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Hydrogen adsorption on fluoro-graphene: an estimate by simulation

氟石墨烯之上的氢吸附：仿真估计

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Abstract - An estimate of the fluoro-graphene adsorption capacity for hydrogen is determined by Monte Carlo numerical simulations. Structure and symmetry of the atom arrangements in fluoro-graphene have been estimated by experiments and ab-initio computations. A comparison of effective and ab-initio potential for gas adsorption on fluoro-graphene materials is done before mesoscopic simulation setting up. These data allow to determine by ab-initio calculations the molecular interactions between gas molecules and the functionalized graphene materials or to estimate approximate effective atom-atom potentials to describe them. In this work on the basis of computed and effective interactions we calculated the fluoro-graphene adsorption properties of hydrogen up to high pressure both at room and low temperature. The estimation of hydrogen storage at 77K on fluoro-graphene is around 9 wt%.

Keywords – fluoro-graphene, DFT, Monte-Carlo simulations, hydrogen storage, physisorption.

I. INTRODUCTION

The adsorption of molecular gas by carbonaceous and porous materials has been studied extensively in the literature [1,2]. Indeed, numerous experimental and theoretical works have established that these materials have excellent adsorption properties which are optimal when the surface adsorption per gram is maximal and the pores have a nanometric size [3]. For pure carbon adsorbents, this maximal surface is obtained when the pore walls are made by a single basal graphite plane, *i.e.* graphene. Such a type of pores corresponds also to a quasi-maximal strength of attractive interaction between the walls and adsorbed gases since, due to the short range of the van der Waals interactions involved in solide-gas physisorption, a wall made by two or more graphite planes has

an interaction very close to that generated by a graphene wall [4]. The van der Waals interaction of one carbon atom in graphene sheet being weak, attempts have been done to increase the adsorption capacity of porous carbons by grafting atoms or molecules on the external graphene plane of pores [5,6]. The functionalized carbon atoms are expected to improve the attractive interaction of graphene on adsorbed gas molecules. However, the superficial density of grafted atoms or molecules is often small and the molecular mass of grafted molecules can decrease the adsorption capacity expressed in term of weight percent an important parameter characterizing the ability of an adsorbent to be used in mobile storage devices. In order to overcome these shortcomings, fluoro-graphene materials, in which each carbon atom is grafted by a fluorine atom, have been developed. For this material the functionalization is maximal: one fluorine atom per carbon atom and the decrease of the weight per cent possibly should be compensated by the increase of the van der Waals attraction of the grafted graphene. It is the main aim of this work to determine to which extent a noticeable improvement of the graphene adsorption capacity can be expected from the functionalization by fluorine. This estimate is performed by Monte-Carlo (MC) simulations in the the grand canonical (GC) Gibbs ensemble. Such computations to be reliable need to be performed with realistic modeling of pores and interactions between adsorbed gas molecules and the functionalized graphene surface. The adsorbent model used in the simulation is described below and one possible approach for describing the interactions is discussed. The simulation data are given for the hydrogen adsorption in porous fluoro-graphene materials. A conclusion summarizes the results of the work.

II. CALCULATION METHOD

II. 1. QUANTUM CHEMICAL CALCULATIONS

Quantum chemical calculations were performed in the frame of periodic DFT by means of the Vienna *Ab initio* Simulation Package (VASP 5.2.11) [7,8]. The electron-ion interactions were described by the projector augmented wave (PAW)[9,10] method, representing the valence electrons, as provided in the code libraries. The convergence of the plane-wave expansion was obtained with a cut off of 500 eV. The generalized gradient approximation (GGA) was used with the functional of Heyd-Scuseria-Ernzerhof (HSE06) [11, 12]. The sampling in the Brillouin zone was performed on a grid of k-points separated by 0.1 \AA^{-1} for the geometry optimizations. To improve the ability of DFT calculations to describe the weak interaction, especially the dispersion interactions, Grimme et al.[13] proposed to introduce an empirical correction of dispersion contribution to the standard density functional (denoted as DFT-D); using this strategy, the estimation of noncovalent interactions can be computed very accurately at the DFT level. All the computations reported in this paper are performed using the dispersion-including DFT Grimme D2 method. DFT-D2 Grimme (G, D2). This method describes the dispersion interactions between a particle and its neighbours in a given radius, via a simple pair-wise force field summed to the pure DFT energy.

