PAPER

Polarisation charge switching through the motion of metal atoms trapped in fullerene cages

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The formation of an endohedral fullerene can lead to charge transfer and the generation of a trapped positively charged metal ion. Using $Ca@C_{60}$ and $[Ca@C_{60}]^+$ endohedral fullerenes as models, density functional theory calculations predict that the motion of a calcium ion within a fullerene is accompanied by large changes in electron density on the surrounding carbon cage. In the case of $[Ca@C_{60}]^+$, partial atomic charge distribution on the carbon cage is split between hemispheres into regions of positive and negative charge as Ca^{n+} moves inside the fullerene cage (non-integer n strongly depends on position of the ion). It is proposed that within tethered fullerene cages the movement of partial atomic charge could form the bases of a molecular polarisation storage bit, and that adopted in the form of $[Ca@C_{60}]^+$ the presence of an overall charge may offer a route to either optical or electronic control.

I. Introduction

A large body of work, both experimental and theoretical, has been devoted to doping fullerene cages with metals,[1–12] much of which has concentrated on encapsulated calcium.[6–12] Previous calculations[6] have shown that in $Ca@C_{60}$, the valence 4s electrons of the encapsulated calcium atom are energetically close to the LUMO of C_{60}, thus allowing the possibility for either zero, one or both 4s electrons to be transferred to the C_{60} shell. These theoretical predictions are consistent with photoelectron spectroscopy experiments.[6,9] Although the C_{60} cage can formally accept one or two electrons from electropositive elements, the actual value of the transferred charge is typically smaller. In the minimum energy configuration, the trapped calcium ion is found to adopt an off-centre position where the $Ca@C_{60}$ complex is stabilized by polarisation of the C_{60} cage; however, for off-centre sites, the gain in polarisation energy is partly compensated by an increase in the repulsive interaction between the trapped ion and the wall of the cage.[10] Chang et al.[11] performed restricted Hartree–Fock (HF) *ab initio* calculations on $Ca@C_{60}$ and $[Ca@C_{60}]^+$ using relativistic effective core potentials with the icosahedral symmetry I_h. This approach predicted the electronic ground state of the $Ca@C_{60}$ to be a triplet $^3T_{1u}$ state ($a_g^1 t_{1u}^1$, where a_g is Ca 4s orbital and t_{1u} is the C_{60} LUMO) and the ground state of the positive ion to be a doublet ^2A_g state. This prediction is inconsistent with the ultraviolet photoelectron spectroscopy (UPS) experiments of Wang et al.,[6] which showed that, unless a_g and t_{1u} are degenerate orbitals, a $a_g^1 t_{1u}^1$ ground state configuration would cause two separate peaks to appear in the UPS spectrum. HF calculations by Wang et al.[6]

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found the ground state of $Ca@C_{60}$ to be a triplet $^3T_{1g}$ (t_{1u}^2) state, where two 4s electrons on the calcium have been transferred to the carbon shell to form $Ca^{2+}@C_{60}^{2-}$. The symmetry in these calculations has been reduced to C_{5v} to show that the calcium ion moves 0.7 Å away from the centre, and the authors did not dismiss the possibility that $Ca@C_{60}$ may have a ground state of even lower symmetry. From a Mulliken population analysis they found the charge on calcium in the ground state to be $+0.59e$, although calculations at the HF level, even with large basis sets, are expected to be of limited accuracy. A study by Lu et al.[12] of $Ca@C_{60}$ with I_h symmetry using discrete variational local density functional predicted a net charge distribution of $Ca^{1.67+}@C_{60}^{1.67-}$.

