

# Structural, electronic, and magnetic properties of heterofullerene C<sub>58</sub>Si with odd number of atoms and a near planar tetracoordinate Si atom

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## Abstract

Density functional calculations and minimization techniques have been employed to characterize the structural and electronic properties of [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub>. Since it has odd number of atoms and a near planar tetracoordinate Si atom on the skeleton of the cage, it has odd number of atoms assembling a cage and is a novel molecule. Vibrational frequencies of the molecule have been calculated at the B3LYP/6-31G\* level of theory. The absence of imaginary vibrational frequency confirms that the molecule corresponds to a true minimum on the potential energy hypersurface. Sixteen <sup>13</sup>C nuclear magnetic resonance (NMR) spectral signals of C<sub>58</sub>Si are characterized, and its heat of formation was estimated in this work. © 2008 Elsevier Inc. All rights reserved.

**Keywords:** Heterofullerene C<sub>58</sub>Si; B3LYP/6-31G\*; Vibrational frequency; NMR; Heat of formation

## 1. Introduction

In the past two decades, a great number of achievements have been acquired for fullerenes, a new form of pure carbon with cage-like structure, where an even number of three-coordinated carbon atoms arrange themselves into 12 pentagons and any number (>1) of hexagons. Fullerenes can be doped in several different ways [1]. If the dopant substitutes the carbon atom(s) on fullerene cage, heterofullerene can be generated. Since heterofullerenes have been shown the remarkable structural, electronic, optical, and magnetic properties [1–4], they have been the focus of attention experimentally and theoretically [5–20] in recent years.

The first heterofullerene ion was reported by the Smalley group in 1991 [5]. So far, successful heterofullerenes contain the elements of B [21], N [20], Si [22–24], O [25], P [26], As [27], Ge [27], Fe, Co, Ni, Rh, and Ir [28]. As we know, every molecule of fullerenes or heterofullerenes reported before contains even number of atoms on the skeleton of the cage. To the author's knowledge, the heterofullerene molecule contain-

ing the odd number of atoms assembling a cage has never been reported before.

In 1970, Hoffmann et al. [29] predicted that the planar tetracoordinate carbon could exist. This prediction has been confirmed by experiments [30]. We think that if an atom, like planar tetracoordinate carbon, has suitable size and can form four bonds in near plane, it can substitute a C–C bond on the surface of fullerene cage, and thus the heterofullerene with odd number of atoms on the skeleton of cage can be formed. We think that the silicon atom is the suitable atom. When a silicon atom substitutes a 6–6 C–C bond (hexagon–hexagon) of C<sub>60</sub>, a molecule of [5,6]-heterofullerene-C<sub>58</sub>Si with odd number of atoms assembling a cage has been obtained. The molecule has 4 pentagons, which containing a Si atom and four carbon atoms, and 10 pentagons and 18 hexagons with only carbon atoms. It has 89 bonds, 4 C–Si bonds and 85 C–C bonds. Its structure is shown in Fig. 1.

The present work is the extension of heterofullerene. We optimized the geometry of [5,6]-heterofullerene-C<sub>58</sub>Si by using DFT method at the B3LYP/6-31G\* level of theory [31]. To verify whether the molecule is a real minimum on the potential energy hypersurface, vibrational frequencies have been calculated at the B3LYP/6-31G\* level of theory, too. Vibrational frequencies confirm that the molecule is a true

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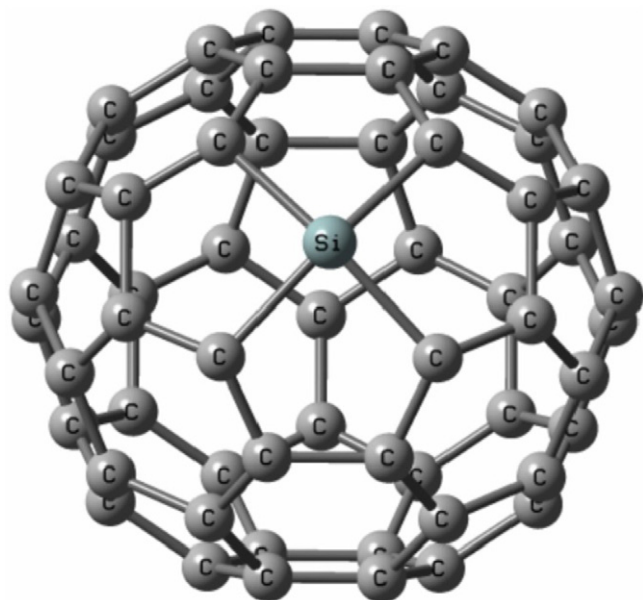


