Adsorption and Encapsulation of Hydrogen Sulfide Molecule using C$_{70}$ Fullerene; DFT Study

Sima Alaf Darbandi $^a$, Zabiollah Mahdavifar $^{*b}$

simadarbandi89@gmail.com

$^a$Department of Chemistry, Science and Research Branch, Islamic Azad University, Khuzestan Iran

$^{*b}$Computational Chemistry Laboratory, Chemistry Department, Faculty of Science, Shahid Chamran University, Ahvaz, Iran

Abstract

In this research work, we investigate the adsorption and encapsulation of hydrogen sulfide (H$_2$S) molecule on the inside and outside of the C$_{70}$ fullerene using DFT calculations at the MPW1PW91 level of theory. Results indicate that the adsorption of H$_2$S gas on the surface of C$_{70}$ fullerene is more stable. Furthermore, the relaxed structures of C$_{70}$-nH$_2$S show that the complexes are stable without breaking bond in C$_{70}$. NBO analysis shows that a considerable degree of charge transfer to the fullerene C$_{70}$ through the process of absorption of H$_2$S gas, to change the electronic properties of C$_{70}$ account.

Keywords

C$_{70}$ fullerene, hydrogen sulfide, encapsulation, adsorption, DFT calculation.
Introduction

Hydrogen sulfide gas occurs naturally in petroleum reservoirs of natural gas, volcanic gases and hot springs there. The gas hydrogen sulfide is a colorless, toxic and flammable with a penetrating odor of rotten eggs. This gas prevents through oxid cytochrome in enzyme function prevents absorb oxygen. The serious effects on health of contact with concentrations above leave behind, and even lead to death. In recent years, bio conjugated nanostructures materials including nanotubes, nanowires, fullerenes and nanoparticles have emerged as a new class of materials for environmental and medical diagnostics applications [1]. Fullerenes and enduring feature of the electrophonic reaction which reduces angle strain by changing the carbon hybridization sp² to sp³ hybridization ones. Other atoms can be trapped inside fullerenes to form inclusion compounds known as the fullerenes endohedral. The properties of fullerenes can be used for the removal of environmental contaminants such as H₂S gas [2].

Computational Details

The initial geometries of fullerene C₇₀, H₂S gas and the C₇₀-nH₂S complexes were fully optimized without any restrictions. The generalized gradient approximation (GGA) in form of Perdew-Wang (MPW1PW91) correction is applied for describing the exchange-correlation term [3]. The calculations were performed at MPW1PW91/6-31G(d) level of theory for all atoms. The relaxed structures are presented in Figure 1. In order to understand the gas–fullerene interactions, the adsorption energy (E_{ads}) of the gas onto fullerene is defined as:

\[ E_{ads} = E_{C70-gas} - (E_{C70} + E_{gas}) \]  

where \( E_{C70-gas} \) denotes the total energy of the fullerene-gas systems and \( E_{C70} \) and \( E_{gas} \) are the total energies of the isolated C₇₀, H₂S molecule, respectively. According to the Eq 1, negative adsorption energy indicates that the formed complex is stable and positive adsorption energy belongs to the local minimum where the adsorption of gas molecule onto the fullerene is prevented by a barrier. It should be mentioned that the adsorption energy encompasses both interaction (\( E_{int} \)) and deformation (\( E_{def} \)) energy contributions, which are both occurred during the adsorption process [2]. The following equations are applied to calculate these contributions.
\[ E_{ads} = E_{def} + E_{int} \]  
\[ E_{int} = E_{C70-gas} - (E_{C70 in complex} + E_{gas in complex}) \]  
\[ E_{def} = E_{def gas} + E_{def C70} \]

where \( E_{C70 in complex} / E_{gas in complex} \) is the total energy of tube/gas and \( E_{def C70} / E_{def gas} \) is the deformation energy of gas/tube in its relaxed geometry. The results of the adsorption energy, interaction energy \( (E_{int}) \), deformation energy \( (E_{def}) \), the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, band gap energy and natural charge are calculated for all components. These results are summarized in Tables 1 and 2.

