

THEORETICAL STUDY OF METHANE ADSORPTION ON GRAPHITE

Albesa, A. G.^a, Vicente, J. L.^a

^a*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Dep. de Química, Fac. Ciencias. Exactas, UNLP, CC 16, Suc. 4 (1900) La Plata, Argentina*

E-mail: alberto.albesa@gmail.com, vicente@inifta.unlp.edu.ar

Received September 1, 2007. In final form December 15, 2007.

Abstract

In the present contribution, we performed PM3 semi – empirical and DFT calculations of increasing numbers of adsorbed methane molecules on a planar polyaromatic substrate, which mimics a graphene plane. In this way we attempt to describe low coverage methane adsorption on a graphite surface. Results show a configuration change of adsorbed molecules from hexagonal to square array as the coverage increases; however methane molecules distance to the surface remains almost unchanged for PM3 and for DFT diminishes from 4.2 Å for one molecule to 3.8.

Keywords: PM3, DFT, methane, graphite, adsorption.

Resumen

En el presente trabajo realizamos cálculos semiempíricos PM3 y DFT de un número creciente de moléculas de metano adsorbidas en un sustrato planar poliaromático que simula un plano de grafeno. De esta forma tratamos de describir la adsorción de metano sobre una superficie de grafito. Los resultados muestran un cambio en la configuración de las moléculas adsorbidas de un arreglo hexagonal a un arreglo cuadrado a medida que el cubrimiento se incrementa; sin embargo la distancia de las moléculas de metano a la superficie se mantienen casi sin cambios (3.89 Å) en los cálculos PM3 y disminuye de 4.2 Å a 3.8 Å en DFT.

Palabras claves: PM3, DFT, metano, grafito, adsorción

Introduction

This paper is part of a study of methane adsorption on different carbonaceous surfaces (from graphite to amorphous and carbon nanotubes).

Natural gas (NG) systems are being developed to provide alternative transportation fuels to traditional liquid petroleum fuels because of their considerable advantages from an environmental point of view and their natural abundance. Environmentally, NG has many advantages over gasoline. It is composed mostly of methane, with lesser amounts of ethane, propane, and butane, contains few or no

contaminants, and burns cleanly and efficiently. However, the major shortcoming of NG as a fuel is the relatively low heat of combustion per unit of volume when compared with conventional fuels [1]. One solution is to compress natural gas, but compressed natural gas (CNG) for use in natural gas fuelled-vehicles require high pressures (up to 25 MPa). The associated disadvantages [2] are related to the weight and bulk of the containment vessel required, the associated safety risks, and the costs associated with multistage compression cycles. Alternatively, adsorbed natural gas (ANG) up to 3.5 MPa onto activated carbons and nanotubes [1-4] offers a very high potential for exploitation in both transport and large-scale applications.

We used a graphite surface as a first step in the study of methane adsorption on several carbonaceous materials. In spite of being the most simple and clean surface, in the adsorption mechanism there are a lot of ambiguities about some aspects such as the pyrolysis reaction [6]. In addition, the graphite surface can also be used to mimic some carbonaceous surfaces [6] at determined scales.

Two recent descriptions [7, 8] about methane adsorption on graphite surfaces tackle the problem from two different points of view: a semiempirical quantum mechanical (SQM) model for the methane-graphite interaction [7] and a grand canonical Monte Carlo (GCMC) simulation [8].

We first looked for a unified description of the adsorption mechanism that was not only based on the two above points of views, but was also in good agreement with our and other experimental information [9, 10].

This paper is organized as follow: after a computation tools description, we show the results of adsorption, from one to four methane molecules on a graphite surface, represented by a polyaromatic molecule. Finally we present the conclusions that become the basis to perform Monte Carlo simulations of bulk methane adsorption on graphite surfaces.

Methodology and computational details

We began by studying the interaction potential, between methane molecules and the graphite surface by employing PM3 semiempirical methods [11] and using Hyperchem software [12] to perform the calculations.