Although the results are sensitive to the adopted level of theory, there exists extensive theoretical support for electron transfer from a metal atom to the cage in endohedral fullerenes, and there is clear experimental and theoretical evidence for the displacement of metal atoms away from the centre of the cage.[13] An off-centre geometry has both static and dynamic implications for $Ca@C_{60}$;[6,10] for example, Ruoff has suggested that free radial motion of the ion may give rise to a low-frequency "rattling" mode, which should be observable by infrared and Raman spectroscopy.[10] The Ca ion is an interesting test system because it has an optical transition at 397 nm that is readily accessible using laser radiation.[14] However, the principle of charge switching through the motion of atomic or molecular species trapped inside fullerene can be also related to other systems. That such motion is possible has been demonstrated through the current-driven rotation of an encapsulated Sc_3N cluster located within a C_{80} fullerene cage.[15] An obvious extension would then be to control the state of an encapsulated species within a fullerene cage by means of electronic or optical stimulation. This has been previously proposed in several single

molecule systems, most notably the $Li@C_{60}$ endofullerene, which is based on charge-transfer excitation.[16] Additionally, a large number of stable compounds $M@C_{60}$ has been reported,[10] where donor elements, M, range from those found in the IA, IIA, III groups of the Periodic Table to lanthanide and actinide groups. In all of these systems, a significant contribution to stabilization comes from the polarisation energy of the enclosed atom, which is located off the cage centre.

In this work, density functional theory (DFT) as implemented in the Q-Chem quantum chemistry software package,[17] is used to show how the extent of charge transfer and the distribution of charge are affected by the presence of a charged species *inside* both a neutral and singly charged fullerene cage. Earlier calculations used DFT to determine the charge density distribution on a C_{60} molecule in the presence of an electric field created by a point charge located *outside* the cage.[18] It was shown that there is a very close match between a DFT calculation of the polarisation response of C_{60} to the gradual displacement of an external point charge and that obtained using classical electrostatic theory as derived in an earlier publication.[19] This study shows that when a charge is located *inside* C_{60} the sign and magnitude of the polarisation response depend very strongly on the precise position of the ion trapped inside the encapsulating cage. It is suggested that this very evident distortion of the charge distribution on a singly charged fullerene cage in response to an applied electric field, is a physical property that could be exploited in the design of a molecular storage bit.

II. DFT predictions of the electronic ground state structure of $Ca@C_{60}$ and $[Ca@C_{60}]^+$

The $B3LYP^{[20,21]}/6\text{-}31G^{*}$ [22,23] DFT calculations were performed to optimise the structures of the neutral $Ca@C_{60}$ and charged $[Ca@C_{60}]^+$ endofullerenes. It was found that in the lowest energy configuration in the electronic ground state corresponding to the neutral $Ca@C_{60}$ system, the encapsulated positive Ca ion is located at a radial distance of $r = 1.22$ Å from the centre of C_{60} facing the centre of hexagon (position A in Fig. 1a). The minimum in the electronic ground state of $[Ca@C_{60}]^+$ ion corresponds to position B, where the Ca ion is 1.21 Å away from the centre of C_{60} and facing the midpoint of an edge between two adjacent hexagons. The electronic ground state is found to be a triplet state for $Ca@C_{60}$ (in agreement with previous results[6,9,12]) and a doublet state for the $[Ca@C_{60}]^+$ cation. In a search for other geometries, which might correspond to local minima for a calcium ion inside the C_{60} fullerene cage, the following positions have been investigated: position C, where the calcium ion is facing a carbon atom on the C_{60} shell; position D, where the calcium ion is located at the midpoint of the edge between adjacent hexagon and pentagon; and position E where the Ca ion is above the centre of a pentagon (all these positions are identified in Fig. 1a).

