An unusual spin-polarized state in fullerene induced by carbon adatom defects

Dexuan Xu,[ab] Yang Gao,[ab] Wanrun Jiang,[ab] Zhigang Wang[ab*]

[a]Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China.

[b]Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun 130012, China.

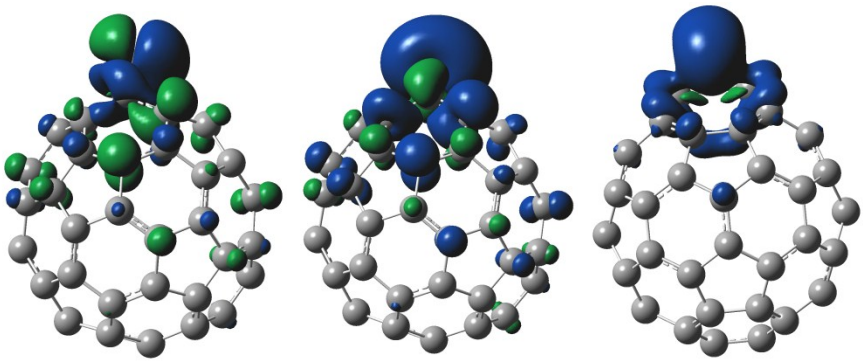
*Corresponding author: wangzg@jlu.edu.cn (Z. W.).

Part 1.

Table S1. Related geometry optimization results (by Gaussian 09) of C_{61}-Def[5, 6] and C_{61}-Def[6, 6] with various DFT methods.1* represents the spin-polarized singlet state.

System	Functionals/Basis set	Multiplicity	ΔE (eV)
Def[5, 6]	BP86/6-31G*	**1***	**0.000**
		1	0.066
		3	0.136
		5	1.518
	PBE/6-31G*	**1***	**0.000**
		1	0.074
		3	0.120
		5	1.506
	B3LYP/6-31G*	**1***	**0.000**
		1	0.091
		3	0.127
		5	1.770
	HSE06/6-31G*	**1***	**0.000**
		1	0.165
		3	0.056
		5	1.685
Def[6, 6]	BP86/6-31G*	1	0.101
		3	**0.000**
		5	1.439
	PBE/6-31G*	1	0.103
		3	**0.000**
		5	1.439
	B3LYP/6-31G*	1	0.090
		3	**0.000**
		5	1.663
	HSE06/6-31G*	1	0.083
		3	**0.000**
		5	1.700

Part 2.



(a) **(b)** **(c)**

Figure S1. The spin density distribution of three spin states. (a) Def[5, 6] spin-polarized singlet state (b) Def[5, 6] triplet state (c) Def[6, 6] triplet state. The blue represents spin-up, the green represents spin-down. Calculation method is PBE/6-31G*, isovalue is 0.002 a.u..

Part 3.

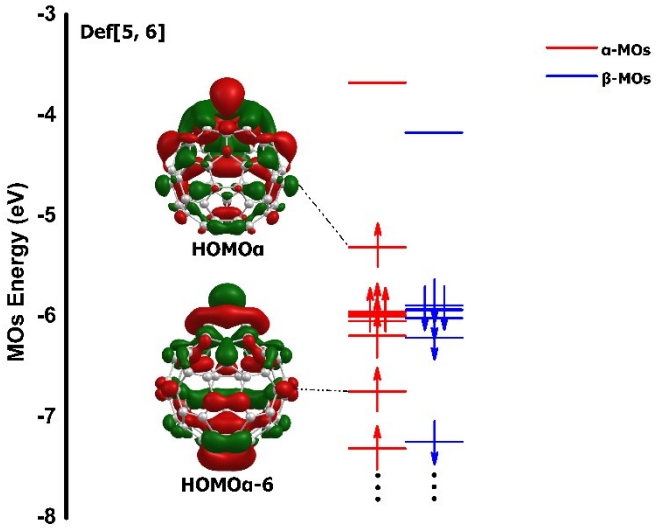


Figure S2. MOs energy diagram of Def[5, 6] structure with triplet state.

Part 4.