Because of the similar chemical characteristics, we modeled the graphite plane with a planar polyaromatic molecule, as is shown in Fig 1.

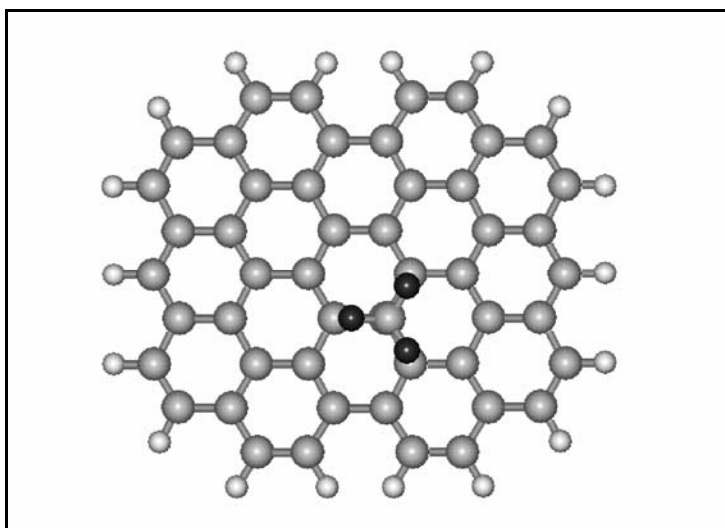


Fig. 1: Optimized geometry of one methane molecule on a planar polyaromatic molecule that mimics a graphite surface (top view).

The interaction energy ΔE_1 for n adsorbed methane molecules was calculated as

$$\Delta E_1 = E(G - n \text{ CH}_4) - [E(G) + n E(\text{CH}_4)] \quad (1)$$

where $E(G - n \text{ CH}_4)$, $E(G)$ and $E(\text{CH}_4)$ are the graphite-methane complex, the isolated graphite sheet and methane molecule respectively.

Then we evaluated the contribution ΔE_2 to the energy due to the methane molecules considering the energy $E_a(n \text{ CH}_4)$, corresponding to the same configuration but without the graphite surface, and its difference with the n methane molecules, that is

$$\Delta E_2 = E_a(n \text{ CH}_4) - n E(\text{CH}_4) \quad (2)$$

and finally we took the interaction energy between methane molecules and graphite as the difference between ΔE_1 and ΔE_2 , or

$$\Delta E = E(G - n \text{ CH}_4) - [E(G) + E_a(n \text{ CH}_4)] \quad (3)$$

The complexes optimized at the PM3 level were subjected to further geometry optimizations using the density functional theory[13,14]. To this end the PW91PW91 [15] functional with the 6-31G basis set as implemented in the Gaussian 03 package[16] was used. The geometry was optimized keeping the graphene molecule's geometry fixed. With the geometry optimized we performed a single point calculation with the same functional and 6-31G(d,p) basis set. The choice of this functional is due because it was found to represent well the intermolecular potential between methane dimers [17]. The basis set dependence is small in the geometry optimization using this functional [18].

3. Results and Discussion

In order to consider the energy interaction when different numbers of methane molecules approach the surface, we first optimized the geometry of the first methane molecule from various relative orientations with respect to the reference plane of graphite [7]. In Table 1 we summarize the results for the PM3 and DFT calculation for the first adsorbed molecule.

Table 1. Charge and bond distance for one methane molecule on the graphite surface for PM3 and DFT calculations.

	PM3		DFT	
	CH ₄ + graphite		CH ₄ + graphite	
Atom	charge [Q]	d _{C-H} [Å]	charge [Q]	d _{C-H} [Å]
C	-0.125		-0.531	
3 H(upper)	0.029	1.087	0.129	1.099
H(lower)	0.038	1.089	0.139	1.098
$\Delta E(\text{KJ/mol})$	-0.642		-2.96	
Distance to the surface	3.82		4.22	

The optimized scheme result for the first molecule on the graphite surface is shown in Fig. 1, with one hydrogen atom pointing to the top adsorption site. There is an increase of the charge in the lower hydrogen atom in both methods, and the bond length in PM3 calculations while in DFT the bond length of the lower hydrogen diminishes.

