Energetics and Electronic Properties of a Neutral Diuranium Molecule Encapsulated in C\textsubscript{90} Fullerene

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Abstract

Scientists have found that the size of the cavity of endohedral metallofullerenes (EMFs) can influence the properties of the inner molecule. In this work, the neutral diuranium molecule was encapsulated into the C\textsubscript{90} fullerene. The neutral U-U dissociation potential energy surfaces of different electronic states confined in the C\textsubscript{90} fullerene were scanned and the quintuple and the septuplet of these states were found to be low-lying. In the fullerene cage, the U\textsubscript{2} molecule easily disintegrates along the axis of the fullerene, and then is chemically adsorbed on the both ends of the fullerene. The charge distribution and the molecular orbit properties of the complex were also uncovered.

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1. Introduction

Carbon cage fullerenes \cite{1,2} can encapsulate various metal atoms or metal clusters and form a kind of the compounds with special structures and properties. They are usually called endohedral metallofullerenes (EMFs)

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Due to their intermolecular electron transfer, the inner metal atoms or/and the outer cage preferentially adopt stable closed-shell electronic configurations [5-7]. Electrochemical study shows that the carbon cage of EMFs will become more active after receiving the electron from the inner metal atoms. Compared with hollow fullerenes (mainly the C_{60}), EMFs have stronger ability to capture and donate electrons, i.e., it is more easily to be oxidized or restored [8].

Actinide elements and their compounds play an important role in nuclear science. The properties of dimetalloendofullerene containing actinide atoms in the cages are very important. In the previous studies researchers found that the size of the fullerene cage cavity can obviously influence the properties of the inner U_2 molecule, such as U_2@C_{60} [9]. The two U atoms have been confined in the center of the C_{60} cage by an unprecedented six fold metal-metal bond [10]. Thus the highly symmetrical U_2@C_{60} structure has been formed with 7A_{2u} ground electronic state. On the contrary, inside C_{70} or C_{84} fullerenes the two U atoms will preferentially bond with the inner wall of the cage [9]. Therefore, if we amplified the size of the cavity, the U_2 molecule would disintegrate and chemically be adsorbed on the inner wall.

In this work, we encapsulated the neutral diuranium molecule into the C_{90} fullerene. The C_{90} has the same size as C_{60} in vertical direction and provides the two uranium atoms with one-dimensional freedom along the tubular axis. We scanned the neutral U-U dissociation potential energy surfaces along the tubular axis to analyse the disintegrate process. And we also analyzed the charge distribution and the molecular orbit bonding properties of every lowest energy structures.

2. Theoretical Methods

Because the unsaturated d and f orbital have significant contribution in bonding, in the system containing actinides, the discrete 5f orbital makes the bonding mode more complicated. Therefore, relativistic effects and strong electron correlations must be taken into account in the calculations of this kind of system. The density functional theory (DFT) has been shown capable to give good results in the research of light element systems. This theory has a significant advantage that it can take electron correlations into account but not obviously increase the computation costs. DFT methods are also widely used in actinides calculations [11-14]. The relativistic pseudopotential basis set is able to take relativistic effects into account with little computation demand [15-17]. The size of pseudopotential core area can influence the analysis of uranium chemistry, as was reported already [18, 19].

In this paper, we adopted Perdew, Burke and Ernzerhof (PBE) method of the DFT for all the calculations. Previous studies showed that the PBE method gives results in good agreement with the CASSCF/CSAPT2 results in term of processing encapsulation energy and predicts the correct bonding of EMFs containing uranium atoms [9, 10]. As the 5f orbital of actinide elements are discrete and take part in bonding, the 5f orbital can not be frozen as core rails [20]. The Stuttgart large-core relativistic effective core potentials (RECPs) basis set with 5f to 7s orbitals treated as valence orbitals (78 core electrons on uranium) was used for the two uranium atoms. In fact, using the large-core RECPs has lower accuracy than the small-core RECPs (60 core electrons on uranium) on the calculation of uranium complex [19]. However, it is highly resource-demanding and time-consuming even if we use the large-core RECPs. In order to study the properties of the U_2@C_{90} system qualitatively, we remain choosing the large-core RECPs. The 3-21g basis set was used for the carbon atoms. The computations of U_2@C_{90} were performed using the Gaussian 03 program [21].

3. Results and Discussion

Using the method and basis set described above, we optimized the geometric structure of different electronic states of the neutral U_2 molecule, and the ground state of U_2 molecule is still septet. The bond distance is 2.48Å,
in good agreement with the result predicted by CASSCF/CASPT2 method (2.43 Å) [22], and it is more accurate than that predicted by PBE/DNP method (2.52 Å) [10].

