5.73, 5.5 and 4.31 eV/atom for coverings of pentagonal, hexagonal and all the faces, respectively. This is in striking contrast to the binding energy of 0.89 eV/atom for the low coverage of K on graphite [11] and shows that Ca atoms are strongly bonded on  $\text{C}_{60}$ . The decrease in the binding energy and charge transfer per adatom with coverage follows the behaviour obtained for K on graphite. Our results suggest that the maximum charge transfer to the fullerene cage could be up to 12e. The optimized

Ca–C bond lengths (Table 1) for the three complexes are smaller than the sum of the covalent radii of C and Ca which is approximately 5.4 a.u. For  $\text{Ca}_{12}\text{C}_{60}$  the Ca–C bond length is 4.63 a.u. and it reduces to 4.41 a.u. for  $\text{Ca}_{20}\text{C}_{60}$ . It is likely due to the fact that for 12 Ca atoms, the charge transfer per calcium atom is higher and the Coulomb repulsion between the calcium ions can be reduced by increasing the Ca–C bond length which effectively increases the Ca–Ca bond length also. As expected from the geometry of  $\text{C}_{60}$ , the Ca–Ca bond length decreases with the increase in the number of Ca atoms but these are significantly longer than those in the isolated Ca clusters. The binding energies shown in brackets are for isolated Ca clusters with the interatomic distances equal to Ca–Ca bond lengths in  $\text{Ca}_x\text{C}_{60}$  complexes. It is clear that the Ca–Ca interaction in the  $\text{Ca}_{12}$  cluster with the bond length of 7.26 a.u. is very weak. However, for  $\text{Ca}_{20}$  and  $\text{Ca}_{32}$ , the Ca–Ca interactions are quite significant and the binding energy is only about  $\sim 3$  eV less. The energy gain upon adsorption is much larger as compared to the binding energy in Ca clusters or Ca bulk. It is also much larger than 0.325 eV/atom in the case [20] for  $\text{Si}_{60}\text{C}_{60}$  with respect to the  $\text{Si}_{60}$  cluster. One of the reasons for this is the large charge transfer from the Ca shell to  $\text{C}_{60}$  which would give significant contribution to the binding energy. The hybridization of the calcium and fullerene states as well as the bonding within the calcium covering contribute further to the binding energy.

In order to compare these results with Li adsorption, we performed calculations for the  $\text{Li}_{12}\text{C}_{60}$  complex at the equilibrium atomic distances obtained in [12] with ab initio molecular dynamics. Similar to the  $\text{Ca}_{12}\text{C}_{60}$  complex and other calculations, we also find a charge transfer of

11.5 electrons from  $\text{Li}_{12}$  to the  $\text{C}_{60}$  molecule. Since nearly all the valence electrons from Li atoms get transferred to  $\text{C}_{60}$ , the total binding energy,  $\sim 34.1$  eV (comparable to 31.2 eV obtained in [12]) between  $\text{C}_{60}$  and the  $\text{Li}_{12}$  layer arises from mostly ionic interaction and the polarization of the electronic charge. In order to show a different bonding character for Ca coverings on  $\text{C}_{60}$ , we have given in Table 2 the percentage of  $\text{H}_u$ ,  $\text{T}_{1u}$ ,  $\text{T}_{1g}$  and  $\text{T}_{2u}$  states near the HOMO on Li, Ca and  $\text{C}_{60}$  for Li and Ca coverings on  $\text{C}_{60}$ . It is clear that strong hybridization occurs between the states of Ca atoms and  $\text{C}_{60}$  in the case of  $\text{Ca}_x\text{C}_{60}$  complexes. But in the case of  $\text{Li}_{12}\text{C}_{60}$ , there is no hybridization of Li and  $\text{C}_{60}$  states in the occupied region but there is only a weak hybridization with the unoccupied  $\text{T}_{2u}$  states.

In Fig. 1, we show a few energy levels near the HOMO for  $\text{C}_{60}$ ,  $\text{Li}_{12}\text{C}_{60}$  and  $\text{Ca}_{12}\text{C}_{60}$ . The Fermi level is shifted to zero of energy. The energy spectrum has almost the same features after the coating of 12 Li or Ca atoms on  $\text{C}_{60}$ . It is to be noted that a rigid band model has been quite successful in understanding the properties of Li intercalation of graphite. For  $\text{Li}_{12}\text{C}_{60}$  and  $\text{Ca}_{12}\text{C}_{60}$ , there is a  $\text{T}_{2u}$  state appearing just above the  $\text{T}_{1g}$  level. This is the LUMO in  $\text{Li}_{12}\text{C}_{60}$  as the  $\text{T}_{1u}$  and  $\text{T}_{1g}$  levels are totally filled due to transfer of electrons contributed by 12 Li atoms. For  $\text{Ca}_{12}\text{C}_{60}$  the HOMO is a  $\text{H}_g$  level which is not completely occupied and therefore, in the ground state there are likely to be distortions in the cluster from the icosahedral symmetry. However, we believe that these may not be very significant as the underlying  $\text{C}_{60}$  cage is quite rigid. Though we have not relaxed the bond lengths in  $\text{C}_{60}$ , we find that the HOMO–LUMO gap of  $\text{C}_{60}$  is decreased after covering with metallic elements in agreement with the results in [12].