$$\Delta E = E_{\text{DFT}} + E_{\text{D2}} \quad (1)$$

The FG (fluoro-graphene) substrate is modelled as a slab, where a unit cell is periodically reproduced in the 3D space. In this approach the surface is infinite in two dimensions (in x and y directions), with a vacuum space (38 \AA) in the z axis direction. This vacuum space should be large enough to enable the hydrogen adsorption and disable its interaction with the consecutive repetition of the system slabs. In the present case, the slabs representing a (2×2) supercell of armchair GF were built from optimized unit cell (See Fig 1.), using Modelview software[14]. The primitive unit cell parameters are: $a=2.59 \text{ \AA}$, $b=2.59 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$, being in a good agreement with previous experiment and theoretical results [15-19].

II. 2. ADSORBENT MODEL

In the simulations where the nanometric scale of the pore network is specifically considered, a good approximate model for the pore shape is a slit with planar walls that, in this work, will be fluoro-graphene planes. The arrangements of functionalized carbon atoms in fluoro-graphene have been studied by *ab-initio calculations* [20-21]. These studies allow defining an approximate reliable model of the quasi bi-dimensional structure of these materials. In our computations, we have chosen to use a chair conformation of the carbon atoms rings that has been identified strongly stable by the DFT computations. In this conformation, the carbon atoms are distributed equally in two parallel planes distant by 0.45 \AA . In a plane, the C atoms are arranged on a triangular lattice, but their two nearest neighbors are located in the other

plane at a distance of about 1.53 \AA . The bond linking the C atom to the F atom is pointing outside the plane external faces and its length is equal to 1.40 \AA . The structure of the adsorbent model is fully defined by the choice of the slit width that, at the considered nanometric scale, is optimal for $1.0 - 2.0 \text{ nm}$ taking into account the size of adsorbed gas molecules and the van der Waals interactions range.

A simple, but approximate, way to describe the interactions between gas molecules and an adsorbent surface is to associate to molecules and adsorbent atoms a pair potential. This way is widely used in the literature on the basis, for instance of Lennard-Jones (LJ) pair potentials:

$$v_{ij}(r) = \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (2)$$

where i and j correspond to a specific site or atom in molecules or the adsorbent. The parameters ϵ_{ij} and σ_{ij} are in general obtained empirically by systematic comparisons with experimental data or derived from the Berthelot rules

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad \text{and} \quad \sigma_{ij} = 0.5(\sigma_i + \sigma_j) \quad (3)$$

where ϵ_i or ϵ_j and σ_i or σ_j are the parameters of LJ potentials defined for the atoms or molecular sites i or j and considered transferable and usable to estimate the cross-interaction ij. Such an interaction potential between hydrogen and fluoro-graphene has been used in ref. [22]. The empirical parametrization of the van der Waals interaction $v_{H_2 F_g}^W$ between H_2 gas molecule and fluoro-graphene solid is made on the basis of a contribution of C and F atoms.

$$v_{H_2 F_g}^W = -\sum_i \frac{C6C}{r_i^6} - \sum_j \frac{C6F}{r_j^6} \quad (4)$$

where r_i and r_j are respectively the distance between the center of mass of H_2 molecules and the C and F atoms, the coefficients $C6C$ and $C6F$ being equal to $9.96 \text{ eV} \cdot \text{A}^6$ and $16.38 \text{ eV} \cdot \text{A}^6$. It is possible to calculate ϵ LJ effective parameters corresponding to C and F atom inside the fluoro-graphene framework using the Berthelot rules. The values of σ LJ parameter estimated in the literature [23] are equal to 3.4 \AA for C and 3.0 \AA for F. The ϵ effective value for C is 21.3 K which is close from a standard value equal to 28.0 K used for adsorption simulation in graphene [24]. The ϵ effective value for F is 125.9 K and can be compared to previous estimates given for instance in ref. [25]. From these values of ϵ and σ , effective LJ potentials for C and F are obtained and summarized in Table 1.

The H_2 LJ potential is localized on the molecular center of mass and is associated with three charges to take into account the linear molecular electric quadrupole: one charge $-2q$ at the center of mass and two charges q localized symmetrically on the molecular symmetry axis at 0.37 nm of the center of mass.

