

Reduction of activation energy barrier of Stone-Wales transformation in endohedral metallofullerenes

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Using *ab initio* calculations, we examine effects of encapsulated metal atoms inside a C_{60} molecule on the activation energy barrier for the Stone-Wales transformation. The encapsulated metal atoms we study are K, Ca, and La which nominally donate one, two, and three electrons to the C_{60} cage, respectively. We find that isomerization of the endohedral metallofullerene via the Stone-Wales transformation can occur more easily than that of the empty fullerene owing to the charge transfer. When K, Ca, and La atoms are encapsulated inside the fullerene, the activation energy barriers are lowered by 0.30, 0.55, and 0.80 eV, respectively compared with that of empty C_{60} (7.16 eV). The lower activation energy barrier of the Stone-Wales transformation implies the higher probability of isomerization and coalescence of metallofullerenes, which require a series of Stone-Wales transformations.

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Since its discovery,¹ the fullerene (C_{60}) has been extensively studied both theoretically and experimentally because of its potential applications in the fields of nanomaterials and biomedical science. Although the fullerene molecule usually has the highest icosahedral symmetry allowed by sixty constituent carbon atoms, transformations to other isomers of lower symmetry are still possible. One of the plausible processes for isomerization of the fullerene is the so-called Stone-Wales (SW) or “pyracylene” rearrangement, which is the 90° rotation of two carbon atoms with respect to the midpoint of the bond.² The SW transformation is also used to describe the structural changes of sp^2 -bonded carbon nanosystems.³ For example, it has been proposed that the fusion process of fullerenes or carbon nanotubes may occur through a sequence of such a rearrangement.^{4–6} One problem in this proposal is that the activation energy barrier of the SW transformation is ~ 7 eV,⁷ due to the breaking of two σ bonds, which is too high to overcome at the temperature in merging processes (1000–1500 °C).^{8,9}

There are several factors that can affect the energy barrier in the SW transformation. Eggen *et al.* found that the activation barrier for the SW rearrangement was substantially reduced in the presence of a loosely bound carbon atom located preferentially in the region of paired pentagons,¹⁰ explaining the growth of fullerenes in terms of autocatalysis by a carbon atom. On the other hand, the energy barrier of the SW transformation could change through certain kinds of endohedral doping into the fullerene cage. While Slanina *et al.* reported the catalytic effect of various kinds of elements or ions in the bowl-shaped $C_{34}H_{12}$,¹¹ relatively few studies have been devoted to the SW transformation of the endohedral metallofullerene. In this paper, we investigate effects of encapsulated metal atoms on the activation energy barrier in the SW transformation of the $M@C_{60}$ molecule, where $M=K, Ca, \text{ or } La$ atoms. The nominal charge transfers from metal atoms to the fullerene will be 1–3 electrons, corresponding to valence states of $K^+, Ca^{2+}, \text{ and } La^{3+}$. We find

that isomerization of the endohedral metallofullerene via the SW transformation can occur more easily than that of the bare fullerene owing to the charge transfer from the encapsulated metal atoms to the fullerene. It is consistent with experiments that metallofullerenes are much easier to fuse than empty fullerenes in peapods.^{12,13}

In this work, we perform *ab initio* pseudopotential calculations using the plane wave basis set¹⁴ within the local density approximation for the exchange-correlation effect. The ultrasoft pseudopotential¹⁵ is adopted with the cutoff energy of 30 Ry. The supercell size is $29 \times 29 \times 29 a_B^3$, where a_B is the Bohr radius, which is large enough to exclude undesirable interactions between supercells. For La, we treat 11 valence electrons ($5s^2 5p^6 6s^2 5d^1$) explicitly since the $5s$ and $5p$ orbitals have chemical interactions with the fullerene molecule.¹⁶ The scalar relativistic effects important in heavy elements such as La are taken into account. The atomic positions are relaxed until the total root-mean-square force of the atoms becomes less than $0.014 \text{ eV}/\text{\AA}$. We use the nudged-elastic-band (NEB) method¹⁷ to calculate the activation energy barrier in the SW transformation of the fullerene. Thirteen replicas are chosen including the initial and final configurations to construct an elastic band. We use the climbing image technique to locate the transition state (TS) precisely.¹⁸

We start with optimizing the La position on a threefold symmetry axis 1.5 \AA away from the center of the cage and obtain the stable position of the La atom in C_{60} . For $K@C_{60}$ and $Ca@C_{60}$, the starting positions for optimization are at the center¹⁹ and on a fivefold axis 1.5 \AA away from the center of the cage,²⁰ respectively. After relaxation, we confirm that the relaxed positions are local minima rather than saddle points by perturbing the final position of the endohedral dopant.

