

SIMULATION OF POLYMOLECULAR ADSORPTION OF HYDROGEN AND OXIGEN ON CARBON NANOTUBES

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Abstract – Polymolecular adsorption and dissociation of hydrogen and oxygen molecules during adsorption on carbon nanotubes are discussed.

I. INTRODUCTION

The developing of the technology of selective deposition of vertically and horizontally oriented with respect to substrate surface carbon nanotube (CNT) arrays seems one of the most promising achievements of modern nanotechnology. Such arrays may consist of single wall and multiwall nanotubes with diameter from dozens to hundreds nanometers and lengths up to several micrometers and present an example of highly ordered dispersive medium with significant contribution of van der Waals interactions to all thermodynamic properties of the material. Main task of simulation of adsorption on carbon nanotube arrays is the determination of the adsorption type (physical or chemical) and the adsorption characteristics (the location of adsorption sites, adsorption bond lengths and energies).

II. SIMULATION AND DISCUSSION

In present paper quantum mechanical calculations were carried out using density functional theory implementation in NWChem quantum chemistry package [1] in local approximation. It is necessary to stress that DFT usually do not describe long-range behavior of electronic density properly because of the rapid decrease of Gaussian functions at long distances. In NWChem there is special correction accounting van der Waals interaction of distant atoms. This correction is described by additional term in interatomic potential:

$$E_{vdW} = -s_6 \sum_{i=1}^{N_{atom}-1} \sum_{j=i+1}^{N_{atom}} \frac{C_6^{ij}}{R_{ij}^6} \left(1 + e^{-\alpha(R_{ij}/R_{vdW}-1)}\right)^{-1} \quad (1)$$

Factor s_6 in (1.43) is defined by the exchange-correlation functional and basis set chosen. For exchange potential B3LYP s_6 is equal to 1.05. Then, $c_6^{ij} = \sqrt{C_6^i C_6^j}$ is the factor of dipole-dipole polarization interaction between i -th and j -th atoms, R_{vdW} и R_{ij} are van der Waals radius and interatomic distance correspondingly. Parameter α is used for control the interaction at intermediate distances. To study multi-molecular adsorption and to take account of the interaction in the adsorbed phase, we used in computation exchange functional of the electron density B3LYP, but in the atomic basis 6-31G. A {16, 16} tube fragment $C_{54}H_{18}$ of larger area was used for the analysis. Quantum mechanically optimized hydrogen molecules were placed above the fragment. The performed computation ascertained that molecular hydrogen is capable of both physical and chemical adsorption on nanotubes and in chemical adsorption, the hydrogen molecule decays into atoms which get attached to different carbon atoms of the nanotube. In physical adsorption, the adsorbed hydrogen forms a lattice, which in the general case is incommensurable with the nanotube lattice when the hydrogen atoms in a molecule are arranged vertically or horizontally with respect to the nanotube surface. In this case it becomes impossible to refer the adsorbed molecule to a certain hexagonal cell of the nanotube, and a single adsorbed hydrogen molecule takes the larger area of the nanotube surface than the area of the stated cell. The effective adsorbing surface of the nanotube diminishes accordingly. It should be noted that in contrast to the molecular-dynamics computation, the vertical orientation of the hydrogen molecules in physical adsorption seems preferable in terms of the energy criterion. For three adsorbed hydrogen molecules, the energy gain in this case is about 21 meV. Moreover, in vertical adsorption, the area taken by one hydrogen molecule is smaller than in the case of horizontal orientation of adsorbed

molecules. The character of hydrogen adsorption on the nanotubes becomes more complicated with due account of chemical adsorption when the hydrogen molecule decays into atoms which bond chemically with the carbon atoms of the nanotube. In physical atomic adsorption, as well as in molecular one, the distance between the hydrogen atom and the nanotube is approximately 2.7 -3.1 Å, while the interatomic distance in the hydrogen molecule is about 0.7 Å. With the distance between the molecule and the nanotube reduced by half (the distance to the carbon atom is 1.4 Å), the hydrogen molecule dissociates and the chemical bonds are formed between the hydrogen atom and the neighboring carbon atoms of the nanotube, with the length of C-H bonds being 1.2 Å. When other hydrogen atoms are added to the system, the chemical bond can either appear or vanish. Various structures of the adsorbate are possible in multi-molecular adsorption, including both chemically and physically adsorbed phases.

Fig. 1 shows the dependence of the depth of the adsorption minimum on the adsorbate structure. It is worth noting that in accordance with the quantum mechanical approach, the value of energy includes the total energy of hydrogen molecules in the ground state. As is seen from the plot, the point 4H2 (four physically absorbed hydrogen molecules) indicates the loss in energy (4.502 eV) in comparison with the structure 3H2 H H (three physically adsorbed hydrogen molecules plus one – chemically adsorbed with dissociation). Thus, physical adsorption is preferable as it gives the energy minimum. It should also be mentioned that in physical adsorption, the mutual orientation of the hydrogen molecules is not fixed. In this regard, taking account of the rotational degree of freedom of the adsorbed phase may appear important for the analysis of the adsorption characteristics of nanotubes. This fact can obscure the kinetics of adsorption processes on nanotubes.