Fig. 1. Structure of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ .

density surfaces corresponding to the HOMO and the LUMO and other some MOs have been studied, too.

### 3. Results and discussion

#### 3.1. Geometries and some properties

We began our study by structural optimization of pure  $C_{60}$  at the B3LYP/6-31G\* level of theory. The calculated bond lengths for 6–6 bonds (hexagon–hexagon) and 5–6 bonds (pentagon–hexagon) are 1.395 and 1.453 Å, respectively, which are in reasonable agreement with the experimental values reported in Ref. [35].

We use a two-dimensional schematic view (Fig. 2) to show how pentagons and hexagons can be distributed in the [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  cage. The optimized structure is shown in Fig. 1 and the optimized bond lengths are given in Table 1 with the numbering system of carbon and silicon atoms in Fig. 2. From Table 1, it can be seen that apart from the C–C bonds surrounding the Si atom, all other C–C bonds lengths are similar to those of pure  $C_{60}$ . The longest C–C bonds are the 6–7 and 12–13 C–C bonds, which 1.508 Å. As for Si–C bonds, being larger than typical Si–C single bond ranging from 1.83 to 1.90 Å [36], is about 1.937 Å. We think that the strain in pentagons containing Si atom makes the Si–C bonds lengths larger.

The optimized bond angles containing-Si atom and surrounding-Si atom for the [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  are  $\angle C_2Si_1C_5 = \angle C_8Si_1C_{11} = 86.2^\circ$ ,  $\angle C_5Si_1C_{11} = \angle C_2Si_1C_{11} = 88.8^\circ$ ,  $\angle C_1C_2C_3 = \angle C_1C_5C_4 = \angle C_1C_8C_9 = \angle C_1C_{11}C_{10} = 111.2^\circ$ ,  $\angle C_1C_2C_{13} = \angle C_1C_5C_6 = \angle C_1C_8C_7 = \angle C_1C_{11}C_{12} = 109.6^\circ$ ,  $\angle C_2C_3C_4 = \angle C_3C_4C_5 = \angle C_8C_9C_{10} = \angle C_9C_{10}C_{11} = 113.8^\circ$ ,  $\angle C_5C_6C_7 = \angle C_6C_7C_8 = \angle C_2C_{13}C_{12} = \angle C_{11}C_{12}C_{13} = 115.8^\circ$ , respectively. The other optimized  $\angle$  CCC bond angles are similar to those of pure  $C_{60}$ .

The total energy and energies of HOMO and LUMO of the [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  are determined at the B3LYP/6-31G\* level of theory. The results are given in Table 2. For the

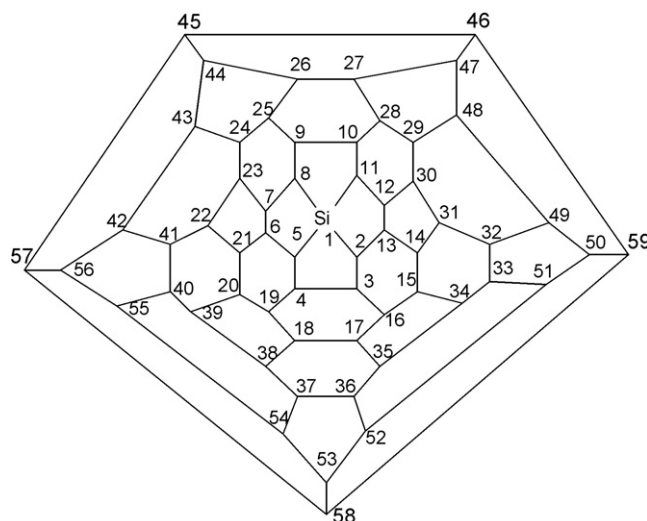


Fig. 2. Numbering system of atoms in [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ .

minimum on the potential energy hypersurface. For future experimental identification of the molecule, its magnetic shielding tensors are calculated. For the sake of understanding the thermodynamic stability, its heat of formation  $\Delta H_f^0$  was estimated, and the natural bond orbital charges and the probability isodensity surfaces corresponding to the HOMO and the LUMO have been also reported in this paper.