The relaxed geometry shows that the K atom prefers to be at the center of C_{60} . On the other hand, the stable positions of the La and Ca atoms are off-centered and the distances from the La and Ca atom to the nearest C atom are 2.5 \AA and

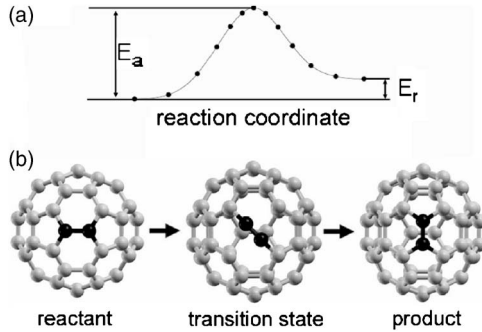


FIG. 1. Schematic energy diagram and the atomic configuration along the reaction coordinate in the Stone-Wales transformation of empty C_{60} . (a) Energy profile along the reaction coordinate. The dots represent the energies of the replicas in the SW transformation in the NEB method. (b) Atomic rearrangement from the I_h isomer to the C_{2v} isomer of the empty C_{60} molecule. Here, the rotating carbon dimer is shown in black.

3.1 Å, respectively. Upon encapsulation of the La atom, the threefold degeneracy of the t_{1u} states is split into 2+1 since the off-centered La atom breaks the icosahedral symmetry of an isolated C_{60} .²¹ Almost three electrons are transferred from the La atom to the doubly degenerate states (fourfold degeneracy including the spin degrees of freedom) of C_{60} .^{21,22} The twofold degeneracy is split again by occupation of the degenerate states with an odd number of electrons.

In Fig. 1, the SW transformation of an empty fullerene is shown with a schematic diagram of the potential energy. In the TS, the rotating carbon dimer [shown in black in Fig. 1(b)] has a bond length of 1.23 Å, with 1.40 Å bonds to each of the two nearest carbon atoms for C_{60} . This result is in agreement with previous studies.^{7,23} To confirm that the energy maximum point along the pathway is actually a transition state with the Hessian index of one, we analyze the Hessian matrix at the highest point. Instead of the full phonon-mode analysis whose computational load is very heavy, we look into a 6×6 Hessian matrix in a configurational subspace constructed by two rotating carbon atoms. We find that only one of the six eigenvalues of the matrix is negative, i.e., the Hessian index of one, and this demonstrates that the NEB method reliably identifies the transition state. Regarding the SW transformation of metallofullerenes with off-centered dopants, we rotate the C-C dimer which is the closest to the metal atom (Ca and La).

Table I lists the computed activation barriers (E_a) of the SW transformations in various fullerenes and a graphene sheet. The activation barrier in the SW transformation of the fullerene (7.16 eV) is lower than that of the graphene sheet (9.2 eV, the highest among the systems we study). The barrier reduction in fullerenes is due to the curvature effect associated with the deviation from the sp^2 bonding.⁶ When K, Ca, and La atoms are encapsulated inside the fullerene, the activation energy barriers are lowered by 0.30, 0.55, and 0.80 eV, respectively, compared with that of bare C_{60} .

To determine the major effect of the encapsulated metal atom on the lowering of the activation barrier, we perform calculations for fullerenes charged with one or two electrons. The results for C_{60}^{3-} are not presented because the third elec-

TABLE I. Activation barrier (E_a) and reaction energy (E_r) of the SW transformation in various sp^2 -bonded carbon systems. All energy values are in eV.