In order to consider two methane molecules, we placed a second one on another top site (see Fig. 2a). The geometry optimization is shown in Fig. 2b. The distance between the two carbon atoms is 3.8 Å, and two hydrogen atoms of each molecule, which we will call laterals, form a straight line C - H ... H - C. Also the lower hydrogen atoms, now form a 168° rather than a 180° angle.

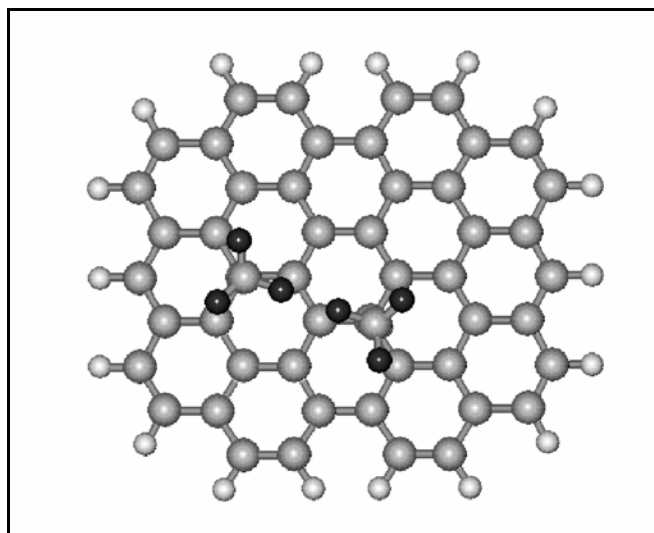


Fig. 2a: Two methane molecules placed on top sites in order to begin the calculations.

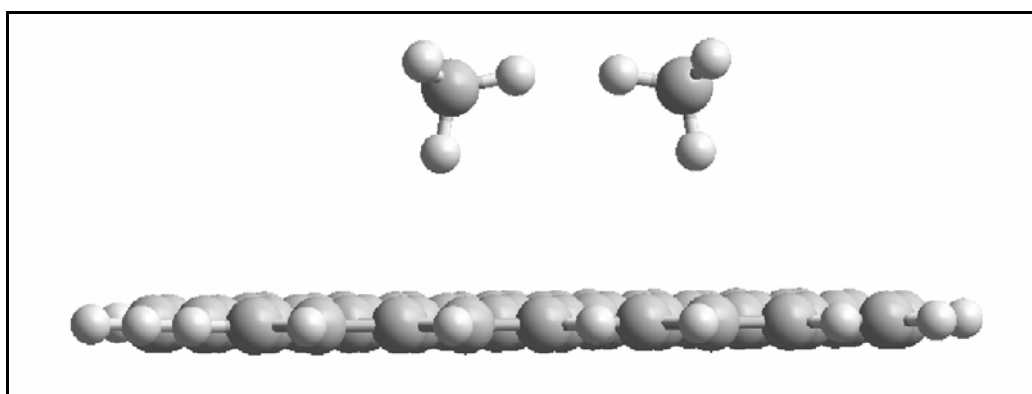


Fig. 2b: Optimized geometry of two methane molecules on a graphite plane (lateral view).

In Table 2 we compare these results with the geometry optimization when the methane molecules are isolated and when they are on the graphite surface.

By employing Eq. (3) we obtain the interaction energy between the two methane molecules and the graphite plane as $\Delta E = - 1.211$ KJ/mol, which means approximately the same contribution of one methane molecule alone.

Table 2a. Charge and bond distance of two isolated methane molecules, and the two molecules on the graphite surface for PM3.