### 2. Computational details

The full geometry optimization for the molecule of [5,6]-heterofullerene- $C_{58}Si$  was performed by using the energy gradient method at the B3LYP/6-31G\* level of theory using Gaussian 98 program system [32]. Since the polarization functions are essential for the realistic expression of geometries of the molecules involving second and third row elements [33], the basis set of 6-31G\* was used in this study. After the optimization of the geometry, its symmetry converges at  $C_{2v}$  group point. Thus we call it [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ . On the basis of the optimized geometry, vibrational frequencies of the molecule were also computed at the B3LYP/6-31G\* level of theory. Vibrational frequencies were determined firstly to verify the nature of the stationary point, second to use the sum of electronic energy and zero-point vibrational energy (ZPE) corrections for calculating the heat of formation of the molecule, and third to predict vibrational frequencies of the unknown stable species for the sake of their future experimental identification by infrared (IR) spectroscopy and the assignment of the observed frequencies. For future experimental identification of the molecule by nuclear magnetic resonance (NMR), its magnetic shielding tensors were calculated by using the gauge-including-atomic-orbital (GIAO) method and the continuous set of gauge transformation (CSGT) procedure [34]. In order to understand the electronic and reactive properties, the net charges with natural bond orbital method and the probability

Table 1  
B3LYP/6-31G(d) calculation of C–C and Si–C bond lengths in molecule C<sub>58</sub>Si

Bond	Site number pairs for bonding	Bond length (Å)
Si–C	(1–2, 1–5, 1–8, 1–11)	1.937
C–C	(2–3, 4–5, 8–9, 10–11)	1.382
C–C	(2–13, 5–6, 7–8, 11–12)	1.437
C–C	(3–4, 9–10)	1.488
C–C	(6–7, 12–13)	1.508
C–C	(3–16, 4–18, 9–25, 10–27)	1.426
C–C	(6–20, 7–23, 12–29, 13–14)	1.412
C–C	(16–17, 17–18, 25–26, 26–27)	1.460
C–C	(15–16, 18–19, 24–25, 27–28)	1.403
C–C	(14–15, 19–20, 23–24, 28–29)	1.448
C–C	(14–31, 20–21, 22–23, 29–30)	1.456
C–C	(21–22, 30–31)	1.388
C–C	(17–35, 26–44)	1.389
C–C	(15–33, 19–37, 24–42, 28–46)	1.449
C–C	(21–38, 22–41, 30–47, 31–32)	1.451
C–C	(32–33, 37–38, 41–42, 46–47)	1.453
C–C	(33–34, 36–37, 42–43, 45–46)	1.400
C–C	(34–35, 35–36, 43–44, 44–45)	1.457
C–C	(33–34, 36–37, 42–43, 45–46)	1.400
C–C	(34–51, 36–52, 43–56, 45–57)	1.447
C–C	(51–52, 56–57)	1.459
C–C	(32–49, 38–39, 40–41, 47–48)	1.396
C–C	(39–40, 48–49)	1.452
C–C	(39–53, 40–55, 48–58, 49–50)	1.452
C–C	(50–59, 53–54, 54–55, 58–59)	1.452
C–C	(50–51, 52–53, 55–56, 57–58)	1.397
C–C	(54–59)	1.398

sake of comparison, those of C<sub>60</sub> are listed in Table 2 as well. Since the HOMO energies for [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> and C<sub>60</sub> are –5.71 and –5.99 eV, respectively, according to Koopman's theorem, its first ionization potential will be lower than that of C<sub>60</sub>. In fact, the energy of LUMO is sometimes considered as an approximation to the electron affinity. The LUMO energies for [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> and C<sub>60</sub> are –3.65 and –3.22 eV, respectively. Its electron affinity will be higher than that of C<sub>60</sub>.

