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A comment on “The interaction of X_2 (X = F, Cl, and Br) with active sites of graphite” [Xu et al., Chem. Phys. Lett., 418, 413 (2006)]

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Abstract

In their article, Xu et al. [1] present the adsorption energies for the chemisorption of the three halogens F_2, Cl_2, and Br_2 on the active sites of graphite. The three investigated systems are the three most stable surfaces, (001), (100), and (110); the latter two are also called zigzag and armchair surface, respectively. Due to some inconsistencies in their article, we re-evaluated the results of Xu et al. in order to investigate the impact on the adsorption energies of the halogens. For the (001) surface, our results agree with Xu et al. However, for the other two surfaces we find major differences. Contrary to Xu et al., we find that the halogens adsorb the strongest on the zigzag surface. The second strongest adsorption is found on the armchair surface for the symmetric configurations, the third strongest for the asymmetric configurations. Several reasons are given which explain this discrepancy. The most striking source of error in the work of Xu et al. is due to the fact that they did not choose the correct spin multiplicities for the model systems which means that they performed the calculations in excited states. This leads to errors between 50-600% for the zigzag surface and 3-42% for the armchair surface.

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In their article, Xu et al. [1] present the adsorption energies for the chemisorption of the three halogens F_2, Cl_2, and Br_2 on the active sites of graphite. The three investigated systems are finite models of the three most stable surfaces, (001), (100), and (110). The latter two are also called zigzag and armchair surface, respectively. These surfaces were modeled by the molecules in a cluster approach (see Figure 1), which is an established technique for these systems [2]. While studying similar systems, we compared our results to the published results and found several discrepancies which, we feel, need some clarification. In their paper Xu et al. state: *"The correct ground state was determined by means of single point energy calculations for different electronic states and the lowest energy electronic state was determined to be the selected ground state (the ground electronic spin multiplicity is 1, 7 and 3 corresponding to the model A, B and C, respectively).“* It is not completely clear to us if this refrains only to the electronic states of the isolated surface models or as well to the systems containing the adsorbed halogens. We assume that these states were selected for both, the isolated models as well as the models with adsorbed halogens. Performing the calculations in the indicated electronic states for both, the adsorbed surface models as well as the isolated models, did not allow us to reproduce the results of Xu et al.; adsorption energies varied up to 20 kcal/mol. Nevertheless, we obtained the same order of the adsorption energies for the different surface models. This leads us to believe that they used this approach.

The ground state of model A has a spin multiplicity of 1 due to the even number of electrons in the system and the two-fold symmetry axis. However, for model B, Montoya et al. showed that the ground state has a spin multiplicity of 5 [2], in contrast to the results of Xu et al. who found a ground state with a spin multiplicity of 7.

Due to this discrepancy, we decided to re-evaluate the results of Xu et al. in order to investigate the impact on the adsorption energies. All calculations were performed with NWChem [3]. To be able to compare our results to those of Xu et al., we also used the B3LYP functional [4, 5] in the spin-unrestricted formulation. Xu et al. optimized the systems with the 3-21G(d) basis [6–8] and recalculated the energies of the resulting optimized structures with the bigger 6-31G(d) basis [6–8]. We decided to optimize the systems with the 6-31G(d) basis to avoid possible errors due to this approach. Additionally, all systems were optimized with the larger Def2-TZVP basis set [9] for better accuracy. All optimizations were performed in C1 symmetry to let the systems relax out of the plane if needed. For model B, all calculations were performed with spin multiplicities 3, 5, and 7; for model C, the spin multiplicities were 1, 3, and 5. VMD was used for visualization and image creation [10].

For model A, our results agree with Xu et al. Only the optimized distances between adsorbent and adsorbate are mostly longer. For the series F_2, Cl_2, and Br_2 the adsorption energies are 0.62 (-0.01), -0.01 (-0.01), and -0.01 (-0.01) kcal/mol for the basis 6-31G(d) (Def2-TZVP). The distances are 3.23 (4.15), 9.55 (9.58), and 10.91 (11.14) Å. However, since there is next to no interaction due to the missing dispersion interaction in the functional, this is likely caused by different convergence criteria. Since we found agreement for this model, we will no longer discuss these properties and refer to the original paper.