2 CH ₄			2 CH ₄ + graphite		
Atom	charge [Q]	d _{C-H} [Å]	Atom	charge [Q]	d _{C-H} [Å]
C	-0.124		C	-0.139	
H(lateral)	0.037	1.092	H(lateral)	0.040	1.092
3 H	0.029	1.087	2 H(up)	0.030	1.087
			H(down)	0.039	1.089

Table 2b. Charge and bond distance of two isolated methane molecules, and the two molecules on the graphite surface for DFT.

2 CH ₄			2 CH ₄ + graphite		
Atom	charge [Q]	d _{C-H} [Å]	Atom	charge [Q]	d _{C-H} [Å]
C	-0.539		C	-0.54	
H(lateral)	0.14	1.099	H(lateral)	0.137	1.099
3 H	0.133	1.099	2 H(up)	0.127	1.099
			H(down)	0.141	1.098

The DFT results are shown in Table 2b. The distance between the methane molecules is 4.60 Å, the same distance that is found when the molecules are isolated. Again it can be observed a shortening in the bond length of the lower hydrogen and an increase of the charge of this hydrogen. The interaction energy, calculated from Eq. (3), is -5.78 KJ/mol for both molecules. The distance of the two methane molecules to the surface is 4.15 Å.

In order to consider the case of three methane molecules, there are two forms to incorporate the third methane molecule, one (arrangement (a)) in an intermediate position between the other two (see Fig. 3a) and the other (arrangement (b)) closer than one of the other two methane molecules (see Fig. 3b,c,d).

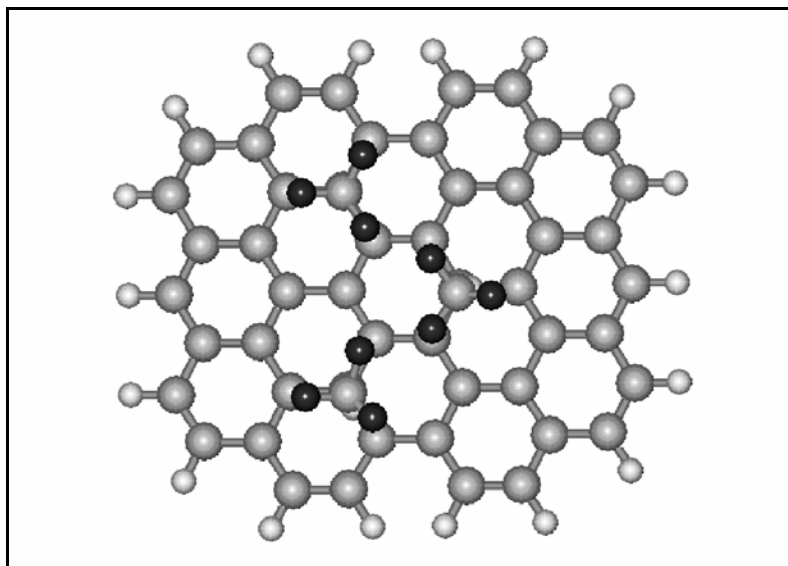


Fig. 3a: Three methane molecules on a graphite surface according to arrangement (a).