Table 2  
Some properties of C<sub>58</sub>Si and C<sub>60</sub> determined at the B3LYP/6-31G\* level of theory

Properties	C <sub>58</sub> Si	C <sub>60</sub>
$E_{\text{HOMO}}$ (eV)	–5.71( $B_1$ ) <sup>a</sup>	–5.99( $H_u$ )
$E_{\text{LUMO}}$ (eV)	–3.65( $A_1$ )	–3.22( $T_{1u}$ )
$\Delta E_{\text{L-H}}$ (eV)	2.06	2.77
$E^c$ (a.u.)	–2499.34761	–2286.17343
Electronic state	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>g</sub>
Point group	C <sub>2v</sub>	I <sub>h</sub>
Dipole moment/debye	0.14	0.0
ZPE <sup>d</sup> (kcal/mol)	226.5	237.6

<sup>a</sup> The orbital symmetry of HOMO and LUMO is given in parentheses.

<sup>b</sup>  $\Delta E_{\text{L-H}}$  is the energy gap between HOMO and LUMO.

<sup>c</sup>  $E$  is the total energy of molecule computed at B3LYP/6-31G\* level by using GAUSSIAN 98 program.

<sup>d</sup> ZPE is the zero-point vibrational energy determined at B3LYP/6-31G\* level, and the value were not scaled.

A large HOMO–LUMO gap has long been recognized as being correlated with kinetic and structural stability while a small gap is associated with reactivity [37–39]. The HOMO–LUMO gaps for [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> and C<sub>60</sub> are 2.06 eV and 2.77 eV, respectively. Since the HOMO–LUMO gap of [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> is smaller than that of C<sub>60</sub>, it will be less stable than C<sub>60</sub>.

### 3.2. Electronic properties

Unfortunately, there is no single way in which to derive accurate electron populations at atoms, the different methods lead to different populations. Here we use the Weinhold's natural population analysis (NPA) [40], which is based on the NBO procedure, to gain the net atomic charges of [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub>. Table 3 lists the NPA charges for all the atoms of [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub>. From Table 3, it can be seen that the silicon atom has very large positive net charges, and the carbon atoms linked to the silicon atom have very large negative net charges, but the other carbon atoms have very small net charges. Its dipole moment is very small, which is 0.143 Debye obtained at the B3LYP/6-31G\* level of theory.

In order to gain insight into the properties of the HOMO and LUMO and other MOs near HOMO or LUMO, we plotted the probability density contours of the MOs from HOMO–4 to LUMO+4 at 0.02 e/(a.u.)<sup>3</sup> isodensity surfaces in Fig. 3. From Fig. 3 one extracts that the Si atom is the active site with additional species willing to act as an electron-acceptor partner, not as an electron-donor partner. The evidence collected in Fig. 3 adds a novel contribution to the understanding of bonding feature in Si-doped heterofullerenes with the odd number atoms.

### 3.3. Vibrational frequencies

To verify whether [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> is a real minimum on the potential energy hypersurface, vibrational

Table 3  
Net atomic charges of [5,6]-heterofullerene-C<sub>58</sub>Si-C<sub>2v</sub> obtained using NBO analysis at the B3LYP/6-31G\* level of theory

atoms	$q/e$
Si <sub>1</sub>	1.878
C <sub>(2,5,8,11)</sub>	–0.468
C <sub>(3,4,9,10)</sub>	0.001
C <sub>(6,7,12,13)</sub>	0.017
C <sub>(14,21,23,30)</sub>	–0.023
C <sub>(15,20,24,29)</sub>	0.006
C <sub>(16,19,25,28)</sub>	–0.015
C <sub>(17,18,26,27)</sub>	0.001
C <sub>(22,31)</sub>	0.025
C <sub>(32,41)</sub>	–0.008
C <sub>(33,40,42,49)</sub>	0.003
C <sub>(34,39,43,48)</sub>	0.000
C <sub>(35,38,44,47)</sub>	–0.001
C <sub>(36,37,45,46)</sub>	0.000
C <sub>(50,51,55,56)</sub>	0.001
C <sub>(52,54,57,59)</sub>	0.000
C <sub>(53,58)</sub>	0.003