Table 1 summarizes the difference in the total energy, ΔE, between the lowest energy configuration and local minima
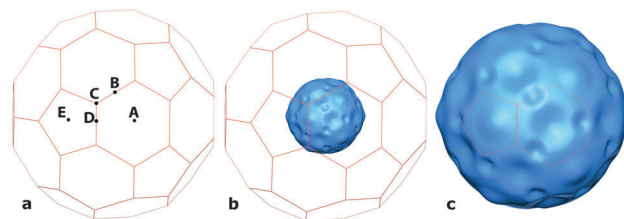

Fig. 1 $Ca@C_{60}$ endofullerene: (a) investigated starting positions of Ca ion inside C_{60}; (A) Ca atom is facing the centre of hexagon; (B) Ca atom is located above the midpoint of the edge between two adjacent hexagons; (C) Ca atom is above carbon atom; (D) Ca atom is facing the midpoint of the edge between adjacent hexagon and pentagon; (E) Ca atom is at the centre of pentagon; (b) the radial minimum energy path at $r = 1.22$ Å from the centre of C_{60}; (c) expanded image of the radial minimum energy path shown in (b).

Table 1   Calculated minima in the electronic ground state of the neutral $Ca@C_{60}$ (triplet) and charged $[Ca@C_{60}]^+$ (doublet) endofullerenes: geometries are defined in Fig. 1a; E is the total energy of the system; ΔE is the energy difference between the lowest energy configuration and the local minimum; radial distance r is an off-centre position of Ca ion inside the fullerene cage

$Ca@C_{60}$				$[Ca@C_{60}]^+$			
Geom.	E (Hartree)	ΔE (eV)	r (Å)	Geom.	E (Hartree)	ΔE (eV)	r (Å)
A	−2963.7635	0.000	1.22	B	−2963.5580	0.000	1.21
B	−2963.7630	0.011	1.22	D	−2963.5570	0.027	1.20
				E	−2963.5554	0.073	1.19

found in the electronic ground state of the neutral $Ca@C_{60}$ and charged $[Ca@C_{60}]^+$ cages; the geometries of the minima are shown in Fig. 1a. In $Ca@C_{60}$ endofullerene only one local minimum has been found which corresponds to position B. In $[Ca@C_{60}]^+$ ion the largest energy difference, $\Delta E = 0.073$ eV, is found to be between the lowest energy minimum (position B) and the local minimum corresponding to position E, where the Ca atom faces a pentagon. A second local minimum is energetically closer ($\Delta E = 0.027$ eV) to the minimum in position B, and it corresponds to position D.

To aid visualisation of the radial minimum energy path, the position of the Ca atom was fixed at a radial distance of $r = 1.22$ Å from the centre of the cage (corresponding to the minimum in the electronic ground state of neutral $Ca@C_{60}$ endofullerene), and a series of single point energy calculations were undertaken to generate the energy surface depicted in Fig. 1b and c. Only very minor fluctuations in the total energy were found along the radial minimum energy path, which implies a free movement of the encapsulated Ca atom throughout the cage at a distance of approximately $r = 1.22$ Å from the centre of C_{60}.

There remains an appreciable energy barrier associated with the movement of a Ca atom through the centre of C_{60} to an equivalent energy minimum position on the other side of the cage. For both neutral $Ca@C_{60}$ and charged $[Ca@C_{60}]^+$ cages, the total energy profiles shown in Fig. 2 have been obtained in a series of single point energy calculations by moving the Ca atom from the lowest energy minimum (A for $Ca@C_{60}$ and B for $[Ca@C_{60}]^+$ as shown in Fig. 1a) through the centre of the fullerene cage. For neutral $Ca@C_{60}$ cage, the energy barrier
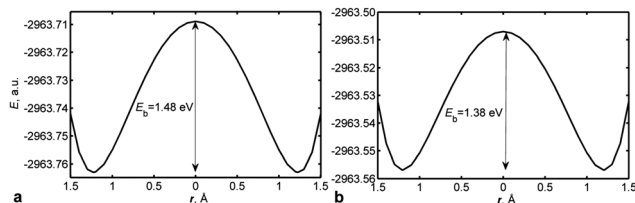
Fig. 2   The total energy profile along the path through the centre of the C_{60} connecting the radial positions of Ca ion (r, in Å) corresponding to the minimum in the electronic ground state: (a) neutral Ca@C_{60} endofullerene (starting position (A) at $r = 1.22$ Å); (b) [Ca@C_{60}]$^{+}$ ion (starting position (B) at $r = 1.21$ Å).

