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Stability of Hydrogen Molecules Confined in Fullerenes [$(H_2)_x@C_y$]

Aicha Bendia – Gustavo Lopez
Bronx community college – Lehman college

Abstract

The thermodynamic properties of various molecular hydrogen inside fullerenes were computed using the path integral formalism. Specifically, the stability of one, two, three and four H_2 molecules inside fullerenes was characterized using alchemical free energy calculation. The interaction between particles was described using Lennard-Jones potential. The fullerenes ranged from 52 to 100 carbons, and the hydrogen molecules were described using 252 beads in the path integral formalism. It was observed that the monomer is stable in all the fullerenes considered. On the other hand, the dimer was stable from C_{70} to C_{100}. However, no stability was observed for trimer and tetramer except $(H_2)_3@C_{94}$. A relation between the stability of the system and the volume/size of the fullerene was established for the monomeric species.

Introduction

During the last few years, scientists have many difficulties studying the interaction of small molecules with fullerene. Particularly, the interaction of species in condensed phase with the external surface of fullerenes has been extensively considered [1]. Additionally, the properties of atoms and molecules entrapped inside fullerenes have been reported [2]. Fullerenes are the third allotropic form of carbon. They are nano-cages that are very stable and easy to synthesize. The purpose of our project is to find a correlation between the stability of the $(H_2)_x@$fullerenes and the structural properties of fullerenes,(i.e. number of carbon atoms, internal area, volume, shape, etc.). Additionally, we want to characterize how effective is to store hydrogen molecules in fullerenes by confining different amounts of hydrogen molecules in various fullerenes and calculating the stability of the $(H_2)_x@$fullerene system. In the previous studies,Turro et al [3] generated $H_2@C_{60}$ and $(H_2)@C_{70}$ and $(H_2)_2@C_{70}$ experimentally. Additional H2 molecules in these fullerenes are not observed. Also Bacic et al [4] used temperature independent techniques to prove that $H_2@C_{60}$ was energetically stable and $(H_2)_2@C_{60}$ was unstable. Moreover, Kruse and Grimme [5] used electronic structure method to show $H_2@C_{60}$ is stable. Cruz and Lopez [6] used temperature dependent simulations to show that $H_2@C_{60}$ is stable and $(H_2)_2@C_{60}$ is unstable. Yakobson et al [7] computationally proposed that it is possible to fit approximately 800 hydrogen molecules in C_{720} because hydrogen is a small molecule. In our study we used path integral replica-exchange Monte Carlo simulations to calculate the thermodynamic stability of monomer, dimer, trimer and tetramer H_2 molecules inside fullerenes.

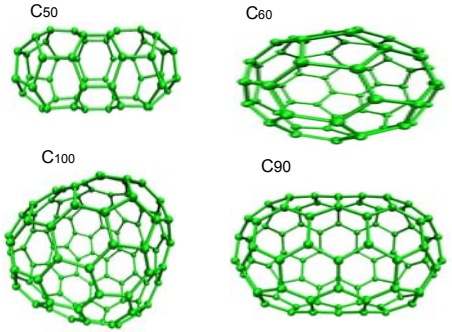
Materials/Methods

- Program Fullerenes: Compute areas, volume, spherical factors.
- VMD (Visual Molecular Dynamics) is a software package for three dimensional visualization, modeling and analysis of molecular systems.
- Path integral home made code.
- Intermolecular potential:
  - $V = V(H2\text{-}H2) + V(H2\text{-}C)$
- Lennard Jones Potential:
  - $V=4\epsilon[(\sigma/r)12-(\sigma/r)6]$
- Alchemical Free Energy Perturbation:

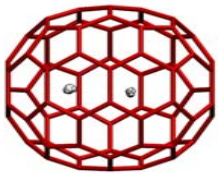
$$\Delta G=-kBT \ln \langle e^{[-\beta(U1-U2)]}\rangle_2$$

- $(H_2)x + C_y \rightarrow (H_2)x@C_y$

Structures of Four Fullerenes Used in This Study

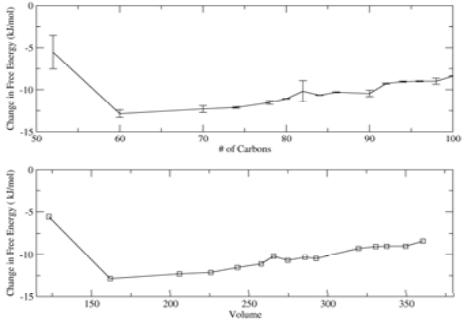


Example of a $(H_2)_2@C_{70}$ Configuration

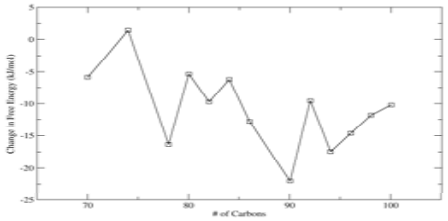


Results

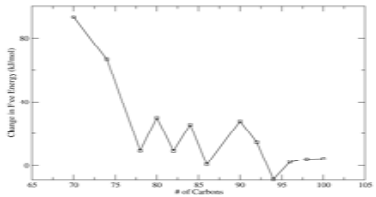
ΔG as a Function of Number of Carbon Atoms or Volume in the Fullerene for H_2



ΔG as a Function of Number of Carbon Atoms in the Fullerene for $(H_2)_2$



ΔG as a Function of Number of Carbon Atoms in the Fullerene for $(H_2)_3$



Conclusion

- One hydrogen molecule is stable in all the fullerenes considered.
- Two hydrogen molecules are stable in fullerenes larger than C_{70}
- Three hydrogen molecules can be accommodated only in C_{94}
- Four hydrogen molecules can not be accommodated in the fullerenes considered.

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