

# Structural, electronic and vibrational study of the endohedral fullerene SiH<sub>4</sub>@C<sub>60</sub> - Ab initio study

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We have done ab initio study of endohedral fullerene C<sub>60</sub>-SiH<sub>4</sub> with help of DFT using 6-31G(d) as the basis set. Firstly we have optimized SiH<sub>4</sub>, C<sub>60</sub> and C<sub>60</sub>-SiH<sub>4</sub>. Secondly, binding energy and HOMO-LUMO gap (band gap) are calculated with optimized geometries. Introduction of SiH<sub>4</sub> into C<sub>60</sub> stabilized the fullerene with transfer of electrons from SiH<sub>4</sub> to C<sub>60</sub>. Harmonic vibrational frequencies of C<sub>60</sub>-SiH<sub>4</sub> are also discussed.

## Introduction

Cislowski found that C<sub>60</sub> cage could act as a polarizable sphere that stabilizes the polar molecules and destabilizes the non-polar (or weakly polar) ones. These results indicate that formation of the endohedral complexes, from nonpolar or slightly polar molecules such as H<sub>2</sub>, N<sub>2</sub> and CO separated molecules is an endothermic process. The C<sub>60</sub> can stabilize molecules such as HF and LiH, encased inside its skeleton [1]. The subject of fullerene molecule C<sub>60</sub> has attracted immense interest and attention due to its fascinating chemical and physical properties [2–5]. Turker and Erkok studied the possible structure and stability of n H<sub>2</sub>@C<sub>60</sub> where n represents the number of H<sub>2</sub> molecules encapsulated in C<sub>60</sub>. Their calculations at the level of AM1 (RHF) level show that the structures of n H<sub>2</sub>@C<sub>60</sub> (n: 9, 12, 15, 19, 21, 24) are stable but highly endothermic [6]. One of the most important challenges for today's medicinal chemistry seems to be development of effective transporter of drug molecules on the whole their pathway to the therapeutic target. Taking into account

the desirable structural properties one expects that just fullerenes may be effective transporter of many drugs. Drug placed inside fullerene cage could be isolated from external environment and due to that protected from inactivation during transport.

As our ongoing research [7-10], here in this paper, our major interest is to study the structure, electronic property, and infrared spectroscopy of endohedral fullerene SiH<sub>4</sub>@C<sub>60</sub>, and predict whether the endohedral fullerene can stably exist. We hope that SiH<sub>4</sub>@C<sub>60</sub> species is sufficiently stable, and our results may provide a reference for further experimental analysis.

## Computational methods

All the DFT calculations were performed with the parallel version of the Gaussian 09 software package [11]. Considering the high computational costs and accuracy, the 6-31G(d) basis set [12] containing one polarization function on each C and H atoms was utilized here.

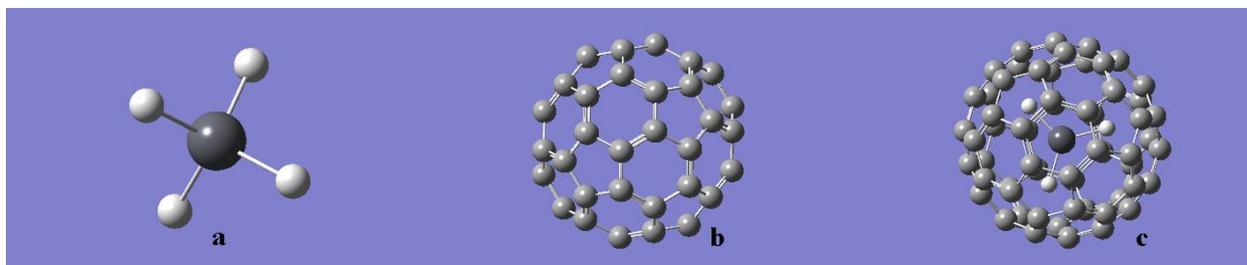


Fig.1 Optimized equilibrium geometries: (a) T<sub>d</sub> SiH<sub>4</sub>, (b) I<sub>h</sub> C<sub>60</sub>, and (c) C<sub>2</sub> axis view of SiH<sub>4</sub>@C<sub>60</sub>