**Results and Discussions**

In this research work, the adsorption of a \( \text{H}_2\text{S} \) molecule and the encapsulation of 2 and 3 \( \text{H}_2\text{S} \) gas molecules inside the fullerene \( \text{C}_{70} \) were investigated. As can be seen in Table 1, a negative energy state to absorb the \( \text{H}_2\text{S} \) has been on the fullerene surface shows that the resulting structure is stable. While attracting positive energy states inside the fullerene molecules are \( \text{H}_2\text{S} \), the structure is unstable. The NBO calculations indicate that the band gap energy decreases in both complexes compared to the pristine \( \text{C}_{70} \). A high band gap signifies greater stability and low reactivity of system. The NBO calculations indicate that the band gap energy decreases in both complexes compared to the pristine nanotube. A high band gap signifies greater stability and low reactivity of system. The decrease of band gap energy in complex III is more than that of complex II, which means that the reactivity of the complex II is less than that complex III.

![Figure 1: Final optimization structures of the adsorption of (a) \( \text{C}_{70}^-\text{H}_2\text{S} \) (Complex I) on the surface (b) \( \text{C}_{70}^-\text{2H}_2\text{S} \) (Complex II) and (c) \( \text{C}_{70}^-\text{3H}_2\text{S} \) (Complex III) inside \( \text{C}_{70} \) molecule.](attachment:image.png)
Table 1: Calculation of the energy optimization ($E_{opt}$) adsorption energy ($E_{ads}$), the interaction energy ($E_{int}$) and deformation energy ($E_{def}$) of complex formation (according to electron volts (eV))

<table>
<thead>
<tr>
<th>Type</th>
<th>$E_{opt}$</th>
<th>$E_{ads}$</th>
<th>$E_{int}$</th>
<th>$E_{def}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex I</td>
<td>-72568.92</td>
<td>-0.0272</td>
<td>-0.022</td>
<td>-0.005</td>
</tr>
<tr>
<td>Complex II</td>
<td>-94301.19</td>
<td>3.420</td>
<td>2.294</td>
<td>1.125</td>
</tr>
<tr>
<td>Complex III</td>
<td>-105161.47</td>
<td>10.900</td>
<td>1.279</td>
<td>9.621</td>
</tr>
</tbody>
</table>

Table 2: HOMO, LUMO and band gap of the C$_{70}$ and C$_{70}$-nH$_2$S complexes.

<table>
<thead>
<tr>
<th>Type</th>
<th>HOMO (eV)</th>
<th>LUMO</th>
<th>Energy Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{70}$</td>
<td>-0.23062</td>
<td>-0.12218</td>
<td>0.10844</td>
</tr>
<tr>
<td>Complex I</td>
<td>-0.23336</td>
<td>-0.12503</td>
<td>0.10833</td>
</tr>
<tr>
<td>Complex II</td>
<td>-0.21833</td>
<td>-0.12472</td>
<td>0.09361</td>
</tr>
<tr>
<td>Complex III</td>
<td>-0.17267</td>
<td>-0.13581</td>
<td>0.03686</td>
</tr>
</tbody>
</table>

Conclusion

In this study, the adsorption and encapsulating of H$_2$S gas inside and outside of the C$_{70}$ molecule are investigated. Obtained data indicate that the H$_2$S molecule can adsorbed into the outer surface of the C$_{70}$ molecule and make more stable complex. Furthermore, by considering the encapsulated of H$_2$S molecules inside of the C$_{70}$, it is observed that C$_{70}$ can encapsulated 3H$_2$S molecules without any breaking bond. In conclusion, the adsorption and encapsulating of H$_2$S using C$_{70}$, we can or more stable form is set to I. H$_2$S gas adsorption on the surface of fullerene C$_{70}$ allows us to conclude that the adsorption on the surface can be an effective way to eliminate environmental pollution H$_2$S.

References style

[1] R. Pandey sensitivity of Boron-Nitride nanotubes toward bimolecular of different polarities,