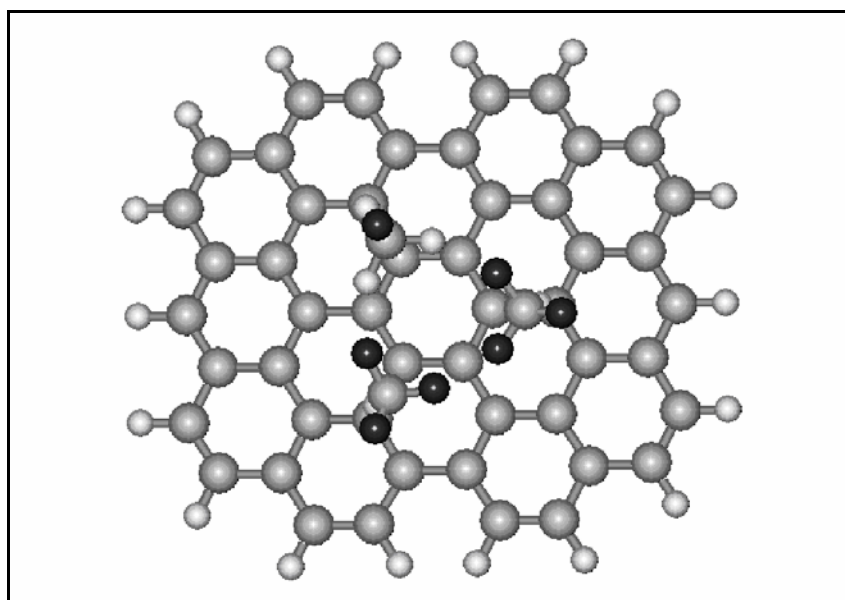


Fig. 3b: Three methane molecules on a graphite surface according to arrangement (b).

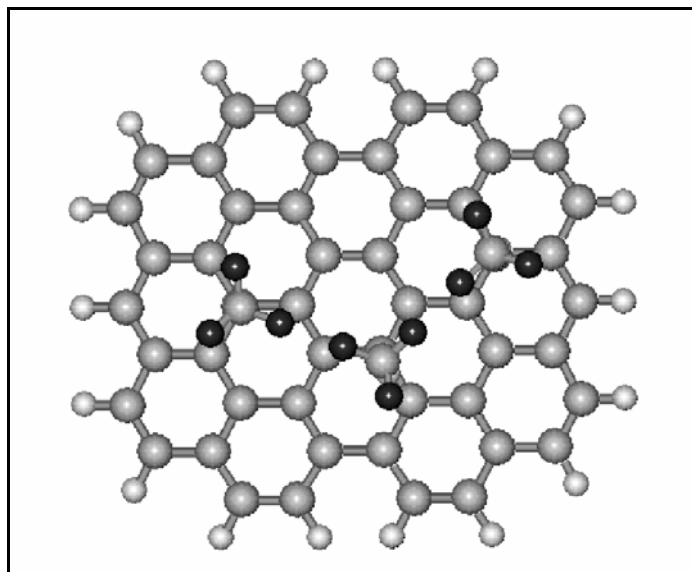


Fig. 3c: Optimized geometry of three methane molecules on a graphite plane (top view).

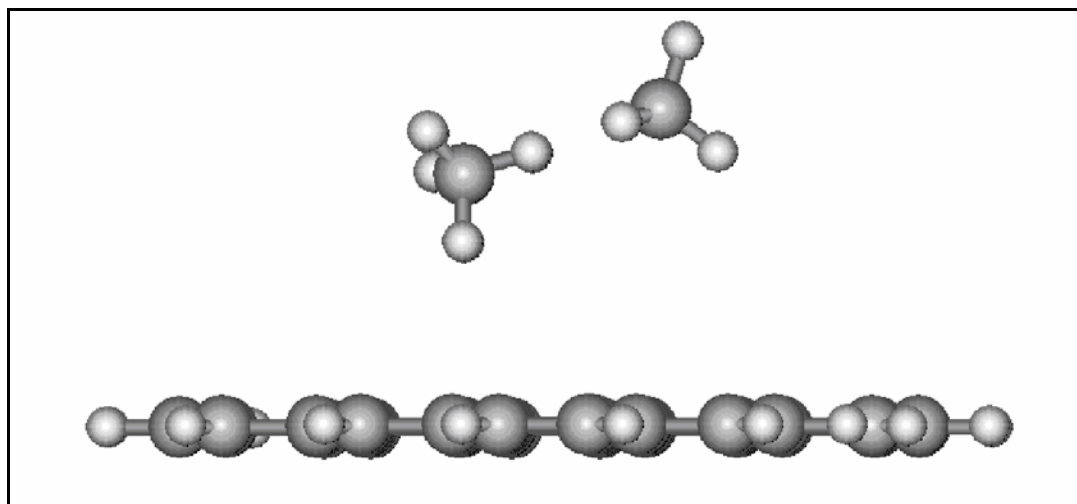


Fig. 3d: Optimized geometry of three methane molecules on a graphite plane (lateral view).