System	E_a	E_r
C_{60}	7.16	1.59
$K@C_{60}$	6.85	1.07
$Ca@C_{60}$	6.61	0.59
$La@C_{60}$	6.36	0.30
C_{60}^-	6.87	1.12
C_{60}^{2-}	6.59	0.67
$C_{42}H_{16}$ (for graphene)	9.20	3.07

tron is found to be unbound. When a fullerene is charged, the activation barrier becomes lower than that of the neutral cage, similar to the endohedral metallofullerenes. The barrier reduction is approximately proportional to the number of donated electrons. E_a in the SW transformation of C_{60}^- (C_{60}^{2-}) is almost identical to that of $K@C_{60}$ ($Ca@C_{60}$). Therefore, one can conclude that the electron donation of the incorporated metal atom lowers the barrier and that the chemical bonding between the metal atom and C_{60} is less important.

The reaction energy ($E_r = E_{product} - E_{reactant}$) shows the same trend as E_a in Table I. The C_{2v} -symmetry C_{60} with two pairs of adjacent pentagons obtained by the SW transformation is 1.59 eV higher in energy than C_{60} with the I_h -symmetry. This value is in good agreement with other results found in the literature.²⁴ By contrast, for $La@C_{60}$, E_r is 0.3 eV, which is much smaller than that of C_{60} (1.59 eV). It implies that an isomer of the metallofullerene which has adjacent pentagons can exist with higher probability compared to empty C_{60} . In the case of $K@C_{60}$ which has an intermediate value of E_r , the K atom at the center of the cage does not move during the process of the SW transformation. By contrast, the La atom in the fullerene moves by 1.0 Å toward the paired pentagons during the dimer rotation. The displacement of the La atom induces a large elongation of the C_{60} cage compared with the empty C_{60} molecule. The geometry of an empty fullerene is governed by the isolated-pentagon rule (IPR),^{25,26} which means that the structure is most stable when all pentagons are surrounded by five hexagons. The IPR-violating cages such as $Sc_2@C_{66}$ and $Sc_3N@C_{68}$, however, are stabilized by the electron transfer between the encapsulated metal atoms and the carbon cage, which significantly decreases the strain energy caused by paired pentagons and thus stabilizes the fullerene.^{27,28} Owing to the 108° bond angles of the pentagon, the apex atoms in the paired pentagon regions of the empty fullerene have a hybridization very close to sp^3 and exhibit a dangling-bondlike character.²⁹ For metallofullerenes, on the other hand, the electron donation from the metal atom weakens the dangling-bondlike character and stabilizes the IPR-violating isomers.

To clarify the role of the encapsulated metal atom, we investigate the electronic structures of C_{60} and $La@C_{60}$ in detail. The inspection of the projected density of states (PDOS) onto the 6s and 5d orbitals of La for each reactant,

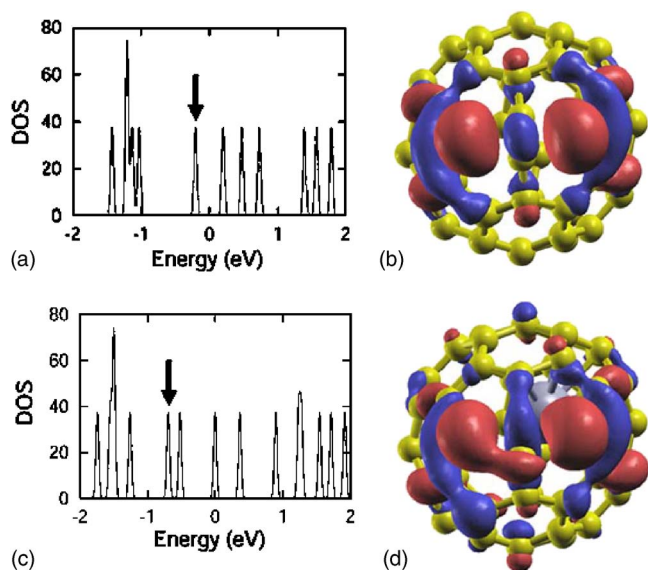


FIG. 2. (Color online) Density of states (DOS) for C_{60} and $La@C_{60}$ in the transition state [(a) and (c), respectively] and the isodensity surface plots of particular states for C_{60} and $La@C_{60}$ [(b) and (d)]. The energy levels of the wave functions in (b) and (d) are indicated by arrows in (a) and (c), respectively. The isodensity value is $0.0014 e/\text{\AA}^3$ and the surface is color-coded according to the sign of the wave functions.