that divides the two minima located at $r = 1.22$ Å on either side of the neutral cage is found to be $E_{b} = 1.48$ eV; for [Ca@C_{60}]$^{+}$ cation, the corresponding minimum position is $r = 1.21$ Å, and the energy barrier has the value of $E_{b} = 1.38$ eV. The energy barriers along the path through the centre of C_{60} originating at any of the symmetry positions A–E are very similar, so that at a radial distance of $r = 1.22$ Å there is a minimum energy trough that embraces the entire cage.

The radial motion of a metal species within a fullerene cage has been demonstrated previously by Akasaka *et al.*[24] for the case of La$_2$@C_{80}, who estimated the barrier to the motion to be of the order of 20 kJ mol^{-1}.[25] As evident from Table 1, Ca ion undergoes free radial motion in C_{60} as all the energy barriers in the radial direction are comparable with its average kinetic energy at room temperature ($\frac{3}{2}kT = 0.038$ eV $= 3.72$ kJ mol^{-1}). Importantly, the radial motion of Ca ion inside a fullerene cage is accompanied by a continuous redistribution of the polarisation charge residing on the cage, such that negative charge on the cage will track the movement of an encapsulated positively charged metal ion (see below). A step forward in the design of a bi-stable dynamical system is the ability to control and modify the profile and the depth of the radial minimum energy path. For example, adsorption of atomic hydrogen on the external surface of endofullerene can significantly alter the total energy profile. As shown in Fig. 3, if one hexagon of the C_{60} cage is functionalised with hydrogen, the barrier between the minima is reduced by about 35–40%, and the energy minimum in the

hemisphere containing the functionalised hexagon is much more shallow (by about 0.23 eV). The total energy profile, as shown in Fig. 3, can be manipulated both in terms of the depth of the minima and the height of the barrier by changing the position and the number of hydrogen atoms adsorbed on the surface of endofullerene.

III. The effect of dynamic re-distribution of the polarisation charge

The exact position of calcium ion inside the cage has a critical influence on polarisation of the C_{60} cage. Fig. 4 shows the distribution of partial atomic charges, as predicted by a Mulliken population analysis,[26] of the [Ca@C_{60}]$^{+}$ cage. Fig. 4a–c depict the distribution of the polarisation charge on fullerene cage in three configurations, which differ by the position of calcium inside a fullerene cage: (a) Ca atom is located in hemisphere 1; (b) Ca atom is in the middle of the cage; (c) Ca atom is found in hemisphere 2. It has been shown previously[18] that Mulliken population analysis can give reliable results for the surface-charge distribution in C_{60} and C_{240} cages. The absolute magnitude of the atomic charges predicted by Mulliken population analysis can be sensitive to the chosen level of theory, and as such can vary between calculations. It is also less realistic when diffuse orbitals on one atom strongly overlap with orbitals on other atoms, such as metal outer s and p orbitals overlapping carbon orbitals. However, the location of charge on the cage, and as a result the degree of polarisation, is predicted reliably provided a consistent basis set is used.
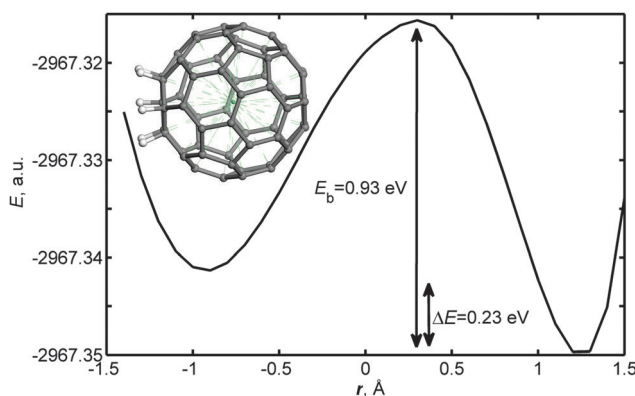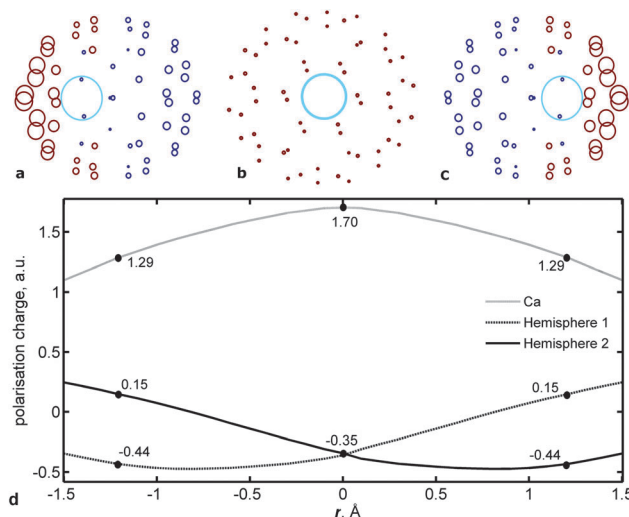