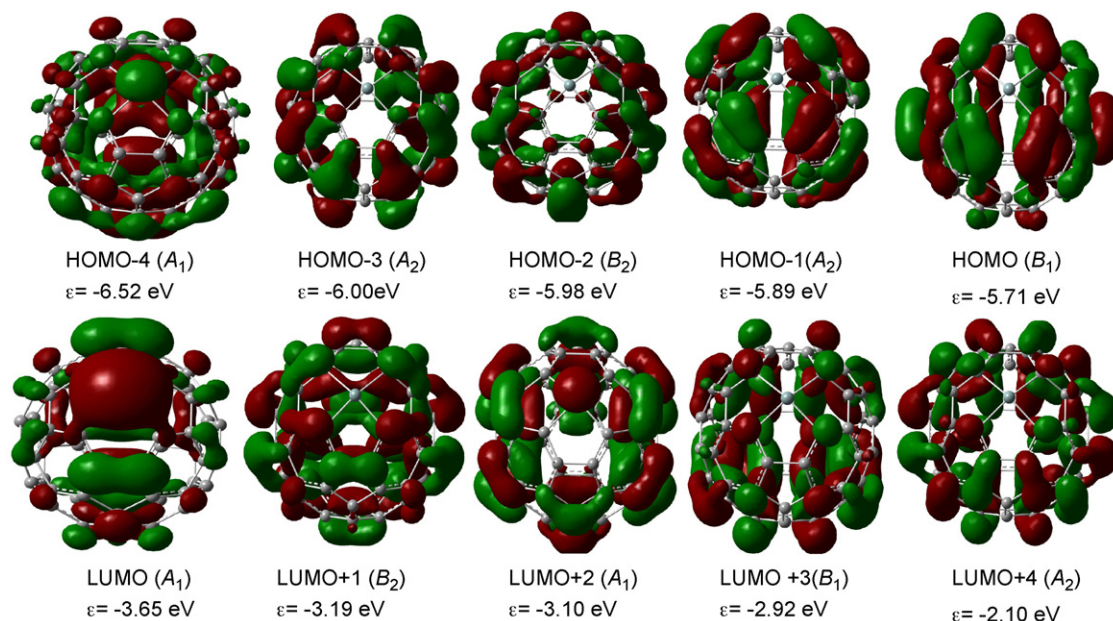


Fig. 3. The HOMO–4 to LUMO+4 molecular orbitals of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ .

frequencies have been calculated at the B3LYP/6-31G\* level of theory. The predicted, unscaled vibrational frequencies are listed in Table 4. The absence of imaginary vibrational frequency confirms that [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  corresponds to a true minimum on the potential energy hypersurface.

Symmetry of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  is helpful in making the assignments of its vibrational frequencies. The reducible representation of vibrational motions of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  is therefore reduced to

$$\Gamma_{\text{vib}} = 45A_1 \left( \frac{\text{IR}}{\text{R}} \right) + 41A_2(\text{R}) + 42B_1 \left( \frac{\text{IR}}{\text{R}} \right) + 43B_2 \left( \frac{\text{IR}}{\text{R}} \right)$$

of which the  $A_1$ ,  $B_1$  and  $B_2$  are infrared active, and all  $A_2$  normal modes are infrared forbidden by symmetry and their infrared intensities are all zero. All normal modes are Raman active.

As is well known, quantum-chemical methods tend to overestimate the values of vibrational frequencies. According to the average scaling factors given in Ref. [41], we scaled all vibrational frequencies in Table 4 and used them to simulate the IR spectrum of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ , see Fig. 4. The simulated IR spectra could be used as evidence to identify the [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ .

### 3.4. Magnetic shielding tensors

For future experimental identification of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  by NMR, its magnetic shielding tensors  $\sigma$  were calculated by using the gauge-including-atomic-orbital method and the continuous set of gauge transformation procedure [34], which is implemented in GAUSSIAN 98 program [33]. In high resolution NMR, the isotropic part  $\sigma_{\text{iso}}$  of  $\sigma$  is measured by taking the average of  $\sigma$  with respect to the orientation to the magnetic field, i.e.,  $\sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ , where  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and

$\sigma_{zz}$  are the principal axis values of  $\sigma$ . The results calculated by using B3LYP hybrid DFT are summarized in Table 5. For comparison, the isotropic part  $\sigma_{\text{iso}}$  of  $^{13}\text{C}$  in the reference tetramethylsilane (TMS) also listed in Table 5.

Table 4

Vibrational frequencies<sup>a</sup> and infrared (IR) intensities of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  calculated at the B3LYP/6-31G\* level of theory

$A_1$	252.0(1.0) <sup>b</sup> , 256.8(0.4), 329.9(1.8), 343.0(0.9), 397.3(0.0), 418.7(9.8), 440.6(0.0), 461.8(1.0), 490.3(1.3), 517.9(9.7), 540.6(14.5), 557.4(4.9), 566.7(1.0), 645.5(12.4), 681.0(0.9), 715.6(1.1), 720.1(0.6), 736.8(1.4), 741.7(0.5), 754.3(1.4), 758.1(0.0), 765.5(0.3), 777.0(0.4), 944.3(6.4), 955.4(0.0), 1076.5(2.1), 1102.6(0.0), 1113.6(0.0), 1194.5(4.0), 1200.0(0.9), 1222.7(1.2), 1272.6(0.0), 1295.8(6.5), 1319.0(1.7), 1337.3(2.8), 1371.2(0.4), 1414.1(0.0), 1453.4(4.4), 1462.4(0.2), 1488.0(0.8), 1499.8(25.0), 1547.0(0.2), 1581.3(0.0), 1607.2(4.6), 1614.5(6.3)
$A_2$	173.3, 272.6, 371.4, 382.8, 413.2, 439.6, 506.1, 532.0, 554.0, 565.4, 583.0, 668.9, 679.0, 699.7, 728.9, 736.8, 746.3, 753.2, 759.0, 765.2, 784.3, 796.3, 859.1, 968.6, 987.3, 1090.9, 1147.3, 1231.6, 1254.4, 1284.3, 1307.6, 1334.4, 1345.0, 1369.3, 1379.6, 1404.8, 1443.7, 1524.0, 1569.9, 1592.2, 1608.2
$B_1$	257.4(0.2), 328.2(0.4), 343.2(0.1), 384.4(3.3), 428.0(0.1), 467.0(0.2), 499.1(7.1), 532.2(10.1), 547.4(17.9), 564.9(2.0), 571.9(9.0), 594.9(3.4), 628.2(0.2), 683.0(2.5), 708.4(4.7), 719.4(0.0), 743.2(1.6), 748.2(3.7), 755.5(0.2), 765.6(18.5), 788.8(0.0), 818.4(4.6), 880.9(6.5), 974.7(1.9), 1018.2(3.0), 1087.6(0.0), 1152.3(0.0), 1179.2(0.1), 1241.0(6.9), 1256.9(2.1), 1279.7(4.1), 1317.3(6.4), 1334.3(0.6), 1360.3(1.2), 1371.1(5.1), 1405.7(4.8), 1455.8(2.6), 1471.8(12.1), 1521.0(0.3), 1560.4(1.1), 1600.0(0.4), 1608.4(0.5)
$B_2$	265.4(0.4), 335.1(1.1), 349.0(0.1), 388.0(5.9), 424.7(0.0), 466.6(2.2), 514.4(18.9), 533.8(17.3), 539.1(0.4), 568.3(0.1), 583.3(1.3), 593.4(11.7), 635.6(4.1), 702.4(0.0), 714.6(3.6), 724.4(9.7), 739.7(3.2), 746.3(2.4), 752.4(0.1), 762.5(4.6), 772.2(0.1), 797.4(0.4), 823.4(1.7), 875.4(13.0), 984.7(0.0), 1030.5(7.0), 1121.6(2.5), 1141.4(7.1), 1216.4(0.8), 1249.0(1.4), 1254.6(0.5), 1280.8(0.2), 1323.1(1.4), 1332.5(0.5), 1356.4(0.0), 1376.4(0.8), 1423.6(0.1), 1447.8(5.0), 1468.5(2.1), 1547.0(5.8), 1551.1(5.6), 1594.2(0.1), 1607.1(0.5)

<sup>a</sup> The unit of vibrational frequencies is  $\text{cm}^{-1}$ .