When putting the neutral U$_2$ molecule into the center of the C$_{90}$ cage and then optimizing the geometric structure, we found that the U$_2$ molecule can easily disintegrate along the axis of the fullerene and finally be chemically adsorbed on the both ends of the fullerene. This phenomenon can be explained by the fact that the C$_{90}$ has the same size as C$_{60}$ in vertical direction but it is wider in the tubular axis direction. As such, the U$_2$ molecule got the one-dimensional freedom along the tubular axis, and thus can easily disintegrate. We scanned the U-U dissociation potential energy surfaces of different electronic states and found that the quintuple and the septuplet of these states are low-lying. For the lower energy parts of the two states, we scanned more carefully in smaller ranges afterward. We found that the septet total energy of the system reached the lowest point when the distance of the two uranium atoms is closed to 2.55Å (see Figure 1a). We can infer that the U-U metal bond was preventing the two uranium atoms from disintegrating. However in the quintet of U$_2$@C$_{90}$, the total energy is always in decline and there is no potential well in the same distance region (see Figure 1a). So the U$_2$ molecule in the quintet is easier to disintegrate than in the septet, and the quintet is an unstable state. When the distance of the two uranium atoms is closed to 6.125Å, in both the quintet and septet energy curves appears a deep potential well (see Figure 1b), and the septet energy of the whole system is lower. Thus it can be seen that the septet of the U$_2$@C$_{90}$ is the most stable state at the distance of the two uranium atoms close to 6.125Å. Obviously, there is no metal bond between the two uranium atoms, and the uranium atoms bond with the carbon atoms of the cage and chemically be adsorbed on the both ends of the fullerene.

Figure 1 .The potential energy curves of the U$_2$@C$_{90}$ system. The squares indicate the quintet states and the white squares indicate the septet states. (a) The distance of U-U is in 2.55 angstrom nearby. (b) The distance is in 6.125 nearby

Figure 2 .The charge distribution of the U$_2$@C$_{90}$ system in both quintet and septet states (R$_{u-u}$ = 6.125 Å)
With a distance between the two U atoms of 6.125 angstrom, the quintet and the septet of the system have the lowest energy. Charge analysis of the quintet and the septet of the system was conducted and the charge distribution of the system is shown in Fig. 2. It is shown that each U atom transfers 0.495 electrons to fullerenes in septet while 0.542 in quintet, indicating that the U atoms in quintet lost more electrons than in septet. No matter for the quintet or the septet, the positive charge is mainly distributed in the region where U atoms locate, while the two ends and the middle area of fullerenes have more negative charges. There is an obvious change of the charge distribution in the middle area in both the quintet and the septet: there is more negative charge in the septet than in quintet, compared with the middle region, and the adjacent domains have the opposite trend of charge variation. In addition to the fullerene ends, this region carries more negative charges in the septet.

From Figure 3, we can clearly see that for the two low energy structures of the septet and the quintet of U₂@C₉₀ system, the metal bond no longer exists between the two U atoms, and the U atoms are chemically adsorbed at the fullerene ends. When the distance between the two U atoms along the axial direction is about 6.125 Å, both of the septet and quintet are stable chemical adsorption states.

![Figure 3](image-url)

Figure 3. The frontier molecular orbitals of U₂@C₉₀ in the septet (a) and quintet (b) (R_u-u = 6.125 Å).

We further analyzed the molecular orbital properties of the two structures. We found that the orbital whose coefficients are greater than or equal to 0.1 has a major contribution. The molecular orbital distributions of the two electronic states from the U atomic orbitals are illustrated in Table 1.
Table 1. The contributions of the U atomic orbitals to U2@C90 molecular orbitals in both quintet and septet states (R_u−u = 6.125 Å).

<table>
<thead>
<tr>
<th>Molecular orbital</th>
<th>Septet</th>
<th>Quintet</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td>7s,6d,5f</td>
<td>5f</td>
</tr>
<tr>
<td>HOMO</td>
<td>5f</td>
<td>7s,6d,5f</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>5f</td>
<td>5f</td>
</tr>
<tr>
<td>HOMO-2</td>
<td>5f</td>
<td>None</td>
</tr>
<tr>
<td>HOMO-3</td>
<td>None</td>
<td>5f</td>
</tr>
<tr>
<td>HOMO-4</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
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<td>5f</td>
<td>5f</td>
</tr>
<tr>
<td>HOMO-6</td>
<td>5f</td>
<td>None</td>
</tr>
</tbody>
</table>

4. Conclusion

The U2 molecule encapsulated in C90 fullerene is easy to be dissociated, no longer keeping metal-metal bond. When the dissociation distance reaches 6.125 Å, the quintet and the septet achieve the minimum value of the energy, with the latter is even lower. The charge distribution of the quintet and the septet is remarkably different in the center region of the system: for the septet, there is more negative charge in the middle region, compared with its adjacent regions, while the quintet shows an opposite trend. The bonding effect is dominated by the 5f atomic orbital of the uranium mainly while the two U atoms are chemically adsorbed on the fullerene ends.

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