Fig. 3   The modified total energy profile for the neutral Ca@$C_{60}H_6$ system containing six hydrogen atoms adsorbed on the external surface of C_{60}.

Fig. 4   Distribution of the polarisation charge in [Ca@C_{60}]$^{+}$ ion: (a–c) polarisation charge on the fullerene cage in three configurations: (a) Ca atom is located in hemisphere 1; (b) the Ca atom is in the middle of the cage; (c) the Ca atom is located in hemisphere 2. Red open circles indicate negative charge and dark blue open circles depict positive charge on C_{60}, and light blue open circle denotes positive charge on the Ca ion. The size of each circle is renormalized to convey the degree of polarisation rather than its magnitude. (d) The polarisation charge, split into two hemispheres and a Ca ion, as a function of the position of calcium ion along a straight line that passes through the center of the cage.

In the case of $[Ca@C_{60}]^+$ cation, a significant delocalization of negative polarisation charge is observed on the fullerene cage when positive Ca ion is located off centre. A pictorial distribution of positive (open dark blue circles) and negative (open red circles) polarisation charge on the cage is shown in Fig. 4a–c, where an open light blue circle indicates the position of Ca ion. Fig. 4d shows the distribution of charge in the $[Ca@C_{60}]^+$ cation, split between two hemispheres and the encapsulated calcium, and depicted as a function of the radial position, r, of calcium along a straight line that passes through the center of the cage (where $r = 0$). When calcium is found in the hemisphere 1 at $r = 1.21$ Å or in the hemisphere 2 at the same distance from the centre, *i.e.* in the trough of the total energy profile, the charge is distributed in the system as $Ca^{1.29+}@C_{60}^{0.29-}$. In this case, a charge of $+1.29e$ resides on the Ca ion, $-0.44e$ is found on the hemisphere that contains the Ca ion, and $+0.15e$ on the surface of empty hemisphere. The total charge, *i.e.* the sum of the contributions from both hemispheres and the Ca ion, always remains unity. It should be stressed again that both the transfer of charge between the calcium atom and C_{60} and the degree of polarisation of the C_{60} cage depend strongly on the exact position of calcium inside the fullerene cage. As calcium moves toward the centre of the cage, the charge on the metal atom increases to the maximum value of $Ca^{1.70+}$; but the *degree of polarisation* of the surface charge on the fullerene cage drops to zero. The negative charge of $-0.70e$ is now uniformly distributed across the surface of C_{60}, as shown in Fig. 4b (in this case, the charge of $-0.35e$ is found to be evenly spread out over each hemisphere). It is therefore an interplay between the amount of charge transferred from the metal onto the cage and the degree of polarisation of the surface charge on the cage that defines the stability of $[Ca@C_{60}]^+$ cation.

