Electronic structure and interaction in CH₄@C₆₀: a first-principle investigation

Ang Jia¹ · He Huang² · Zhong-fu Zuo² · Yong-jin Peng²

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Abstract
CH₄@C₆₀ was the first example within which an organic molecule has been embedded in C₆₀. CH₄ can rotate freely in the molecular cage, and the carbon skeleton structure of the C₆₀ has no obvious deformation. The electronic structure of CH₄@C₆₀ and interaction between C₆₀ and CH₄ were studied under quantum mechanical calculation method. The different reaction sites on C–C bonds in C₆₀ and the weak Van der Waals interaction between CH₄ and C₆₀ were shown clearly. These results and the orbital interaction between CH₄ and C₆₀ were helpful for understanding and further application of this unique biggest organic molecule CH₄ contained in C₆₀ structure so far.

Keywords C₆₀ · Electronic structure · Interaction · First principle

Introduction
C₆₀ is a carbon allotrope consisting of 60 C atoms in the shape of a soccer ball. Since C₆₀ has a hollow molecular cavity, it is also envisaged to use C₆₀ as a molecular cage and embed other small molecules in C₆₀. In theory, this process is simple: specific chemical means are used to cut the C–C bonds of several consecutive five-membered carbon rings and six-membered carbon rings on one side of the C₆₀, open a gap, introduce small molecules, and finally close the rings one by one by the same chemical method to suture the sphere.

In the past, small inorganic molecules such as H₂, H₂O, and HF have been embedded into C₆₀ [1–19]. In order to plug larger molecules into the C₆₀, a larger gap has to be opened on its surface. However, over opening prevents further stitching of the C₆₀, thus limiting the size of the embedded molecules.

Professor Richard J. Whitby’s team opened a large gap on one side of a C₆₀ molecule, a 17-carylic ring containing an S atom, and then tucked the CH₄ into the cavity of C₆₀ at high pressure [20]. The next step was the key suturing step, in which the sulfide in the gap was partially oxidized to sulfoxide, and desulfonylation occurred under photoinitation to complete the first closing, and then, the structure of C₆₀ was reduced by mature cyclization and aromatization processes. With the shielding of C₆₀, the quantum properties of C atom in a single CH₄ molecule can be studied in this structure.

The stability and interaction in the structure of encapsulation of small molecules into fullerene nanocages have been studied by some previous theoretical work [3, 6, 16, 21–24], whereas the CH₄@C₆₀ structure was probed using some new quantum mechanical calculation methods in this work and the interaction between C₆₀ and CH₄ was shown more clearly.

Methods
The wB97X-D3 [25] and M06-2x [26] exchange–correlation functional conjunction with def2-TZVP basis set [27] in vacuum were employed for geometric structure optimization and electronic structure calculation within the ORCA 4.2.1 code [28]. This combination of functional and basis set was shown to be reliable especially for the quantum mechanical calculation of carbon materials [29]. All analyses were finished by using the Multiwfn 3.7 code [30] and some isosurface maps were rendered by means of the VMD 1.9.3 software [31].
The most stable optimized geometric structure of CH$_4@C_{60}$ was obtained with the lowest energy and the number of the imaginary frequency of vibration was checked to be zero.

Results and discussion

From the isosurface map of electron density in Fig. 1a, the symmetrical distribution of electron in CH$_4@C_{60}$ was clearly shown. The electron density along the C–C bonds shared by one five-membered and one six-membered carbon ring ([5,6] bond, labeled by 1 in Fig. 1) was smaller than C–C bonds shared by two six-membered carbon rings ([6,6] bond, labeled by 2 in Fig. 1). This character was also clearly shown in isosurface map of gradient norm (Fig. 1b) and laplacian (Fig. 1c) of electron density.

The value of the laplacian function was defined as the trace of the electron density Hessian matrix at a point, which was the result of the Laplace operator applied to the electron density. The positive value of laplacian function means that the electron density was mainly divergent; otherwise, the negative value mean that aggregation of electron density was dominant. In the isosurface map of laplacian of electron density of CH$_4@C_{60}$ (Fig. 1c), the positive value was indicated by green color and the purple color was used to indicate negative value. It can be clearly seen that the positive laplacian value at the center of carbon and the negative laplacian value along the C–C bonds and the center of hydrogen atom which indicated the flow direction of the electron in this molecule. The symmetrical distribution of electron density and the difference between the [5,6] and [6,6] bonds were also clearly shown in isosurface map of laplacian of electron density (Fig. 1c).

To illustrate the interaction between CH$_4$ and the C$_{60}$ in detail, the $\delta g$ [32] function of interaction area in the molecule was obtained through the multi wavefunction analysis software Multiwfns 3.7 and shown in Fig. 2. It can be clearly shown that only the weak Van der Waals interaction of C–H...π exist between the CH$_4$ and C$_{60}$ which was same as the results of experiments before [20].