transition state, and product indicates that the $6s$ and $5d$ energy levels of the La atom mainly lie above the Fermi level. It means that almost three electrons transfer from La to the fullerene in $La@C_{60}$. In Fig. 2(a), the highest occupied molecular orbital (HOMO) at -0.2 eV (indicated by the arrow) corresponds to the dangling-bond-originated state as illustrated in Fig. 2(b). This state is above the HOMO of C_{60} (i.e., the fivefold degenerate states originating from the HOMO of empty C_{60} which are split off now). The energy level which has the dangling bond character in $La@C_{60}$ is at -0.7 eV (HOMO-2) as shown in Fig. 2(c) by the arrow and the wave function in Fig. 2(d). Here one can observe three electrons coming from the La atom occupy the upper one and half levels which are the lowest unoccupied molecular orbital (LUMO) and LUMO+1 levels in the transition state of C_{60} . The overall shape of the two wave functions [Figs. 2(b) and 2(d)] is similar except for small changes due to the perturbation of the La atom.

Figures 3(c) and 3(d) show the PDOS onto $2p$ orbitals of two carbon atoms [labeled as A , B and A' , B' in Figs. 3(a) and 3(b)] which have the dangling bonds in the transition state. In the case of empty C_{60} , the PDOS of A and B are exactly same. For $La@C_{60}$, on the other hand, the charge density of nonbonding states at site A' (between -1 and 0 eV) is not identical to the density at site B' . This difference arises from the hybridization between the La atom and the C atom at site B . In the TS configuration of empty C_{60} , the HOMO and LUMO are both localized states within the

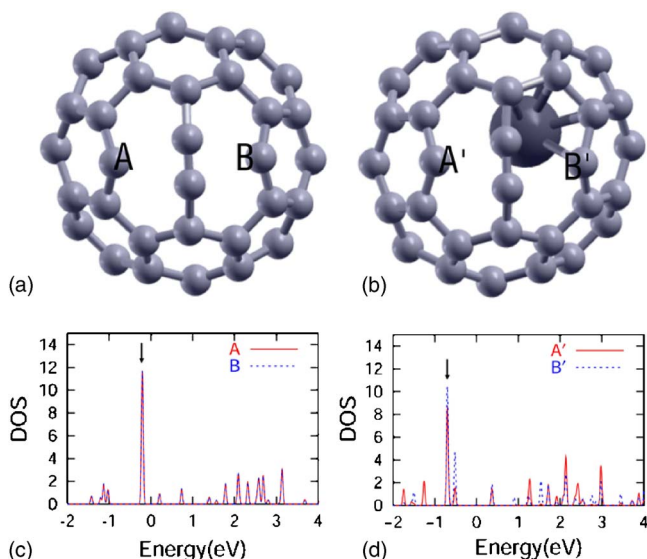


FIG. 3. (Color online) Atomic structures of the transition state configuration for (a) C_{60} and (b) $La@C_{60}$, and PDOS of two atoms [labeled A , B and A' , B' in (a) and (b), respectively] which have dangling bonds in the transition state, for (c) C_{60} and (d) $La@C_{60}$. The defect states due to the dangling bonds or distorted bonding configurations are indicated by arrows. The red solid and blue dotted lines are the PDOS onto $2p$ orbitals of A , A' and B , B' atoms, respectively.

hemisphere containing two dangling atoms while the HOMO and LUMO in the TS of $La@C_{60}$ are delocalized on the whole cage. Consequently, the electron transfer and hybridization between the fullerene and metal atom reduce the activation energy barrier of the SW transformation in the endohedral metallofullerene.

In summary, we have studied the effect of encapsulated metal atoms inside a C_{60} molecule on the activation energy barrier of the SW transformation. The metal atoms in our study are K, Ca, and La, which donate one, two, and three electrons to the C_{60} cage, respectively. We have found that isomerization of the endohedral metallofullerene by the SW transformation can occur more easily than that of the empty fullerene owing to the charge transfer. The reduction of the activation energy barrier by the electron transfer may also explain the fact that metallofullerenes are much easier to coalesce than empty fullerenes inside nanotubes.

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