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DFT investigation of the encapsulation potential of calix[4]arene towards methane (CH_4).

Ibtissem Meriem ASSABA*, Youghorta BELHOCINE**, Mahamadou Seydou***

*Petrochemical engineering department, Skikda University, Algeria
** Petrochemical engineering department, Skikda University, Algeria
*** UFR de chimie, Paris Diderot, France
E-mail: ibtissem1994assaba@gmail.com, chimieskikda@gmail.com, mahamadou.seydou@univ-paris-diderot.fr

Abstract

As a redoubtable pollutant, there has been a growing interest in finding a practical way for methane (CH_4) adsorption. In this concept the most urgent needs nowadays is to develop new chemical materials for environmental purification able to adsorb pollutants like methane effectively. The aim of this study was to test the effectiveness of calix[4]arene to capture and store CH_4 and to demonstrate their high selectivity toward this gas by computational means. We performed a computational study based on the interaction of CH_4 molecules with calix[4]arene by using the functional B97-3c implemented in ORCA 4.0. We defined first the adsorption energy of the studied molecule on calix[4]arene, the adsorption energy noted E_{ads} was calculated. Based on the results (the value of adsorption energy obtained), calix [4]arene materials shows remarkable CH_4-adsorption selectivity.

Keywords: Adsorption, storage, encapsulation, methane, Calix[4]arenes, DFT, environnement.

1. Introduction

The incredible modern life style, technology, new industrial challenges, economic growth …etc contributed to build a strict relationship with gas emissions, which lead inevitably to environmental degradation. Several studies showed and proved that increasing gas emissions like methane the main component of natural gas fuels directly contributes to climactic instability.

Understanding the impact of economic growth on the environmental quality and responding to the perceived threat is becoming increasingly important. Gas storage in solids is an increasingly important research area with applications in the field of energy, environment, biology and medicine [1]. However from energetic and environmental standpoints the most urgent needs is about finding a cost-effective, harmless and eco-friendly viable way to selectively capture/storage CH_4.

Several different types of porous materials such as carbon materials, zeolites, silica gels, MOFs and polymers have been recently examined in addition to organic crystalline microporous solids and nonporous ones, but no ideal candidates have emerged so far [1]. In this paper, we wish to report on the methane adsorption properties of calix[4]arene.

Calixarenes a group of macrocyclic phenol-formaldehyde condensates [2], having a rigid natural cavity, which can recognize ions and organic molecules [3]. Owing to their potential applications in various areas such as VOCs or other gas detection [4], heavy metal absorption [2], catalysis [2], alkali metal complexation, transport [2] and more recently as active agents in potentiometric sensors [2]; calixarenes have captured and attracted researcher's interest.

In addition, the growing interest in calixarenes materials comes from their easy synthesis, thermal stability, their recognition properties and the use as selective complexation agents in sensors [3]. Particularly, due to their ability to occlude guest molecules in their cavities [4], calixarenes cavities can be synthesized with various size according to the requirements [3].

Herein, we report a theoretical study of the encapsulation potential of calix[4]arene towards methane, and we evaluate the interest of such materials in capturing small molecules, pollutants for environmental purification use.

2. Our approach

The exceptional stability of this organic material encouraged researchers to evaluate the potential application of calix[4]arene as a gas-adsorbent.

In order to test the effectiveness of those materials calix[4]arene to capture methane (CH_4) and to demonstrate their high selectivity toward this gaz. We performed a computer-based study based on the interaction of CH_4 molecules with calix[4]arene by using the functional B97-3c [5] implemented in ORCA 4.0 [6].

2.1. DFT

DFT: Density Functional Theory, as a tool for calculating atomic and molecular properties has strongly influenced the evolution of quantum chemistry during the past 15 years. Based on the famous Hohenberg and Kohn theorems, DFT provided a sound basis for the development of computational strategies for obtaining information about the energetics, structure, and properties of atoms and molecules at much lower costs than traditional techniques. [7]

3. Results and Discussion

We first define the adsorption energy of the studied molecules on calix[4]arene .The adsorption energy noted Eads is calculated with the following equation:

$$\mathbf{E_{ads} = E(_{calix[4]arene\ -\ CH4}) - (E_{\ calix[4]arene} + E_{\ CH4}).}$$

After calculation, the complexation energy obtained is negative and it is around: $\mathbf{E_{ads}}$**=-19.80 kj/mol.**

Based on the result:

- We notice that the calix[4]arene materials shows remarkable CH_4-adsorption selectivity.
- The negative value of energy obtained demonstrate the encapsulation potential of calix[4]arene towards methane.

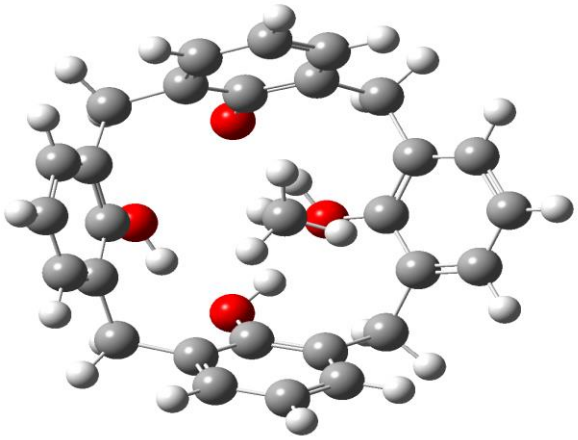

Figure 1. 3-D representation of the optimized structure of calix[4]arene-methane complex.

4. Conclusion

- Our results confirm the interest of calix[4]arene for CH_4 capture and storage.
- Results provide a glimpse into the vast encapsulation potential of calix[4]arene towards small molecules especially pollutants from environmental purification stand point.

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