TABLE 1, Parameters of empirical LJ potentials for H₂ molecule, C and F atoms of fluoro-graphene. ϵ is in unit of Kelvin degree, σ and distance in unit of nanometer, and electric charge q in unit of the electron charge. Cross-interactions are obtained from the Berthelot rules

LJ parameters	ϵ	σ	q charge
H ₂ molecule	36.7	0.2958	0.480
C of fluoro-graphene	21.3	0.3400	
F of fluoro-graphene	125.9	0.3000	

III. RESULTS AND DISCUSSION

In figure 1, the full DFT interaction between hydrogen and a fluoro-graphene plane is given at HSE0 level. The variation of the interaction potential in xy plane is shown on Figures 1-b-d. Figure 1-a shows the variation of the interaction potential when hydrogen molecule is located above one carbon atom, just between two fluorine atoms. The position of molecule is set in a position for which the axis of hydrogen molecule is perpendicular to the surface.

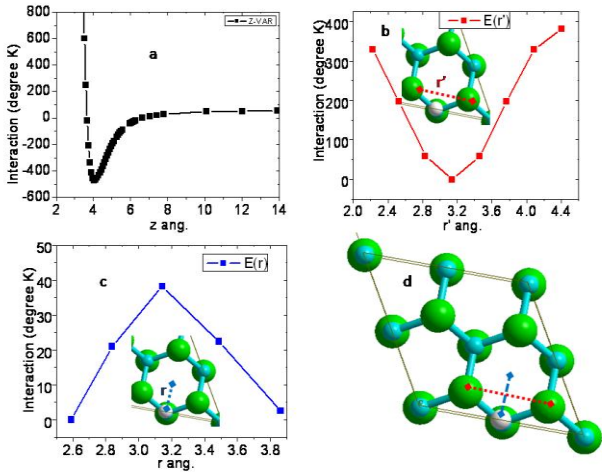


Fig.1, HSE06-D2 interaction between H₂ and fluoro-graphene toward z axis (a) and xy plane (b and c). The structure of the chosen supercell showing the hydrogen molecule displacement directions in xy plane (d).

One can observe that the minimum of the interaction along z axis is found to be equal to -470K with an equilibrium distance of 4.05Å from the surface. The variation of the interaction in xy plane reaches 340K and the hydrogen most stable position is found to be locating in a bridge between two fluorine atoms. The total interaction can decrease down to -800K depending on the position in xy plane. Previously, the minimum interaction energy was found to be equal to -677K at PBE-D2[20] level and the equilibrium position was found between two fluorine atoms. Using Moller Plesset method a minimum interaction energy of 349 K was obtained by Reichenbacher et al.[26]

In figure 2, the full effective interaction between hydrogen and a fluoro-graphene plane is given. The contributions to this interaction of the C and F atoms are also plotted. The minimum of interaction is equal to about -620K and is located at 4.8Å from the fluoro-graphene plane. The interaction value is greater than the HSE06-D2 value (-470K) due probably to the parameter significantly different for fluorine.

The equilibrium distances are also different of about 0.75Å and the interaction becomes repulsive fewer than 4.05 and 4.80Å for the effective and DFT potentials, respectively.

The figure 3 shows that, when the contributions of the two walls are added, in the central part of the smallest pore the interaction minimum is equal to -1100.0K.

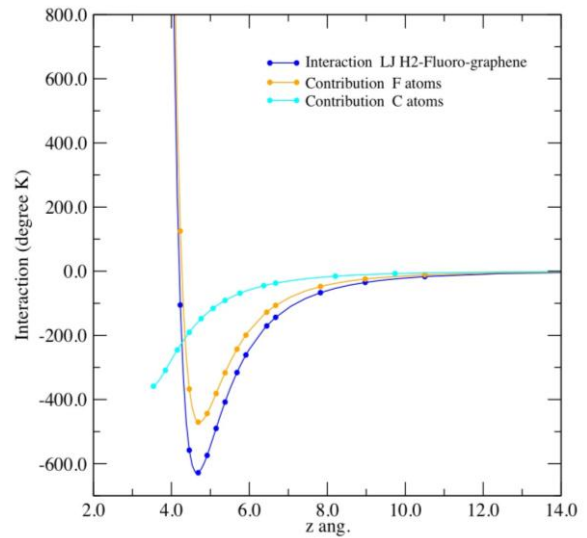


Fig.2 Effective interaction between H₂ and fluoro-graphene expressed in kelvin (K)