For the zigzag and armchair surface (models B and C), the relative energies of the different electronic states with respect to the ground state are given in Table 1. They were obtained with the 6-31G(d) basis to compare our results to Xu et al.

For model B, our results agree with Montoya et al.; the ground state has a spin multiplicity of 5. However, this state shows a significant amount of spin contamination. The expectation value of S^2 is 6.22 compared to the theoretical value of 6. To validate that the order of the electronic states is not wrong due to spin contamination, separate ROHF calculations were performed. In agreement with Montoya et al., the same order as presented in Table 1 was recovered. This gives us confidence that the unrestricted formulation of the used density functional yields reliable results.

For model C, the ground state has a spin multiplicity of 1. This state is 1.44 eV lower than the triplet state.

At this point, we want to reiterate that Xu et al. report ground state spin multiplicities of 7 and 3 for models B and C, respectively. This indicates some systematic error in their results due to the choice of excited states as references.

The optimized ground state structures for adsorption of F_2, Cl_2, and Br_2 on models B and C obtained with the basis Def2-TZVP are shown in Figures 2 and 3. In Table 2, the adsorption energies obtained with the two different basis sets are given. The reference values of Xu et al. are also given for comparison.

For model B, the ground state has a spin multiplicity of 3 after halogen adsorption due to the formation of two covalent bonds. Since Xu et al. chose an excited state as ground state for the adsorbed and the isolated surface models, this has a large impact on the adsorption energies. Our results are consistently higher by about 80 kcal/mol. This gives an error of 50-600% for the results of Xu et al.!

For model C, the ground state spin multiplicity of the adsorbed species depends on the adsorption site. For structures M3 and M5 the ground state has a spin multiplicity of 3. For M1, the energies of the singlet and the triplet state differ only by 0.004 eV. The singlet state is the ground state. This difference with respect to M3 and M5 is probably due to substantial spin contamination. The expectation value of S^2 is 1.03 compared to the theoretical value of 0. For the larger basis Def2-TZVP, the triplet state is the ground state. In addition, no spin contamination is observed for the singlet state. For M2, M4, and M6, the ground state has a spin multiplicity of 1. Our results for this surface show the same trend as Xu's. However, all our adsorption energies are lower. Depending on the system, the discrepancy is about 10-30 kcal/mol. This gives errors up to 42% for this surface.

Thus, Xu et al. chose the right ground state for the (001) surface, whereas they chose excited states for the other two investigated surfaces. This leads to adsorption energies of poor quality. We agree with Xu in the findings, that the order for the adsorption energies with respect to the halogens is $F_2 > Cl_2 > Br_2$. However, as can be seen in Table 2, the relative stabilities for adsorption on the zigzag and armchair surfaces show some important differences between our results and those of Xu et al. We find, that the halogens adsorb the strongest on the zigzag surface. For hydrogen, the same trend was shown by several authors [11, 12]. The second strongest adsorption is found on the armchair surface for the symmetric configurations (M2, M4, and M6), the third strongest for the asymmetric configurations (M1, M3, and M5).

Lifting symmetry restrictions for optimization of these structures is also important. This is especially true for the adsorption of Cl_2 and Br_2 on the zigzag surface. In C_S symmetry, the ground state has a spin multiplicity of 5. By performing the optimization in C_1 symmetry, the triplet becomes the ground state. We also want to point out that the reported adsorption energies with and without basis set superposition error (BSSE) in Table 1 on Xu et al. seem to be interchanged since correcting for the BSSE should result in lower adsorption energies.

To summarize, the determination of adsorption energies by Xu et al. seems to be flawed by several errors. By calculating the adsorption of halogens on graphite surface models in excited states, their adsorption energies differ up to 80 kcal/mol from our results. Even more so, their results are also qualitatively wrong. They predict stronger adsorption of the halogens on the armchair surface than on the zigzag surface. However, in fact the opposite behavior is observed as shown by our results. Our results show that in fact, the halogen systems show the same trend of stability as hydrogen. The zigzag surface binds the halogens the strongest. The adsorption energies for the armchair surface are significantly lower. Here, adsorption in the symmetric configuration is more stable than in the asymmetric one.

Acknowledgement

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Table 1: Total energies in eV of the different electronic states of the model systems relative to the ground state obtained with B3LYP/6-31G(d). ZZ denotes the model of the zigzag surface and AC the model of the armchair surface.

