The density functional calculations on the structural and electronic properties of the endohedral fullerene dimer $(N_2@C_{60})_2$*

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The generalised gradient approximation based on density functional theory is used to study the structural and electronic properties of the endohedral fullerene dimer $(N_2@C_{60})_2$. Four N atoms sit at the cage centres in the form of two N_2 molecules. The density of states and Mulliken charge analysis explore that the energy levels from –6 to –10 eV are mainly influenced by the N_2 molecules.

Keywords: $(C_{60})_2$, $(N_2@C_{60})_2$ dimer, electronic property, density functional
PACC: 3640B, 7115M, 7125W

1. Introduction

Fullerenes have attracted much interest since the discovery of C_{60}.[1] The endohedral derivatives of C_{60}, which enclose atoms or molecules, can exhibit unique physical and chemical properties.[2,3] Experimentally, fullerene polymers are prepared by polyreaction under certain condition.[4–6] For example, the D_{2h} symmetrical $(C_{60})_2$ dimer has been obtained by the high speed vibration milling method,[7] and its dumbbell-shaped structure has already been determined through x-ray diffractometry.[8] Theoretically, the $(C_{60})_2$ dimer with dumbbell-shaped structure and two adjacent cages linking by parallel double bonds has the lowest energy.[9–11] As reported, Komatsu *et al.*[12] have synthesised $H_2@C_{60}$ and its dimer. Although Cao *et al.*,[13] Suetsuna *et al.*,[14] and Peres *et al.*[15] have isolated $N_2@C_{60}$,[16] the experimental preparation of $(N_2@C_{60})_2$ dimer is being under study. In this paper, the main aim is to study the structural and properties of $(N_2@C_{60})_2$ dimer, we hope the results can direct the developing of the experimental work.

2. Theoretical methods and computational details

The generalised gradient approximation[17] based on density functional theory[18] is used in the calculations. We choose the BLYP functional (Becke gradient exchange functional[19] combines with Lee–Yang–Parr correlation functional[20]) and DNP basis set[21] (double numerical basis functions together with polarisation functions). The electronic structure is obtained by solving the Kohn–Sham equations self-consistently[22] with the spin unrestricted scheme. Self-consistent field procedure is carried out with a convergence criterion of 10^{-6} a.u. on the energy and electron density. The geometry optimisations are performed with a convergence criterion of 10^{-3} a.u. on the gradient, 10^{-3} a.u. on the displacement, and 10^{-5} a.u. on the energy.[23,24] The optimized bond lengths for the single and double bonds of C_{60} are 1.46 Å and 1.40 Å (1 Å = 0.1 nm), respectively, in good agreement with the experimental values of 1.43–1.46 Å and 1.39–1.40 Å.[25–27] The calculated energy gap (E_g) between the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule or-

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bital (LUMO) of C_{60} is 1.66 eV, which compares well to the first excitation energy of 1.70 eV in previous experiment.[28] Therefore, the computational scheme is suitable to study the fullerene system.

3. Results and discussion

3.1. The structure

According to the previous studies,[9−11] the $(C_{60})_2$ dimer with two C_{60} cages linked by two parallel double bonds should be most stable. In order to find out the most stably combined style of four N atoms in the lowest-energy $(C_{60})_2$, we place the four N atoms along the X, Y, and Z axes in both C_{60} cages separately. The distance between two N atoms (R_{N-N}) is at first four times the N–N bond length in free N_2 molecule, and then decreases to half and quarter successively.

Table 1 lists the initial R_{N-N}s, optimised R_{N-N}s, binding energies (BEs), and doped energies (DEs) of the nine structures. It is discovered that when the initial R_{N-N} is four times of the N–N bond length in free N_2 molecule, the interaction between two N atoms will be smaller than that between N and C, thus, two N atoms are isolated from each other in the cage. However, when the initial R_{N-N} decrease to half and quarter of its value, the interaction between the two N atoms is greater than that between N and C, hence, the two N atoms are combined to one N_2 molecule in each cage. Commonly, the thermodynamic stability of a fullerene is determined by its BE,[29] which is defined as the difference between the energy sum of all free atoms constituting the molecule and the total energy of the molecule. The higher BE leads to the more thermodynamic stability. As computed, the BEs of the cages enclosing two N_2 molecules are about 27.71, 25.29 and 25.31 eV higher than that of the structures encaging four isolated N atoms respectively along the X, Y, and Z axes. The DE is defined as DE = $E[(N_2@C_{60})_2]$-$\{E[(C_{60})_2]+4E(N)\}$,[30−32] where $E[(N_2@C_{60})_2]$, $E[(C_{60})_2]$, and $E(N)$ are the total energies of $(N_2@C_{60})_2$, $(C_{60})_2$, and single N atom respectively. The negative DE means the exothermic reaction, and the larger absolute value of DE leads to the greater stability. It is found from Table 1 that the structures enclosing two N_2 molecules all have negative DE. Thus, the reaction to dope two N_2 molecules into the $(C_{60})_2$ cages is exothermic and energetically favoured. However, we do not know whether the two N_2 molecules are at or off the cage centre. Totally, twelve sites are chosen to place them, as shown in Fig. 1. We find that the N_2 off the centre are all back to the cage centre after optimisation. Thus, the N_2 molecules are most stable at the cage centre, acting the same as the noble gas atoms[33] and the $N_2@C_{60}$.[16]