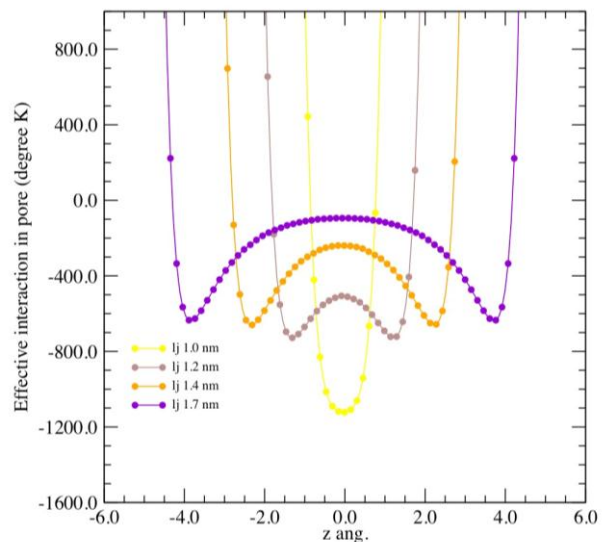


Fig. 3 Interaction of H₂ expressed in kelvin (K) molecule inside pores of different widths with fluoro-graphene walls.

In figure 4, the molecular simulation results for the excess adsorption are given. The excess adsorption is defined as the difference between the total adsorption and the adsorption due to the compression, *i.e.* the gas amount which, in any case, would be inside the pore volume in the absence of a molecule-wall interaction.

In the small pore of width equal to 1.0 nm, when the pressure increases, the excess adsorption is maximal around 200bars and, for larger pressures, it does not increase due to the steric effects between adsorbed molecules. For larger pores (widths equal to: 1.2, 1.4 and 1.7nm) the excess adsorption increases up to 500bars, but is larger for the width equal to 1.4nm because the inter-molecular steric effects are reduced compared to the case of the smallest width and the interaction between the gas molecules and pore wall is stronger than in the larger pores (cf. fig. 3).

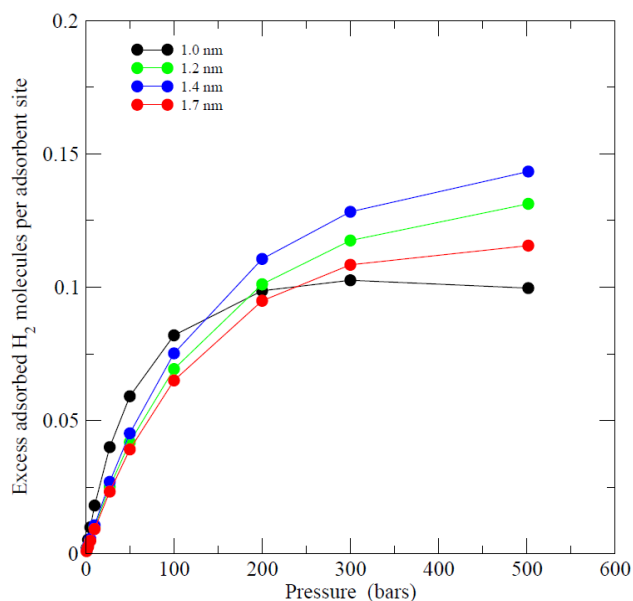


Fig.4 Excess adsorption of H₂ molecule per site at 293.16 K. A site is defined as one C atom of the fluoro-graphene plane. The ratio between the excess weight per cent and the excess adsorption per site is equal to 6.45.

The estimation of hydrogen storage at 77K on fluoro-graphene is around 9 wt%, higher than the pristine graphane (5 wt%) estimation and more close to the values found for graphane doped by sodium (10.3 wt%) or lithium (12.3 wt%)[27] ; values to be compared to the DOE target [28].

IV. CONCLUSION

The adsorption properties of the fluoro-graphene for H₂ at room temperature have been determined using an effective interaction and compared with DFT calculations. In the case of graphane where such a comparison is being done, a good agreement is obtained [29] between the adsorption estimated from the effective and theoretical interactions. Such a result reinforces our confidence that the present estimate of the adsorption capacity of fluoro-graphene is reliable. The

adsorption of H₂ on fluoro-graphene expressed in excess weight per cent is not significantly different from that of graphane being equal to ~ 1.0% at high pressure and room temperature [3, 29].

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