Table 3. Charges and bond distances of three methane molecules on the graphite surface, with arrangements (a) and (b), respectively.

arrangement (a)			arrangement (b)		
PM3					
CH ₄	charge [Q]	d _{C-H} [Å]	CH ₄ (central)	charge [Q]	d _{C-H} [Å]
C	-0.152		C	-0.152	
H	0.029	1.086	H(lat.)	0.041	1.092
H(lat.)	0.041	1.092	H(lat.)	0.041	1.092
H(lat.)	0.040	1.092	H	0.029	1.086
H(lower)	0.039	1.088	H(lower)	0.040	1.089
CH ₄			CH ₄		
C	-0.152		C	-0.139	
H(lat.)	0.042	1.092	H	0.028	1.087
H	0.029	1.086	H	0.029	1.087
H(lat.)	0.041	1.092	H(lat.)	0.040	1.092
H(lower)	0.039	1.088	H(lower)	0.039	1.089
CH ₄			CH ₄		
C	-0.144		C	-0.139	
H(lat.)	0.041	1.092	H(lat.)	0.041	1.092
H(lat.)	0.041	1.092	H	0.029	1.087
H	0.028	1.086	H	0.028	1.087
H(lower*)	0.033	1.086	H(lower)	0.039	1.089
DFT					
CH ₄	charge [Q]	d _{C-H} [Å]	CH ₄ (central)	charge [Q]	d _{C-H} [Å]
C	-0.543		C	-0.551	
H	0.125	1.099	H(lat.)	0.139	1.099
H(lat.)	0.138	1.099	H(lat.)	0.139	1.099
H(lat.)	0.138	1.099	H	0.126	1.099
H(lower)	0.137	1.099	H(lower)	0.142	1.099
			CH ₄		
			C	-0.541	
			H	0.125	1.099
			H	0.125	1.099
			H(lat.)	0.139	1.099
			H(lower)	0.142	1.099

Arrangement (a):

The geometry optimization causes a shift of the molecules from the top to the bridge sites, but there is a rotation of the third molecule, with one of the hydrogen atoms higher up. This configuration gives distances of the carbon atom to the graphite surface

of 4.92 Å for the upper methane and 3.92 Å for the other two methane molecules, respectively, which means that they are further apart than in the previous cases.

We note a stretching of the distances C-H between the lateral hydrogen that participate in the bond C-H...H-C, and also with the lower hydrogen.

The energy interaction with the surface is -1.106 KJ/mol, lower than the case of two methane molecules. This can be due to the stronger bond between the three methane molecules, but in all cases the methane-graphite system is energetically more stable than three isolated methane molecules.

The DFT results show that the three methane molecules are equivalent, i.e. the three molecules are at the same distance to the surface (3.90 Å). It can be observed the C-H...H-C bond, so the molecules form a perfect triangle. The interaction energy is -13.92 KJ/mol, largest than in the case of the two methane molecules.