## Results and discussion

### Optimized equilibrium parameters

The optimized equilibrium geometries of T<sub>d</sub> SiH<sub>4</sub>, C<sub>60</sub> and SiH<sub>4</sub>@C<sub>60</sub> are shown in Fig. 1. Their equilibrium parameters are listed in Table 1. Our results show that the equilibrium Si–H bond length is 1.50 Å in the T<sub>d</sub> SiH<sub>4</sub> molecule, which is in excellent agreement with the other theoretical values (1.536 Å) [13] and

the stretching frequency of SiH<sub>4</sub> is 2190 cm<sup>-1</sup>, which is not too far from the other theoretical values ( 2089 cm<sup>-1</sup>) given in literature [13]. For I<sub>h</sub> C<sub>60</sub> fullerene,

The optimized equilibrium C–C bond length is 1.449 Å for pentagon–hexagon edge and 1.393 Å for hexagon–hexagon edge. These values are almost the same as the experimental value 1.455 Å and 1.391 Å [14]. It is indicated that our calculations are reliable and accurate, and this level of theory will provide reliable data for this system. Additionally, the equilibrium X (center)–C

bond length of  $C_{60}$  is 3.541 Å obtained by this method.

For endohedral fullerene  $SiH_4@C_{60}$ , it is obtained that its ground-state structure has  $C_2$  symmetry. The energy minimum is found by full geometry optimization without symmetry limitation at the DFT/6-31 G (d) level of theory. As seen from Table 1, the equilibrium Si–H bond length is shorter when the  $SiH_4$  molecule is placed inside a fullerene cage than when it is isolated molecule by 0.08 Å, approximately. The shortened Si–H bond length in  $SiH_4@C_{60}$  suggest that the central  $SiH_4$  molecule is more compact and the  $C_{60}$  cage may stabilize the highly symmetric Td  $SiH_4$  molecule, which is consistent with the previous study [15]. The H–Si–H bond angles (109.46-109.47) shows that  $PbH_4$  remains keep sp<sup>3</sup> hybridized Si atoms in the endohedral fullerene. Compared with the equilibrium C–C bond length of the  $C_{60}$  cage, the C–C bond lengths of  $SiH_4@C_{60}$  are a little change by 0.01 and 0.02 Å, respectively. All these changes of the bond lengths and bond angles thus lead to symmetry-reducing distortion of the cage. In the endohedral fullerene, the distance from the center to the cage is obviously changed. It is shown that the cage may be elongated and become slightly thinner. Additionally, the distances between C atom in  $C_{60}$  and H atom in  $SiH_4$  are 2.342-3.729 Å, implying that the encapsulated Td  $SiH_4$  only exists in molecular form inside the fullerene and not absorb to the internal surface of the fullerene.

### 25 Stabilities and electronic properties

The relative stability of endohedral fullerene can be reflected from the inclusion energy ( $E_{inclu}$ ). The inclusion energy can be calculated according to the following reaction:

$$E_{inclu} = E(SiH_4@C_{60}) - E(SiH_4) - E(C_{60})$$

$E$  represents the total energies of the ground-state  $SiH_4$ ,  $C_{60}$  and  $SiH_4@C_{60}$ , respectively.

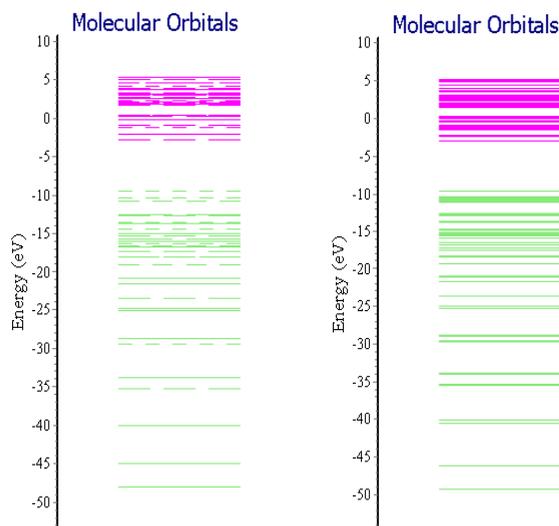
Our calculated results show that the formation of  $SiH_4@C_{60}$  from the free  $C_{60}$  and Td  $SiH_4$  is endothermic with inclusion energy of 44.16 kcal/mol. It is suggested that  $SiH_4@C_{60}$  may exist as stable species. Now we discuss the electronic structure of  $C_{60}$  and  $SiH_4@C_{60}$ . Their electronic energy levels obtained by DFT/6-31 G (d) level of theory are shown in Fig. 2. For  $C_{60}$ , the calculated HOMO–LUMO energy gap corresponds to 6.59 eV is in good agreement with the value given in literature [16] (listed in Table 2). For the endohedral fullerene  $SiH_4@C_{60}$ , the HOMOs are lowered by 0.13 eV and LUMOs are also lowered by 0.27 eV. Its energy gap between HOMO and LUMO is 6.45 eV. It is in good agreement with the value of the  $C_{60}$  cage. A large HOMO–LUMO gap can be associated with high-kinetic stability because it is energetically unfavorable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO and so to form the activated complexes of any potential reaction [17]. Thus, the endohedral fullerene  $SiH_4@C_{60}$  is predicted to be very kinetic stable species. To further understand the HOMO and LUMO properties, we have plotted the HOMO-LUMO pictures of the complexes shown in Fig. 3. It is seen that the electron distributions of HOMO and LUMO are associated with the carbon cage other than the  $SiH_4$  site. It is indicated that that the energy gap between HOMO and LUMO has close relations with the interaction of the carbon cage.