The distribution of molecular orbital of CH$_4@C_{60}$ was illustrated by density of states (DOS) map in Fig. 3. The DOS curve reflected the number of molecular orbitals in unit energy interval at corresponding energy. The total DOS (TDOS) of CH$_4@C_{60}$ and the partial DOS (PDOS) of maps contributed by C$_{60}$ and CH$_4$ respectively were simultaneously shown in Fig. 3. Meanwhile, isosurface maps of three molecular orbitals (orb92, HOMO, LUMO) with energy at about $-22.42$ eV, $-8.10$ eV, and $-2.12$ eV respectively at the current wb97XD3/def2-TZVP level were also drawn in the figure for comparison. It can be seen from Fig. 3 that the HOMO and LUMO of the CH$_4@C_{60}$ molecule were almost solely contributed by the C$_{60}$ structure yet without the admixture of CH$_4$ part. Within the occupied orbitals,

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Fig. 1 CH$_4@C_{60}$ isosurface maps of a electron density, value = 0.25; b gradient norm of electron density, value = 0.25; c laplacian of electron density, value = ±0.7

Fig. 2 $\delta g$ function of interaction area in CH$_4@C_{60}$

Fig. 3 DOS curve of CH$_4@C_{60}$
there were only several molecular orbitals with energy about $-23 \text{ eV}$, $-16 \text{ eV}$, and $-13 \text{ eV}$ in which the CH$_4$ component made the contribution. This conclusion can also be deduced by the isosurface maps of molecular orbitals in Fig. 3.

The charge decomposition analysis (CDA) method was a valuable tool to analyze quantitatively the interactions between two molecular fragments in terms of the linear combination of the donor and acceptor fragment orbitals’ donation and polarization using quantum mechanical calculations [33]. Within the CH$_4$@C$_{60}$ molecule, the C$_{60}$ and CH$_4$ were defined as two fragments to be analyzed using CDA method. According to the results of CDA analysis, the orbital interaction between two fragments of C$_{60}$ and CH$_4$ was illustrated in Fig. 4. The solid and dashed horizontal bar in Fig. 4 indicated the occupied and unoccupied molecular orbital respectively. The CH$_4$@C$_{60}$ molecular orbital was connected by red line with the fragments’ orbital which contributed more than 10% in that molecular orbital. It can be also seen in Fig. 4 that mostly the CH$_4$@C$_{60}$ molecular orbitals including HOMO and LUMO were contributed by the C$_{60}$ structure. The CH$_4$ part just played a role in few occupied and unoccupied CH$_4$@C$_{60}$ molecular orbitals which agreed with the conclusion from Fig. 3 mentioned before and the non-covalent interaction concept which was discussed in the reference [34, 35] based on the Hellmann–Feynman theorem.

Fukui function and related dual descriptors were very popular methods defined under the framework of conceptual density functional theory for predicting reaction sites. Fukui functions and related dual descriptors were fine for most systems. However, for some systems which had higher order point group symmetry (tended to degenerate the front-line molecular orbitals), the Fukui function and the dual descriptor may give meaningless results, such as the distribution of the function did not satisfy the symmetry of the system, and therefore obviously violated the basic chemical intuition. Ricardo et al. put forward the concept of orbital-weighted Fukui function and dual descriptor of orbital...
weighted [36, 37]. Compared with the general form of Fukui function and double descriptors, the orbital-weighted form had the advantage that it can be reasonably applied to the system of line orbital (quasi) degeneration.

Here the orbital-weighted double descriptors of CH$_4$@C$_{60}$ obtained from Multiwfn were illustrated in Fig. 5 to present the reaction sites of the molecule. The negative value of orbital-weighted double descriptors on [6,6] bond (purple) indicated it was most easily electrophilic attacked. Otherwise, the positive value of orbital-weighted double descriptors on [5,6] bond (green) indicated it was most easily nucleophilic attacked. This result was similar as the former study on C$_{60}$ and reflected the weak interaction between CH$_4$ and C$_{60}$. To further understand the vibrational properties of CH$_4$@C$_{60}$, the IR spectrum was calculated and displayed in Fig. 6. The red arrows in Fig. 6 which indicated the vibration modes at different wavenumbers showed the most vibration modes were almost contributed by C$_{60}$ part and the negligible interaction between C$_{60}$ and CH$_4$ at this energy level.

**Conclusions**

In summary, the electronic structure and interaction between fragments inside the CH$_4$@C$_{60}$ molecule were studied using quantum chemical method based on density functional theory. The different reaction sites on [5,6] and [6,6] bonds and the weak Van der Waals interaction between CH$_4$ and C$_{60}$ were shown clearly. The calculated IR spectrum indicated the negligible interaction between C$_{60}$ and CH$_4$ at the vibrational energy level. These results and the orbital interaction between CH$_4$ and C$_{60}$ were helpful for understanding and
further application of this unique biggest organic molecule CH₄ contained in C₆₀ structure so far.

Author contribution Ang Jia performed the calculation; He Huang and Zhong-fu Zuo performed the data analysis; Yong-jin Peng designed and analyzed the data.

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Data availability All the data can be shared in the supporting information online.

Code availability The software ORCA and VMD used in this work can be downloaded freely.

Declarations

Competing interests The authors declare no competing interests.

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