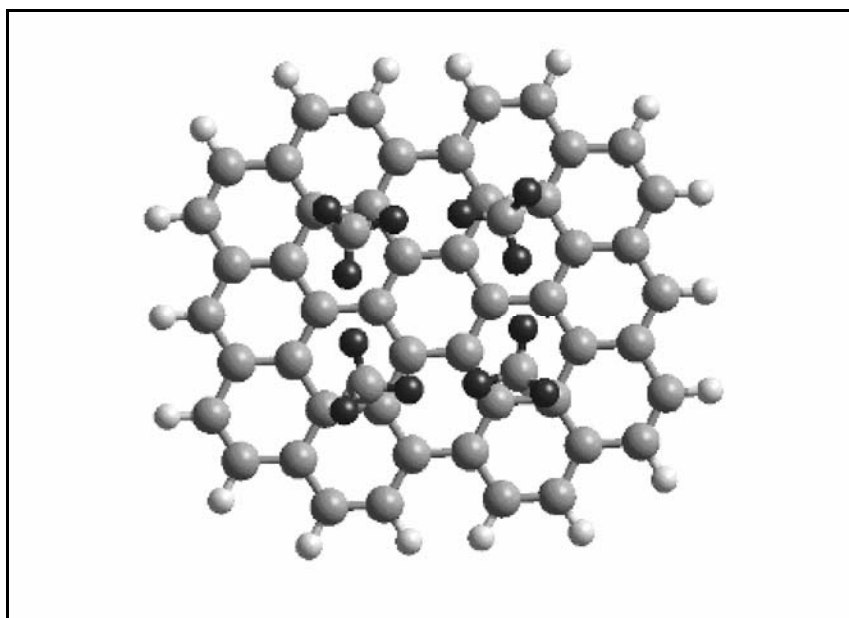


Fig. 4: Optimized geometry of four methane molecules on a graphite plane (top view).

Arrangement (b):

Here we also note bond formation C-H...H-C between methane molecules but in this case the distance of all molecules to the surface is 3.83 Å for PM3 and 3.95 for DFT results. The energy interaction with graphite is -1.785 KJ/mol for PM3 and -8.92 KJ/mol for DFT.

Finally we incorporated a fourth methane molecule to the previous arrangements. In this case we obtained the four molecules on the same plane at a distance 3.89 Å, for both methods, from the graphite surface as is shown in Fig. 4. The geometry optimization is given in Table 4.

Table 4. Geometry of four methane molecules, hydrogen atom (a) lower, (b) upper.

PM3				DFT			
CH ₄ (1)	charge [Q]	d _{C-H} [Å]	d _{C-G} [Å]	CH ₄ (1)	charge [Q]	d _{C-H} [Å]	d _{C-G} [Å]
C	-0.150		3.89	C	-0.549		3.79
H	0.041	1.092		H(up)	0.125	1.099	
H	0.029	1.086		H(lat)	0.139	1.099	
H	0.038	1.088		H(down)	0.136	1.099	
H	0.041	1.092		CH ₄ (2)			
CH ₄ (2)				C	-0.151		3.80
C	-0.151		3.89	H	0.039	1.099	
H	0.039	1.088		H	0.029	1.099	
H	0.029	1.086		H	0.041	1.099	
H	0.041	1.092		H	0.041	1.099	
H	0.041	1.092		CH ₄ (3)			
CH ₄ (3)				C	-0.15		3.82
C	-0.150		3.89	H	0.038	1.099	
H	0.038	1.088		H	0.029	1.099	
H	0.029	1.086		H	0.041	1.099	
H	0.041	1.092		H	0.041	1.099	
H	0.041	1.092		CH ₄ (4)			
CH ₄ (4)				C	-0.151		3.83
C	-0.151		3.89	H	0.039	1.099	
H	0.039	1.088		H	0.041	1.099	
H	0.041	1.092		H	0.029	1.099	
H	0.029	1.086		H	0.041	1.099	
H	0.041	1.092					

5. Conclusions

From the calculations we can conclude that the interaction energy between one, two, and three methane molecules adsorbed on a graphite surface, corresponding to the most favorable configuration, is almost the same ($\Delta E \approx -2.9$ KJ/mol).

From DFT results we note that the distance of the methane molecules to the surface diminishes from 4.2 Å for one molecule to 3.8 Å in the case of four and for PM3 these distance is always about 3.89 Å.