Table 2  
Percentage of the  $\text{C}_{60}$  and metallic covering components for a few levels near the Fermi energy<sup>a</sup>

Level	$\text{Ca}_{12}@\text{C}_{60}$			$\text{Li}_{12}@\text{C}_{60}$		
		$\text{Ca}_{12}$	$\text{C}_{60}$		$\text{Li}_{12}$	$\text{C}_{60}$
LUMO	$\text{A}_g$	30	70	$\text{T}_{2u}$	16	84
HOMO	$\text{H}_g$	46	54	$\text{T}_{1g}$	0.0	100
HOMO-1	$\text{T}_{2u}$	48	52	$\text{T}_{1u}$	0.0	100
HOMO-2	$\text{T}_{1g}$	31	69	$\text{H}_u$	0.0	100

<sup>a</sup> Hybridization between the calcium shell and  $\text{C}_{60}$  for the HOMO is clearly observed.

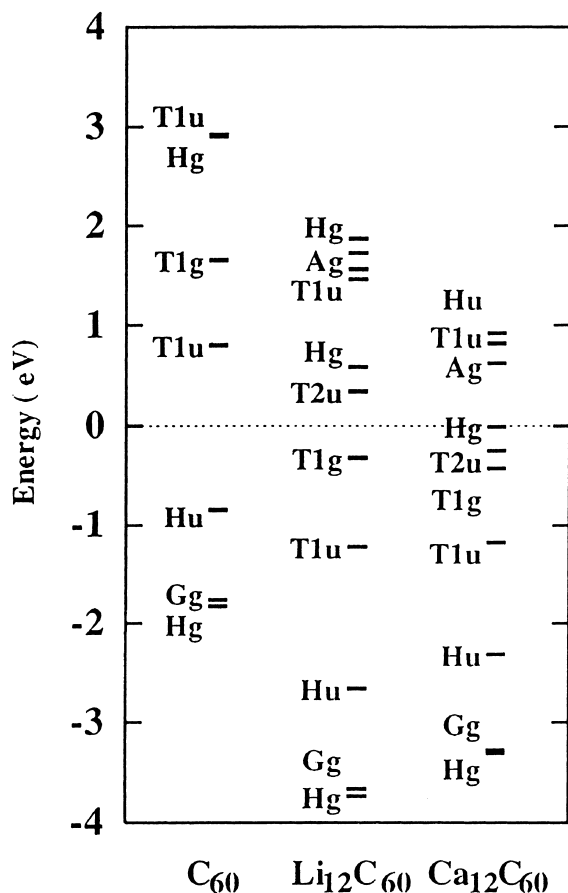


Fig. 1. Kohn-Sham energies for  $C_{60}$ ,  $Li_{12}C_{60}$  and  $Ca_{12}C_{60}$ . The zero of energy is the HOMO of  $Ca_{12}C_{60}$ .

In Fig. 2 we have shown the electronic density of states (DOS) for the  $Ca_xC_{60}$  complexes. The DOS were obtained by broadening the eigenstates in the form of Lorentzians. From the figure, we can see that the main features of the  $C_{60}$  spectrum remain nearly intact after adsorption as seen from the partial density of states of  $C_{60}$  in  $Ca_xC_{60}$  complexes. But certainly a rigid band picture is not appropriate. Near  $E_F$  a clear shift of  $C_{60}$  states towards higher binding energies can be observed. Also there is significant hybridization of  $C_{60}$  states with those of calcium in this region. The total DOS at  $E_F$  is large as in metals and the dominant contribution comes from the calcium atoms. It increases further with an increase in the Ca coverage as one can see clearly from the DOS curves at and