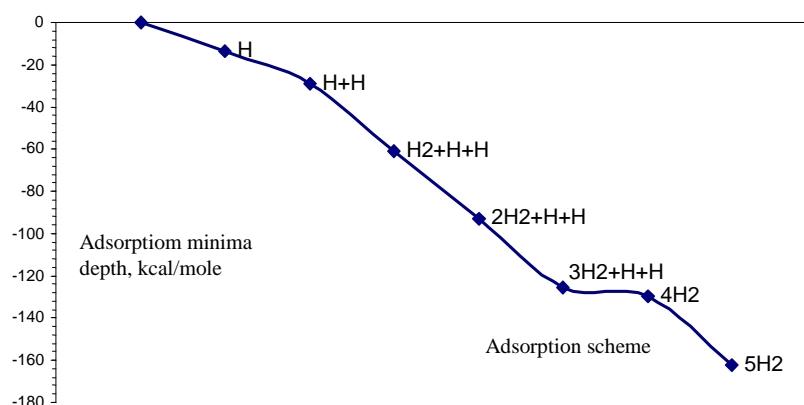


Figure 1 – Adsorption energy for different structures of the adsorbed phase.

The obtained data enable us to state that the hydrogen molecules form quasi-regular structures on the basis of the triangle lattice with the period independent of the period of the graphene lattice. Since in process of adsorption of hydrogen molecules, they may dissociate into atoms, particular attention was given to studying adsorption of two hydrogen atoms on the external wall of the nanotube {16,16} in a wide range of interatomic distances and the distances between the atoms and the nanotube. The hydrogen atoms move along the basis vector of the graphene lattice, the motion starts far from the carbon atom. The height of the hydrogen atoms over the nanotube fragment is from 0.8 Å до 2.6 Å, the van der Waals interaction is taken into account. The binding energy of the hydrogen atoms on the nanotube surface is calculated as follows:

$$E_{Sorb} = E_{System} - E_{Tube} - 2 \cdot E_H \quad (2)$$

where E_{System} is the energy of the nanotube fragment {16,16}, E_{Tube} is the energy of the structure consisting of the nanotube fragment 16×16 and hydrogen atoms, E_H is the energy of the hydrogen atom. The research results are given in Figure 2.

Computation was made on the grid cluster BY-BNTU.

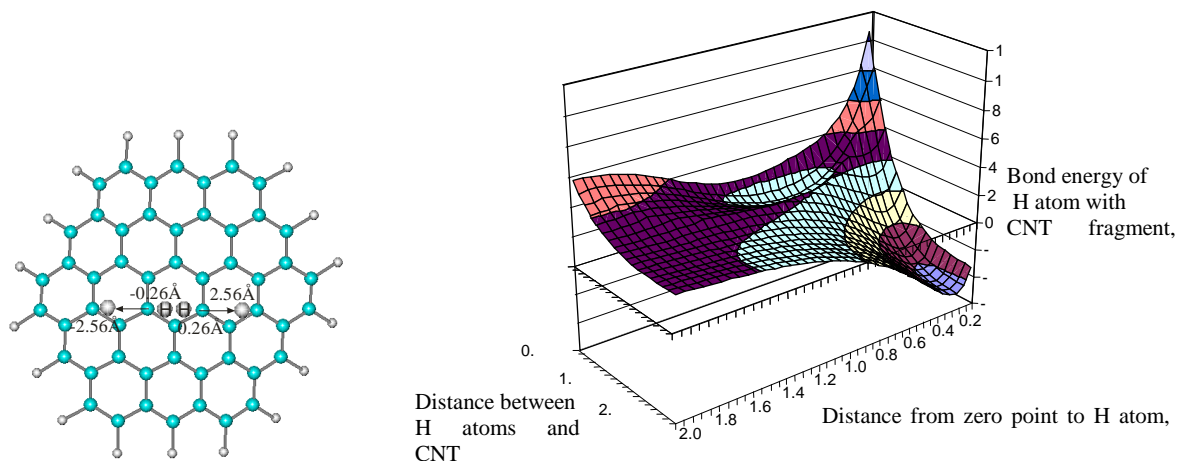


Figure 2 - The structure of the system “two hydrogen atoms – the fragment of carbon nanotube” and the dependence of the hydrogen binding energy with the CNT fragment on the position of the hydrogen molecule over the surface of the nanotube fragment

III. CONCLUSION

The simulation task of the adsorption of gas molecules on carbon nanotube arrays has hierarchical nature. It begins at quantum mechanical level where electronic properties of adsorption system are studied and the physical or chemical character of adsorption is determined with calculation of corresponding parameters of adsorption sites. Then interaction in adsorbed phase is studied and spatial distribution of adsorbed molecules is obtained. In the cases where physical adsorption dominates the molecular mechanics methods can be used for these studies.

REFERENCES

- [1] Valiev M., Bylaska E.J., Govind N., Kowalski K., Straatsma T.P., van Dam H.J.J., Wang D., Nieplocha J., Apra E., Windus T.L., de Jong W.A. (2010) NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations. *Comput. Phys. Commun.* **181**, 1477.