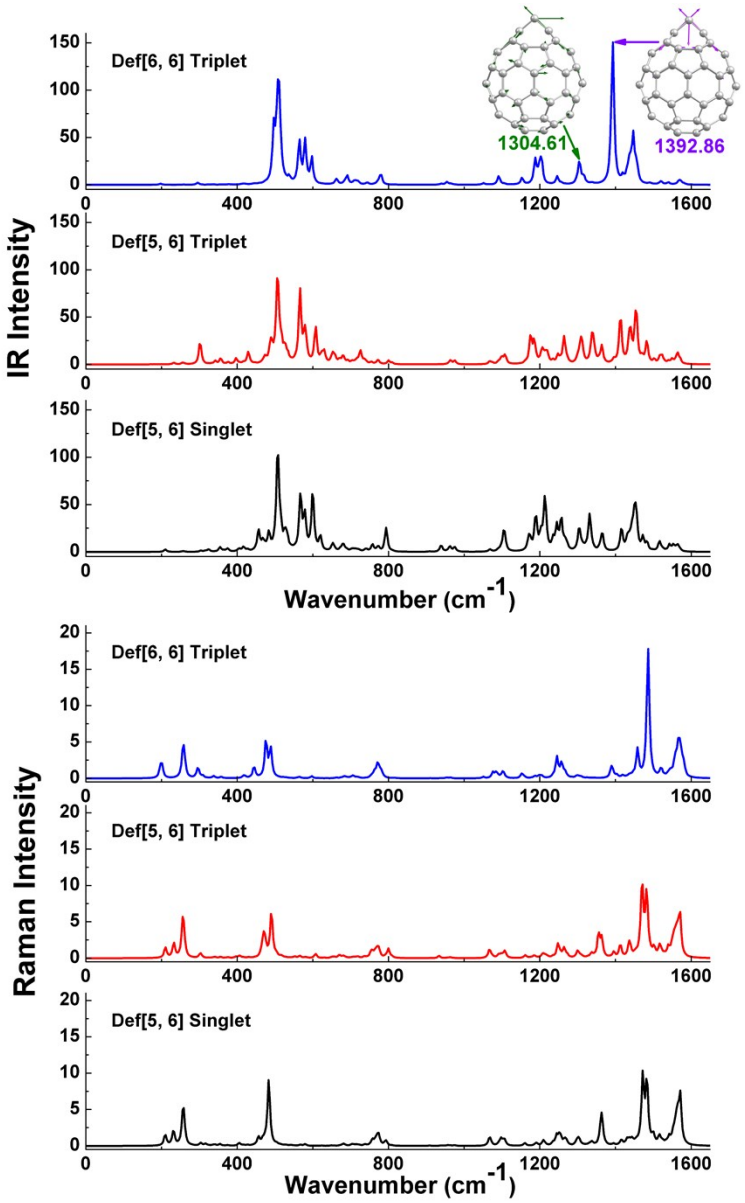


Figure S3. IR and Raman spectra of Def[5, 6] and Def[6, 6] adsorption structures. The black lines, red lines and the blue lines represent the singlet state of Def[5, 6], the triplet state of Def[5, 6] and the triplet state of Def[6, 6] respectively. The same colors correspond to the same vibration modes.

Part 5.

Table S2. Relative energy of C_{61}-Def[5, 6], C_{61}-Def[6, 6] with corresponding most stable electron state.

System	Def[5, 6]-spin polarized singlet	Def[6, 6]-triplet
∆E (eV)	0	0.208

Part 6.

Table S3. Binding (E_{bin}), interaction (E_{int}) and preparation (E_{prep}) energies (in eV) of Def[5, 6] and Def[6, 6].

System	Def[5, 6]	Def[6, 6]
E_{bin}	3.58	3.37
E_{int}	6.87	7.09
E_{prep}	3.29	3.72

To assess the thermodynamic stability of the Def[5, 6], its binding, interaction and preparation energies are computed and listed in Table S3, compared with the values of the Def[6, 6]. For characterizing the stability of a carbon adatom in fullerene, we difined its binding (E_{bin}), interaction (E_{int}) and preparation (E_{prep}) energies as:

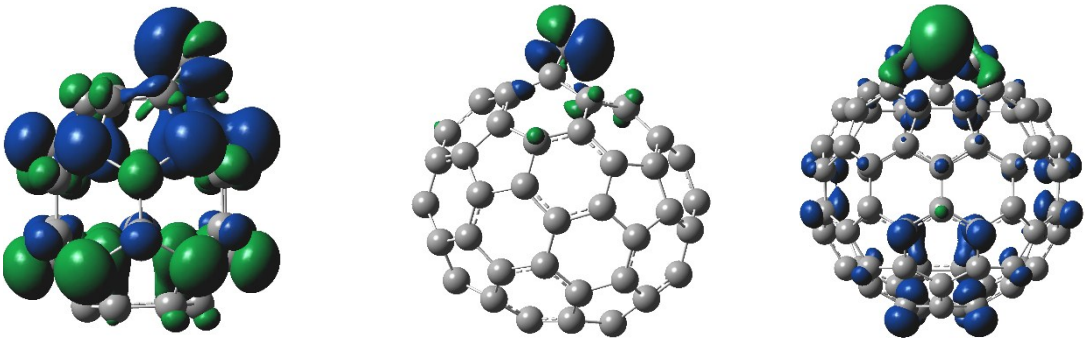
$$E_{bin/int} = (E_{iso/relaxed(C60)} + E_{adatom}) - E_T$$

$$E_{prep} = E_{int} - E_{bin}$$

where E_T is the total energy of defective fullerene, $E_{iso(C60)}$ represents the energy of the isolated C_{60}, $E_{relaxed(C60)}$ denotes the energy of C_{60} in its relaxed geometry, and E_{adatom} is the energy of carbon adatom. The final E_{int} was obtained after taking basis set superposition error (BSSE) into account. The E_{int} represents a measure of the strength of

the chemical interaction between the carbon adatom and C_{60}, a positive E_{int} means an attractive interaction; while the E_{bin} encompasses not only the energy gained due to the chemical interaction E_{int}, but also the energy paid to deform the C_{60} from its ideal configuration to the relaxed adsorption structure (i.e., preparation energy, E_{prep}).

Part 7.



(a) **(b)** **(c)**

Figure S4. Typical spin density distribution of other considered fullerenes in the spin polarized singlet state (a) C_{37}-Def[5, 6], (b) C_{71}-Def[5, 6], (c) C_{81}-Def[5, 6]. Blue represents spin-up, green represents spin-down. Calculation method is PBE/6-31G*, isovalue is 0.002 a.u..