The Ionization Energies and Electron Affinities of Endohedral Metallofullerenes MC_{82} (M = Sc, Y, La): Density Functional Calculations

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By means of density functional calculations, the ionization energies and electron affinities of ScC_{82}, YC_{82} and LaC_{82} are predicted and compared with those of typical empty fullerenes such as C_{60} and C_{70}; endohedral metallofullerenes can be regarded as a sort of super atom.

Endohedral metallofullerenes [fullerenes with a metal(s) inside the cage] have long attracted special attention as new chemical entities with novel properties. Thus, great efforts have been made for their production and extraction, as summarized in a recent review.[1] It has been shown that Group 3 metals (M = Sc, Y, La) can be trapped inside the much less abundant C_{82} (compared with C_{60} and C_{70}) to form soluble and air-stable metallofullerenes. In addition, recent important progress is the successful purification and isolation in milligram quantities.[2–4] However, little is still known about their properties. Thus, we have undertaken the density functional (DF) calculations of the vertical ionization energies (E_i) and electron affinities (E_{ea}) of MC_{82} to characterize the electronic properties.

The spin-polarized calculations in the self-consistent Kohn–Sham formalism[5] were carried out using the standard local spin density approximation (LSDA)[6] and two recently developed non-local density functional methods (B-LYP and B-P).[7–9] The B-LYP and B-P methods include density gradient correction with the Becke (B) functional[7] for the exchange part while they include the gradient-corrected correlational functional developed by Lee, Yang and Parr (LYP)[8] and by Perdew (P),[9] respectively. Relativistic effective core potentials and basis sets developed by Stevens *et al.*[10] were used on M but the outermost core electrons were explicitly treated as valence electrons. The split-valence double-zeta basis set was used for C.[11] This gives 769 contracted Gaussian functions on MC_{82}. The most stable structures of MC_{82} were taken from our previous theoretical study.[12] As Fig. 1 shows, the metal atom, at an off-centre position, is strongly bound to one hexagonal ring in the C_2-symmetry cage of C_{82}.[12,13] This structural feature was recently proved by EXAFS measurements of Y and La in YC_{82}[14] and LaC_{82}.[15]

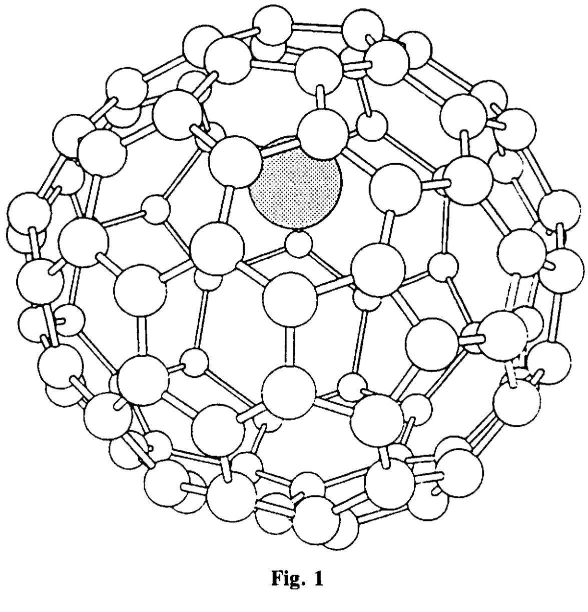

Fig. 1

In an attempt to calibrate the present calculations, the E_i and E_{ea} of C_{60} were first calculated for which experimental values are available.[16,17] The calculated values at several levels are summarized in Table 1 together with those obtained with the traditional Hartree–Fock (HF) molecular orbital method. As in a recent theoretical study,[18] the HF calculations greatly underestimate the E_{ea} value because of the neglect of electron correlation. On the other hand, the E_i and E_{ea} values are overestimated at the LSDA level. In contrast, the gradient-corrected DF methods at the B-LYP and B-P levels give values much closer to those obtained experimentally. The E_i and E_{ea} values at the B-P level agree to within 0.1–0.2 eV of the experimental values. This suggests that the B-P calculations are most suitable for the present purpose.