<sup>b</sup> The unit of IR intensity is  $\text{km/mol}$  and given in the parentheses. The IR intensities of all inactive modes are all zero, and not given in this table.

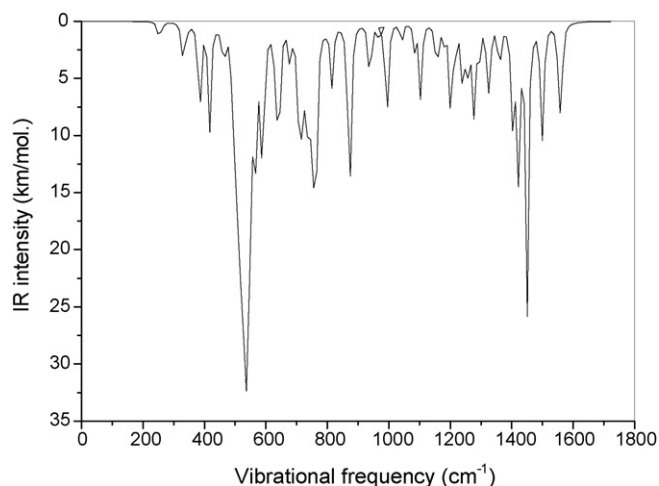


Fig. 4. Simulated IR spectrum of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ .

We find that [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  has sixteen  $^{13}C$  NMR spectral signals, indicative of the 16 unique carbon sites in its structure. The Ref. [42] pointed out the CSGT procedure provides better NMR results than GIAO procedure. So we calculated the  $^{13}C$  NMR chemical shift  $\delta = \sigma_{iso}^{TMS} - \sigma_{iso}^{sample}$  with respect to the reference tetramethylsilane for  $C_{58}Si$  at the B3LYP/6-31G\* level of theory by using the CSGT method, also listed in Table 5.

### 3.5. The stability of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$

What is the stability of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ ? To answer this, the approach calculates the energy change of the

Table 5

B3LYP/6-31G\* calculations of the absolute isotropy,  $\sigma_{iso}$  in ppm (parts per million), of the nuclear magnetic shielding tensor  $\sigma$  for atoms in  $C_{58}Si$  and tetramethylsilane (TMS) found by using both GIAO and CSGT methods

Site number $\{n_i\}$	$\sigma_{iso}$		
	$\sigma_{iso}^a$	$\sigma_{iso}^b$	$\delta$ (ppm) <sup>c</sup>
$^{13}C$ {2, 5, 8, 11}	34.9	33.3	155.3
$^{13}C$ {3, 4, 9, 10}	47.7	42.8	145.8
$^{13}C$ {6, 7, 12, 13}	41.0	35.8	152.8
$^{13}C$ {14, 21, 23, 30}	51.2	45.8	142.8
$^{13}C$ {15, 20, 24, 29}	41.5	37.4	151.2
$^{13}C$ {16, 19, 25, 28}	59.7	54.8	133.8
$^{13}C$ {17, 18, 26, 27}	56.3	51.3	137.3
$^{13}C$ {22, 31}	47.7	43.4	145.2
$^{13}C$ {32, 41}	51.8	47.0	141.6
$^{13}C$ {33, 40, 42, 49}	44.4	39.9	148.7
$^{13}C$ {34, 39, 43, 48}	46.8	42.1	146.5
$^{13}C$ {35, 38, 44, 47}	52.6	47.7	140.9
$^{13}C$ {36, 37, 45, 46}	51.7	46.9	141.7
$^{13}C$ {50, 51, 55, 56}	49.9	45.3	143.3
$^{13}C$ {52, 54, 57, 59}	45.1	40.6	148.0
$^{13}C$ {53, 58}	41.5	37.4	151.2
TMS $^{13}C$	189.8	188.6	

<sup>a</sup> The  $\sigma_{iso}$  obtained at the B3LYP/6-31G\* level of theory by using the GIAO method.