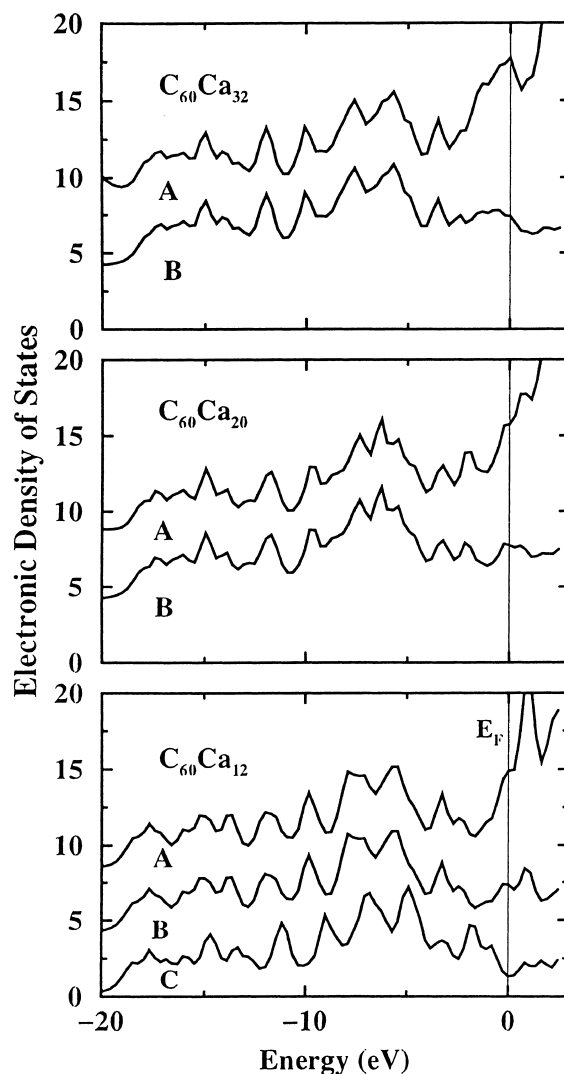


Fig. 2. Density of states obtained from broadening the electronic levels with Lorentzian for  $Ca_xC_{60}$  complexes. A, B and C are respectively the total DOS for the complex, partial DOS for  $C_{60}$  in the complex and the total DOS for pure  $C_{60}$ .

near the Fermi energy. At the bottom of the DOS curve the position of the peaks does not shift much, but there are small changes in the shape. In contrast to this, the spectrum of  $Li_{12}C_{60}$  shows a shift in the whole energy range and a gap at  $E_F$ . In going from 12 to 20 Ca atoms on  $C_{60}$ , we find the changes in the  $C_{60}$  states to be more significant. This is due to a decrease in the Ca–C bond length. In going further to 32 atoms, the hybridization

weakens slightly due to an increase in the bond length. This increase in the Ca–C bond length arises from the fact that charge transfer from each calcium atom decreases and the bond length would be expected to attain its value close to the sum of the covalent radii of Ca and C atoms. The latter is larger than the value of the Ca–C bond length in  $\text{Ca}_{32}\text{C}_{60}$ .

### 3. Summary

In summary, we have performed local density functional calculations for calcium coatings on  $\text{C}_{60}$ . We find that there are almost 12 electrons transferred from the metallic layer to  $\text{C}_{60}$  and we expect it to be so also for Sr and Ba. The charge transfer remains nearly the same after 12 Ca atoms have been adsorbed. But the interaction between the shell of metal atoms and  $\text{C}_{60}$  is strongly dependent on the element. For Li, we have found that the interaction between the Li shell and  $\text{C}_{60}$  is mostly ionic while in the case of Ca covered  $\text{C}_{60}$ , there is strong ionic interaction as well as hybridization of Ca and C states. This leads to a large binding energy for Ca atoms on  $\text{C}_{60}$ . However, this value is smaller than the binding energy of  $\text{C}_{60}$  so that the latter is not broken. On the other hand the large binding energy should be very favorable against coalescence of such complexes as Ca–Ca bonding is much weaker. The stability of 32 Ca atoms on  $\text{C}_{60}$  is suggested to be geometric in origin, since we did not find any significant feature such as a large HOMO–LUMO gap in the electronic spectrum which could suggest an electronic origin. The interatomic distance between calcium atoms after coating on  $\text{C}_{60}$  is slightly longer than in pure  $\text{Ca}_{12}$ ,  $\text{Ca}_{20}$  and  $\text{Ca}_{32}$  clusters. This result suggests that a good symmetrical geometric match is made at  $\text{Ca}_{32}$  leading to its high abundance. However, the elongation in the Ca–Ca bond length after coating on  $\text{C}_{60}$  as compared to the isolated  $\text{Ca}_{32}$  shell, as well as the short Ca–C bond lengths when compared with the sum of the covalent radii of Ca and C, suggest that there could be a possibility of accommodating more Ca atoms in the shell. This could happen when a second layer Ca starts depositing on the complex. This would tend

to bring the Ca–Ca bond lengths closer to the bulk value and may facilitate more packing in the first layer. As the binding energy with  $\text{C}_{60}$  is much higher than the Ca–Ca interaction, this is very plausible. Accordingly we speculate that the peaks at 35 and 38 calcium atom covering could be related to further incorporation of respectively 3 and 6 atoms in the calcium layer. This idea could also find support from the experimental data on Ba coatings for which the peaks at 35 and 38 are much weaker. This is likely to be due to the bigger size of Ba atoms compared with Ca. The large charge transfer from the metal layer to  $\text{C}_{60}$  could lead to significantly different properties of the metallic shell. These complexes with a metallic shell could offer novel catalysts and serve as species for developing new cluster materials.

### Acknowledgements

This work was performed when the authors were at the International Centre for Theoretical Physics, Trieste, Italy and XGG would like to thank the members of the condensed matter group there for the hospitality and the staff of the microprocessor laboratory for allowing the use of their computer. V.K. is grateful to Prof. Y. Kawazoe for the hospitality and support at the Institute for Materials Research, Tohoku University as well as support from cooperation between Japan and China. He is also thankful to Profs. R.B. Tao and X.G. Gong for their hospitality in China. X.G.G. also gratefully acknowledges support from the NNSF of China, the special funds for major state basic research project and the CAS project.

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