Table 1. The initial R_{N-N}s, optimised R_{N-N}s, BEs and DEs of $(N_2@C_{60})_2$.

the axis for locating N atoms	initial R_{N-N}/Å	optimized R_{N-N}/Å	BEs/eV	DEs/eV
X axis of $(C_{60})_2$	4.44,4.44	3.94, 3.94	842.16	7.53
	2.22,2.22	1.11,1.11	869.87	–20.19
	1.11,1.11	1.11,1.11	869.87	–20.19
Y axis of $(C_{60})_2$	4.44,4.44	4.07,4.07	844.54	5.14
	2.22,2.22	1.11,1.11	869.83	–20.14
	1.11,1.11	1.11,1.11	869.83	–20.14
Z axis of $(C_{60})_2$	4.44,4.44	3.99,3.99	844.49	5.20
	2.22,2.22	1.11,1.11	869.80	–20.11
	1.11,1.11	1.11,1.11	869.80	–20.11

Figure 1 also shows 31 different sites which the N_2 molecules will point to. The calculated BEs and DEs of these 31 structures are almost isoenergy. It should be noticed that the DE defined here is the total energy difference of $(N_2@C_{60})_2$ minus those of $(C_{60})_2$ and two N_2 molecules. Therefore, the thermodynamic stability of the $(N_2@C_{60})_2$ dimer has no relation with the orientation of N_2 molecules. We next take D_{2h} symmetrical $(N_2@C_{60})_2$-20 as an example to analyse its electronic properties. The calculated E_g of $(C_{60})_2$ is 1.44 eV, about 0.22 eV smaller than that of C_{60}, 1.66 eV, indicating that the dimer is more reactive. While, $(N_2@C_{60})_2$-20 has an E_g approximate to that of $(C_{60})_2$, 1.47 eV, indicating their similar kinematic stabilities.