<sup>b</sup> The  $\sigma_{iso}$  obtained at the B3LYP/6-31G\* level of theory by using the CSGT method.

<sup>c</sup>  $\delta = \sigma_{iso}^{TMS} - \sigma_{iso}^{sample}$  is at the B3LYP/6-31G\* level of theory by using the CSGT method and its unit is parts per million (ppm).

Table 6

The data for calculating the heat of formation  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$

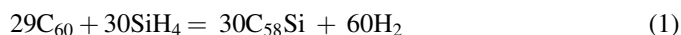
Species	$E^a$ (a.u.)	ZPE <sup>b</sup> (kcal/mol)	$\Delta H_f^0$ (kcal/mol) <sup>c</sup>
$C_{60}$	-2286.17343	237.6	609.6
$C_{58}Si$	-2499.34761	226.5	
$SiH_4$	-291.88369	19.6	8.2
$H_2$	-1.17548	6.4	0.0
Si	-289.37173	0.0	108.4

<sup>a</sup>  $E$  is the total energy obtained at the B3LYP/6-31G\* level of theory.

<sup>b</sup> ZPE is the zero-point vibrational energy obtained at the B3LYP/6-31G\* level of theory, too.

<sup>c</sup> The experimental  $\Delta H_f^0$  of  $C_{60}$ ,  $SiH_4$  and Si was taken from Refs. [43–45].

homodesmic reaction (1) in  $\Delta H_r$  from the sum of electronic and zero-point vibrational energy computed at the B3LYP/6-31G\* level of theory,



The energy change  $\Delta H_r$  of the homodesmic reaction (1) and the experimental heats of formation  $\Delta H_f^0$  of  $C_{60}$ ,  $SiH_4$  and  $H_2$  lead to  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ . The data used to calculate  $\Delta H_r$  of Eq. (1) and  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  are listed in Table 6.

The energy change  $\Delta H_r$  of the homodesmic reaction (1) was calculated as follows:

$$\begin{aligned} \Delta H_r &= 30(E + ZPE)_{C_{58}Si} + 60(E + ZPE)_{H_2} \\ &\quad - 30(E + ZPE)_{SiH_4} - 29(E + ZPE)_{C_{60}} \\ &= 2573.4 \text{ (kcal/mol)} \end{aligned}$$

Using the  $\Delta H_r$  of the homodesmic reaction (1) and heats of formation of  $C_{60}$ ,  $SiH_4$  and  $H_2$  in Table 6, the  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  can be estimated by

$$\begin{aligned} \Delta H_{f,C_{58}Si}^0 &= \frac{29\Delta H_{f,C_{60}}^0 + 30\Delta H_{f,SiH_4}^0 + \Delta H_r - 60\Delta H_{f,H_2}^0}{30} \\ &= 683.3 \text{ (kcal/mol)} \end{aligned} \quad (2)$$

The  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$  is 683.3 kcal/mol.

We also used the Eq. (3) to estimated the  $\Delta H_f^0$  of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ , and the  $\Delta H_f^0$  is 689.3 kcal/mol, which coincides with the result of the homodesmic reaction (1).



## 4. Summary

In summary, we have performed DFT calculations of bonding, natural population analysis, vibrational frequencies, IR intensities, magnetic shielding tensors, and heats of formation of [5,6]-heterofullerene- $C_{58}Si-C_{2v}$ . The absence of imaginary vibrational frequency confirms that the molecule corresponds to a true minimum on the potential energy hypersurface. It has 130 IR-active independent vibrational modes and 171 Raman-active independent vibrational modes,

respectively. All IR- and Raman-active vibrational frequencies are assigned. Sixteen  $^{13}\text{C}$  NMR spectral lines for the molecule are characterized. Its heat of formation is estimated. Comparing the stability of [5,6]-heterofullerene- $\text{C}_{58}\text{Si-C}_{2v}$  with that of  $\text{C}_{60}$ , only from the thermodynamic point of view, it is less stable than  $\text{C}_{60}$ .

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