**Table 1.** Optimized equilibrium parameters of  $SiH_4@C_{60}$ ,  $C_{60}$ , and  $SiH_4$ .

Molecule	Parameter	DFT/6-31 G (d)
$SiH_4$	Si–H	1.500
	H–Si–H	109.47
	Stretching frequency	2190
$C_{60}$	Pentagon–hexagon edge	1.449
	Hexagon–hexagon edge	1.393
	X(center of $C_{60}$ )–C( $C_{60}$ )	3.541
$C_{60}\text{-}SiH_4$	Si–H	1.425
	Pentagon–hexagon edge	1.466-1.469
	Hexagon–hexagon edge	1.388-1.467
	Si( $SiH_4$ )–C( $C_{60}$ )	3.559-3.582
	H( $SiH_4$ )–C( $C_{60}$ )	2.342-3.729
	H–Si–H	109.46-109.47

**Table 2.** The calculated energies of  $SiH_4@C_{60}$ ,  $C_{60}$ , and  $SiH_4$ .

Molecule	Symmetry	$E_{HOMO}$	$E_{LUMO}$	$E_{Gap}$
$SiH_4$	$T_d$	-9.71 eV	1.63 eV	11.35 eV
$C_{60}$	$I_h$	-9.47 eV	-2.88 eV	6.59 eV
$C_{60}\text{-}SiH_4$	$C_2$	-9.60 eV	-3.15 eV	-6.45 eV



**Fig 2.** Electronic energy levels of  $C_{60}$  and  $C_{60}\text{-}SiH_4$  obtained with the DFT/6-31 G (d) method, solid and dashed lines refer to the occupied and unoccupied states, respectively.

## Infrared spectra

To verify whether the endohedral fullerene  $\text{SiH}_4@C_{60}$  is a real minimum on the potential energy surface, the harmonic vibrational frequencies have been calculated with the DFT/6-31 G (d) method. Our predicted calculation finds that there are 5 infrared active modes in the  $\text{SiH}_4@C_{60}$ . The harmonic vibrational frequencies and intensities of these modes are 588 (6), 1386 (11), 1704 (2), 1726 (34), and 2543(1); IR intensities (in km/mol) of active modes are in parenthesis. The stronger IR spectroscopic signal with IR intensity of 34 km/mol is determined at the frequency 1726  $\text{cm}^{-1}$ .