Table 2: Adsorption energies in kcal/mol for the different systems obtained with B3LYP/6-31G(d) and B3LYP/def2-TZVP, respectively. The results of Xu et al. are given for comparison. ZZ denotes the model of the zigzag surface and AC the model of the armchair surface.

Figure 1: Models for a) the (001) surface, b) the (100) surface, and c) the (110) surface.

Figure 2: Optimized geometries of adsorbed F_2 (M1 and M2), Cl_2 (M3 and M4), and Br_2 (M5 and M6) on the armchair surface of graphite. Distances are given in Å.

Figure 3: Optimized geometries of adsorbed a) F_2, b) Cl_2, and c) Br_2 on the zigzag surface of graphite. Distances are given in Å.

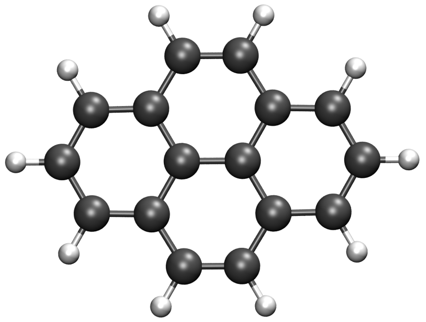
Table 1

	Multiplicity		
System	3	5	7
ZZ	1.07	0.00	1.04
F_2/ZZ	0.00	1.13	5.27
Cl_2/ZZ	0.00	1.05	4.36
Br_2/ZZ	0.00	1.05	6.37
	Multiplicity		
	1	3	5
AC	0.00	1.44	2.72
F_2/AC-M1	0.00	0.00(4)	1.39
F_2/AC-M2	0.00	1.40	2.79
Cl_2/AC-M3	1.78	0.00	1.60
Cl_2/AC-M4	0.00	1.43	2.87
Br_2/AC-M5	1.44	0.00	1.39
Br_2/AC-M6	0.00	1.41	2.83

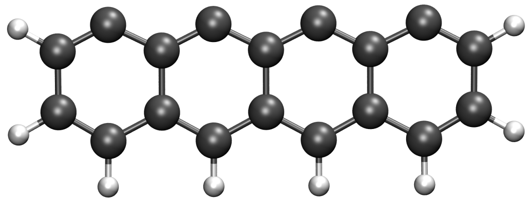
Table 2

System	6-31G(d)	def2-TZVP	Ref.[1]
F_2/ZZ	212.6	209.3	138.7
Cl_2/ZZ	124.4	118.1	48.2
Br_2/ZZ	100.2	97.1	17.3
F_2/AC-M1	149.9	142.5	177.7
F_2/AC-M2	185.0	179.6	201.4
Cl_2/AC-M3	51.1	40.5	61.9
Cl_2/AC-M4	103.1	94.1	116.1
Br_2/AC-M5	26.0	18.9	37.4
Br_2/AC-M6	80.0	74.3	82.0