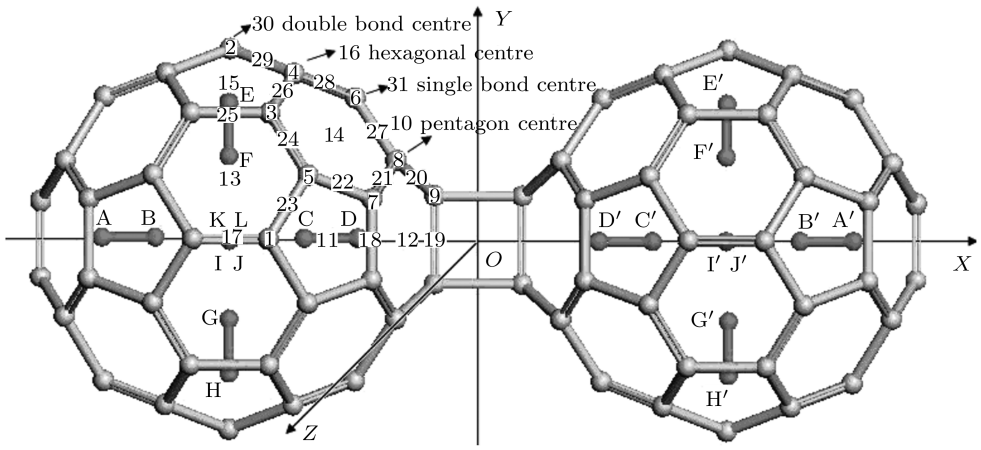


Fig. 1. (A-B, C-D, E-F, G-H, I-J,K-L), (A'-B', C'-D', E'-F', G'-H', I'-J') are the possible stable positions of N_2 molecules in the cage. Three cases in X axis: I = (A-B, A'-B'), II = (A-B, C'-D'), III =(C-D, C'-D'); two cases in Y axis: IV = (E-F, E'-F'), V = (G-H, E'-F'); two cases in Z axis: VI = (I-J, I'-J'), VII = (K-L, I'-J'); five cases in two axes: VII = (A-B, E'-F'); VIII = (A-B, I'-J'); IX = (C-D, E'-F'); X = (C-D, I'-J'); XI = (E-F, I'-J'). The numbers 1 to 31 are 31 directions which the N_2 molecule point to: 1–9 are nine different carbon atoms; 10, 11, 15 are three different pentagon centres; 12, 13, 14, 16 are four different hexagonal centres; 18, 20, 22, 23, 25, 26, 27, 29, 31 are nine different single bond centres; 17, 19, 21, 24, 28, 30 are six different double bond centres.

3.2. The electronic structure

Figure 2 shows the total density of states (TDOSs) of $(C_{60})_2$ and $(N_2@C_{60})_2$-20, and the partial density of states (PDOS) of the N_2 molecules in $(N_2@C_{60})_2$-20. The DOS is obtained by a Lorentzian extension of the discrete energy levels, with weights being the orbital populations in the levels and a summation over them. The broadening width parameter is chosen to be 0.15 eV and the Fermi energy (E_F) is taken to be zero. We find that there are small difference between –6 to –10 eV below the E_F in the TDOSs of $(C_{60})_2$ and $(N_2@C_{60})_2$-20, indicating that the energy levels in this range are maninly influenced by N_2 molecules. In addition, there is almost no peak appearing around E_F in the PDOS of N_2 molecules in $(N_2@C_{60})_2$-20, showing that N_2 molecules have no influence on the frontier orbital. This can be clearly seen from the HOMO and LUMO of $(N_2@C_{60})_2$-20 shown in Fig. 3, in which the wave functions are distributed in the carbon cage, while there is no distribution in the nitrogen molecules at the centre of carbon cage.

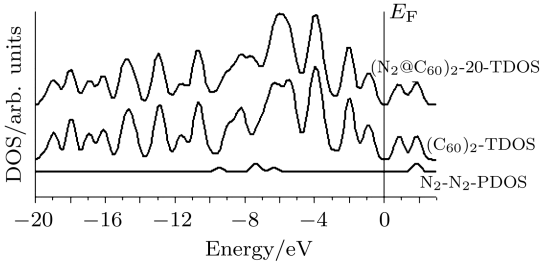
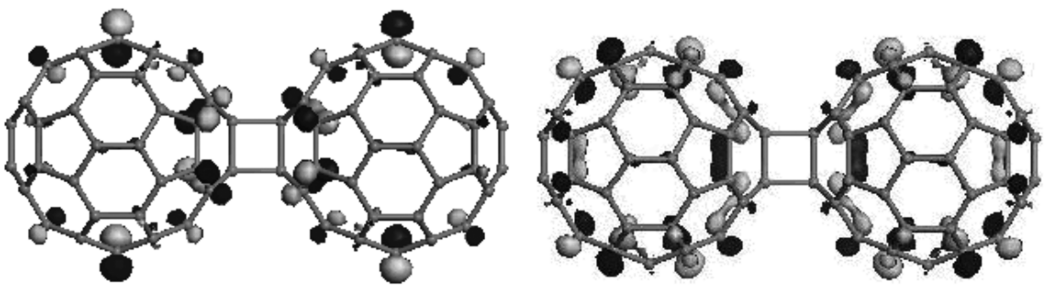


Fig. 2. TDOSs of $(N_2@C_{60})_2$-20 and $(C_{60})_2$, PDOS of N_2 molecules in $(N_2@C_{60})_2$-20.



HOMO of $(N_2@C_{60})_2$-20 LUMO of $(N_2@C_{60})_2$-20

Fig. 3. The HOMO and LUMO of $(N_2@C_{60})_2$-20.

Next, we carry out the Mulliken charge analysis of $(N_2@C_{60})_2$-20. We find that, the electrons of each N atom are 0.002 e, while the charge of every C atom is less than 0.098 e. Therefore, the electrons of each N atom and C atom are almost unchanged in the formation of $(N_2@C_{60})_2$-20, showing the small effect of N_2 molecules on the cage, as well.

The VIP is the total energy difference between the one electron positively charged and neutral clusters. The VEA is evaluated by adding one electron to the neutral cluster in its equilibrium geometry and taking the difference between their total energies. The calculated VEA of $(C_{60})_2$ and $(N_2@C_{60})_2$-20 are 3.13 and 2.77 eV, while the VIPs of $(C_{60})_2$and $(N_2@C_{60})_2$-20 are 6.48 and 6.49 eV, respectively. Obviously, the VEA of $(N_2@C_{60})_2$-20 decrease much while the VIP of it changes little, indicating that $(N_2@C_{60})_2$-20 is much difficult to obtain electrons. Therefore, the ability for obtaining electron of the cage is obviously affected by the two N_2 molecules.