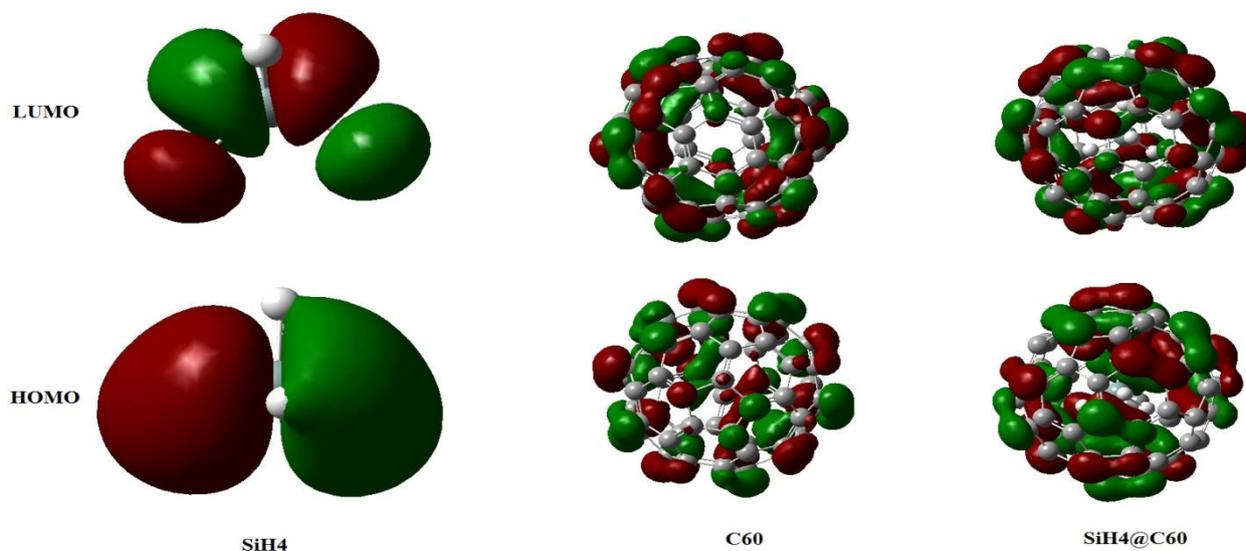


Fig. 3. HOMO-LUMO pictures of  $\text{SiH}_4$ ,  $C_{60}$ , and  $\text{SiH}_4@C_{60}$

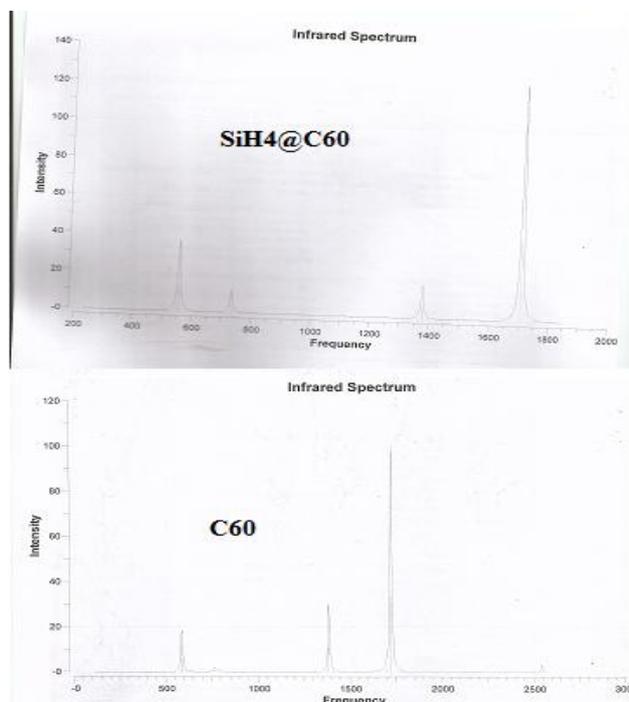


Fig. 4. Calculated IR spectra of  $\text{SiH}_4@C_{60}$  and  $C_{60}$

The calculated IR spectrum of  $\text{SiH}_4@C_{60}$  is shown in Fig. 4. For comparison, the IR spectrum of  $C_{60}$  cage obtained at the same level of theory is also given in fig 4. As can be seen from Fig. 4, the main absorption peaks of  $\text{SiH}_4@C_{60}$  appear to be quite similar in general shapes with those of  $C_{60}$  cage. However, the IR intensities of the endohedral fullerene are slightly stronger than those of  $C_{60}$  cage. To our knowledge, there are no experimental or theoretical data regarding these properties for this system. Our results may thus provide a suitable path for further study.

## Conclusion

We have studied the structure, electronic property and infrared spectroscopy of endohedral fullerene  $\text{SiH}_4@C_{60}$  using the density functional theory. It is found that  $\text{SiH}_4$  molecule is more compact when it is placed inside a fullerene cage than when it is isolated molecules, and the  $C_{60}$  cage may stabilize the high Td  $\text{SiH}_4$  molecule. The formation of  $\text{SiH}_4@C_{60}$  from the free  $C_{60}$  and Td  $\text{SiH}_4$  is endothermic with inclusion energy of 44.16 kcal/mol. The energy gap of  $\text{SiH}_4@C_{60}$  is very close to the values of  $C_{60}$  cage. Therefore, it is confirmed that the  $\text{SiH}_4@C_{60}$  seems to be the kinetic stable species. Additionally, there are 5 infrared active modes in the  $\text{SiH}_4@C_{60}$ , and its main absorption peaks appear to be quite similar in general shapes with those of  $C_{60}$  cage. However, its IR intensities are weaker than those of  $C_{60}$ . These calculated properties of the endohedral fullerene may provide a reference for further experimental analysis.

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## Notes and References

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