Table 2 summarizes the E_i and E_{ea} values of MC_{82} as well as those of C_{60}, C_{70} and C_{82} at the B-P level. It was suggested early that metallofullerenes have lower ionization energies than empty fullerenes.[19] This can be now confirmed quantitatively by the present calculations. The E_i of 6.19 eV calculated for LaC_{82} is 1.59 and 1.45 eV smaller than those for C_{60} and C_{70}, respectively. On the other hand, the E_{ea} of 3.22 eV for LaC_{82} is 0.65 and 0.53 eV larger than those for the empty fullerenes. These are well consistent with the shifts of the first oxidation and reduction potential peaks measured recently in solution for LaC_{82}, relative to those of C_{60} and C_{70}.[20] In addition, the present calculations suggest that the E_i and E_{ea} values of YC_{82} are very similar to those of LaC_{82}.

As Table 2 shows, E_i and E_{ea} values tend to increase and decrease upon going to ScC_{82}, respectively. As already pointed out,[12] the electronic structures of metallofullerenes depend on the nature of the encapsulated metal atoms. As the calculated positive charge on La is +2.92 (Table 2), the electronic structure of LaC_{82} can be formally described as

Table 1 The ionization energies (E_i) and electron affinities (E_{ea}) of C_{60} at several levels of calculations

	E_i/eV	E_{ea}/eV
HF	8.05	0.94
LSDA	8.45	3.10
B-LYP	7.27	2.09
B-P	7.78	2.57
exp	7.57–7.61[a]	2.65[b]

[a] From ref. 16. [b] From ref. 17.

Table 2 The ionization energies (E_i) and electron affinities (E_{ea}) of MC_{82}, C_{60} and C_{70} and the charge densities on M in MC_{82}, MC_{82}^+ and MC_{82}^- calculated at the B-P level

			Charge on M		
	E_i/eV	E_{ea}/eV	Neutral	Cation	Anion
ScC_{82}	6.45	3.08	2.16	2.18	2.18
YC_{82}	6.22	3.20	2.59	2.61	2.60
LaC_{82}	6.19	3.22	2.92	2.97	2.90
C_{60}	7.78	2.57			
C_{70}	7.64	2.69			
C_{82}	6.96	3.37			

$La^{3+}C_{82}^{3-}$ as a result of the transfer of three valence electrons on La to the LUMO and LUMO + 1 of C_{82}. On the other hand, electron transfer is decreased upon going to YC_{82} to ScC_{82}, as calculated charges of +2.59 (Y) and +2.16 (Sc) indicate, and the electronic structure $Sc^{2+}C_{82}^{2-}$ is increasingly favoured in ScC_{82} owing to the more compact and lower-lying d orbitals of Sc.[12]

As shown in Table 2, the charges on M are little changed even when MC_{82} loses or accepts an electron. This allows the formal view that electron removal and gain take place on the C_{82} cage, with the metals acting as a positive core in a sort of 'super atom'. Therefore, it is not surprising that LaC_{82} has a smaller E_i than ScC_{82} since the original LUMO + 1 of C_{82} is responsible for the ionization in the former while it is the LUMO in the latter. Nevertheless, the E_i difference between LaC_{82} and ScC_{82} is small (0.3 eV). This indicates that the energy gap between the LUMO and LUMO + 1 is only 0.6 eV.[12,13] On the other hand, LaC_{82} has a larger E_{ea} value than ScC_{82}. This can be ascribed to an effective attraction resulting from the higher positive charge on La (+3) *vs.* Sc (+2). In this context, it is interesting that the electron affinity of LaC_{82} is comparable to that of C_{82}, despite the fact that LaC_{82} has already three extra electrons on the C_{82} cage.

In an attempt to confirm this view, E_i and E_{ea} values of C_{82}^{3-} and C_{82}^{2-} were calculated by placing point charges of 3+ and 2+ instead of the La and Sc atoms, respectively. This model calculation gives E_i and E_{ea} values of 6.28 and 3.66 eV for C_{82}^{3-} and 6.63 and 3.45 eV for C_{82}^{2-}. These values agree reasonably well (in both magnitude and order) with those calculated for LaC_{82} and ScC_{82}. In the absence of the point charges, it was calculated that further electron attachment to C_{82}^{2-} and C_{82}^{3-} are not significantly bound or unbound at the present theoretical level. This supports again the view that metallofullerenes are composed of a positively charged core atom and a negatively charged cage.

It is hoped that the predicted E_i and E_a values as well as the 'super atom' view are helpful in disclosing further the properties and reactivities of endohedral metallofullerenes.

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