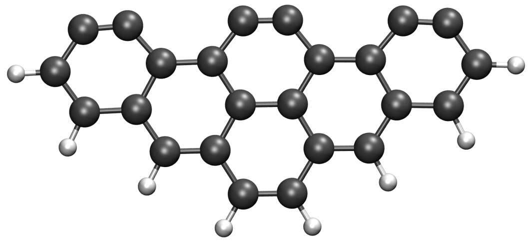
Figure 1



(a) Model A

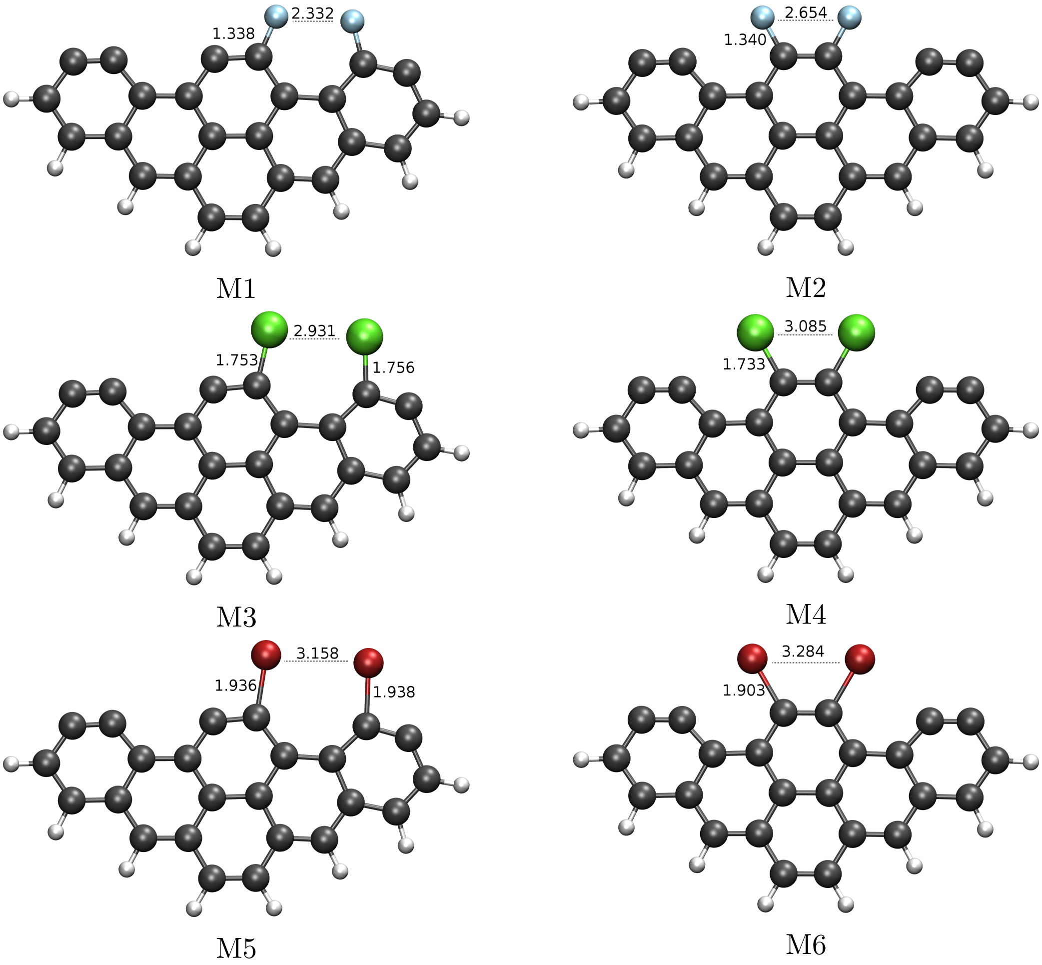


(b) Model B



(c) Model C

Figure 2



M1

M2

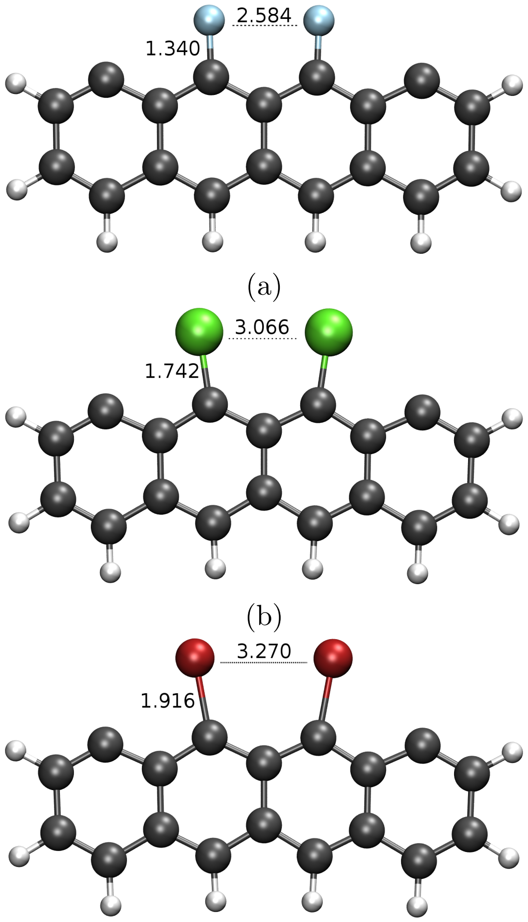
M3

M4

M5

M6

Figure 3



(a)

(b)

(c)