In neutral $Ca@C_{60}$ endofullerene, the overall polarisation charge behaviour is less profound. When the calcium atom is displaced by 1.22 Å from the centre of the cage, the net charge transfer is $Ca^{1.24+}@C_{60}^{1.24-}$ (similar to the case of a singly charged cage), but the polarisation charge on the cage remains negative in both hemispheres for all radial positions of calcium. The value of the charge transferred from metal on a neutral cage is very close to that in a singly charged cage for all radial positions of encapsulated metal. For example, at the point of highest degree of polarisation, *i.e.* at the centre of the cage, the charge on the metal atom increases to $Ca^{1.71+}$ (the same as in a singly charged cage). As shown in Fig. 2, the values of the central barrier are also very close for the neutral and singly charged fullerenes indicating that the nature of the main barrier is due to charge transfer from the encapsulated metal and is not affected by a change in the degree of polarisation of the cage.

An alternative representation of polarisation charge residing on fullerene cage is shown in Fig. 5 for the $[Ca@C_{60}]^+$ cation. When a positive calcium ion is located in hemisphere 1, negative charge on the fullerene cage is drawn to it as shown in Fig. 5a. Indeed, this is also the case when a calcium ion is found in hemisphere 2 (Fig. 5c). Since the charge distribution is calculated for a fixed incremental angle, the surface area, over which the partial atomic charge is summed, varies from the
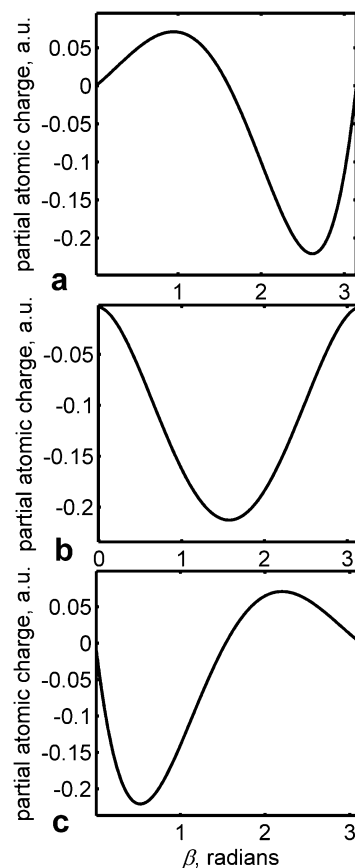

Fig. 5 For the $[Ca@C_{60}]^+$ cation, the partial atomic charge distribution on C_{60} calculated at three different positions of the encapsulated Ca atom: (a) Ca is located in hemisphere 1; (b) Ca is in the middle of the cage; (c) Ca is located in hemisphere 2.

maximum at the centre, to the minimum for the angles close to 0 and 3.14 radians. This explains the non-uniform nature of the charge distribution in Fig. 5b depicting the case when calcium atom resides at the centre of the fullerene cage.

IV. Conclusions

$Ca@C_{60}$ and $[Ca@C_{60}]^+$ endohedral fullerenes are representative of a large group of molecular cages, which can be reversibly toggled between two stable states defined by different physical features, in this case by the distribution of the polarisation charge. Transitions between the stable states are generally achieved as a response to external stimuli such as light, pH, temperature or a potential difference. It has been shown that endohedral fullerenes containing a single metal ion exhibit a pattern of behaviour characterised by marked transitions in charge density on the carbon cage in response to motion of the ion; illustrated in this case by Ca^{n+}. Similar motion within a tethered $[Ca@C_n]^+$ cage could form the basis of a molecular polarisation switch. The energy barriers identified for $[Ca@C_n]$ and $[Ca@C_n]^+$ can be moderated through addition of atomic hydrogen or fluorine to the carbon cage. Such additions can

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either change the relative stability between bi-stable states or even remove the barrier to motion completely.

Acknowledgements

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