Furthermore, the first three methane molecules form arrangements according to both methane and graphite symmetries. This means methane molecules form a hexagonal configuration of 4.5 Å side, at almost the same distance of 3.95 Å from the surface. This situation is compatible with lower coverage, but when the coverage increases (i.e. four methane molecules) the structure changes. There is a change of the distance between the methane molecules and the graphite surface from 3.95 Å to 3.80 Å, and the interaction energy is $\Delta E \approx -3.77$ KJ/mol, now the hexagonal configuration changes to a square one, with the same average side of 4.5 Å.

Another point to take into account is that the energy interaction between methane and the graphite surface, at low coverage, is almost the same from one

adsorption site to another. In other words the graphite structure does not play a very important role in methane adsorption on graphite surface at temperatures over 80 K.

We used these conclusions to perform a study and comparison between Monte Carlo simulations and our [10] and other experimental [11] results. According to our preliminary calculations there is a very good agreement between all of them.

Acknowledgments

The authors gratefully acknowledge financial support from the UNLP (Universidad Nacional de La Plata), CICPBA (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) and CONICET (Consejo de Investigaciones Científicas y Tecnológicas).

References

- [1] K. Wagner, *Methane (international thermodynamics tables of the fluids state volume 13)* (IUPAC chemical data series), Blackwell Science, Boston, 1996.
- [2] N. D. Parkyns, D. F. Quinn; in *Porosity I Carbons*, Patrick, J.W.; Arnold, E. (Eds.) London, 1995, p. 302.
- [3] R. F. Cracknell, P. Gordon, K. E. Gubbins; *J. Phys. Chem.*, 1993, 97, 494.
- [4] M. Muris, N. Dufau, M. Bienfait, N. Dupont-Pavlovsky, Y. Grillet, J.P. Palmari, *Langmuir*, 2000, 16, 7019.
- [5] S. Bammidipati, G. D. Steward, S. A. Gakoglu, M. J. Purdy; *AIChE J.*, 1996, 42, 3123.
- [6] Bandosz, T. J.; Biggs, M. J.; Gubbins, K. E.; Hattori, Y.; Iiyama T.; Kaneko, K.; Pkunic, J; Thomson, K. T., *Molecular Models of Porous Carbons*, in: Radovic, L. R. (ed.), *Chemistry and Physics of Carbon*, Marcel Dekker Inc., New York, 2003, vol. 28.
- [7] H. Sabzyan, M. Babajani; *J.Molec.Struct.:THEOCHEM* 2005, 726, 155.
- [8] D. D. Do, H. D. Do; *J. Phys. Chem.*, 2005, 109, 19288.
- [9] F. Jensen; *Introduction to Computational Chemistry*, Wiley, Chichester, 1999.
- [10] A. G. Albesa, J. L. Lanos, J. L. Vicente, to be published.
- [11] N. N. Avgul, A. V. Kiselev; in: Walker P. L. (ed.); *Chemistry and Physics of Carbon*; Marcel Dekker Inc., New York, 1970, vol. 6.
- [12] Hyper Chem. Release 7.0 for Windows, *Molecular Modeling System: Hyper Cube*, <http://www.hyper.com>, 2002.
- [13] W. Kohn, L. J. Sham; *Phys. Rev. A*, **1965**, 140, 1133
- [14] R. G. Parr, W. Yang; *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- [15] Y. Wang, J. P. Perdew; *Phys. Rev B*, **1991**, 44, 13298.
- [16] M. J. Frisch et al., GAUSSIAN 03, Revision B.02, Gaussian, Inc., Pittsburgh PA, 2003.
- [17] A. H. T. Li, S. D. Chao; *J.Chem. Phys.*, **2006**, 125, 94312.
- [18] S. Tzuzuki, H. P. Lüthi; *J.Chem. Phys.*, **2001**, 114, 3949.