4. Conclusion

The geometry optimisations show that the four N atoms are located at the cage centres in the form of two N_2 molecules. The electronic analysis indicates that the Eg of $(N_2@C_{60})_2$-20 is close to that of $(C_{60})_2$. The energy levels from –6 to –10 eV are mainly influenced by the N_2 molecules.

References

[1] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162

[2] Salas R E E and Valladares A A 2008 *J. Mol. Struct: Theochem.* **869** 1

[3] Ren X Y and Liu Z Y 2005 *Struct. Chem.* **16** 567

[4] Wang Y, Holden J M, Bi X X and Ekiund P C 1994 *Chem. Phys. Lett.* **217** 413

[5] Iwasa Y, Srima T, Fleming R M and Siegrist T 1994 *Science* **264** 1570

[6] Pekker S, Janossy A, Mihaly L, Chauvet O, Carrard M and Forro L 1994 *Science* **265** 1077

[7] Pederson M R and Quong A A 1995 *Phys. Rev. Lett.* **74** 2319

[8] Wang G W, Komatsu K, Murata Y and Shiro M 1997 *Nature* **387** 583

[9] Haufler R E, Wang L S, Chibante L P F, Jin C M, Conceicao J, Chai Y and Smalley R E 1991 *Chem. Phys. Lett.* **179** 449

[10] Adams G B, Page J B, Sankey O F and O'Keeffe M 1994 *Phys. Rev.* B **50** 17471

[11] Kürti J and Németh K 1996 *Chem. Phys. Lett.* **256** 119

[12] Komatsu K, Murata M and Murata Y 2005 *Science* **307** 238

[13] Cao B, Peres T, Cross R J, Saunders M and Lifshitz C 2001 *J. Phys. Chem.* A **105** 2142

[14] Suetsuna T, Dragoe N, Harneit W, Weidinger A, Shimotani H, Ito S, Takagi H and Kitazawa K 2002 *Chemistry* **8** 5079

[15] Peres T, Cao B P, Cui W D, Khong A, Cross R J, Saunders M and Lifshitz C 2001 *Int. J. Mass Spectrom.* **210** 241

[16] Gao H, Zhu W H, Tang C M, Geng F F, Yao C D, Xu Y L and Deng K M 2010 *Acta. Phys. Sin.* **59** 1707 (in Chinese)

[17] San D 1996 *Dmol. Biosym. Technologics* CA

[18] Tang C M, Yuan Y B, Deng K M and Yang J L 2006 *Acta. Phys. Sin.* **55** 3601 (in Chinese)

[19] Becke A D 1988 *J. Chem. Phys.* **88** 1053

[20] Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864

[21] Delley I B 1990 *J. Chem. Phys.* **92** 508

[22] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133

[23] Tang C M, Zhu W H and Deng K M 2010 *Chin. Phys.* B **19** 033604

[24] Tang C M, Cao Q S, Zhu W H and Deng K M 2010 *Chin. Phys.* B **19** 033603

[25] Hawkins J M, Meyer A, Lewis T A, Loren S and Hollander F J 1991 *Science* **252** 312

[26] Leclercg F, Damay P, Foukani M, Foukani M, Chieux P, Bellissent-Funel M C, Rasat A and Fabre C 1993 *Phys. Rev.* B **48** 2748

[27] Hedberg K, Hedberg L, Bethune D S, Brown C A, Dorn H C, Johnson R D and Vries M D 1991 *Science* **254** 410

[28] Pederson M R and Quong A A 1995 *Phys. Rev. Lett.* **74** 2319

[29] Lu G L, Yuan Y B, Deng K M, Wu H P, Yang J L and Wang X 2006 *Chem. Phys. Lett.* **424** 142

[30] Lu L H, Chen C and Sun K C 1998 *Int. J. Quant. Chem.* **68** 273

[31] Chang Y F, Zhang J P, Hong B, Sun H, An Z and Wang R S 2005 *J. Chem. Phys.* **123** 094305

[32] Hong B, Chang Y F, Qiu Y Q, Sun H, Su Z M and Wang R S 2006 *J. Chem. Phys.* **124** 144108

[33] Saunders M, Cross R J, Jimenez-Vazquez H A, Shimshi R and Khong A 1996 *Science* **271** 1693