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Effect of Temperature on thermodynamic parameters and chemical properties at adsorption process nitrite on the Graphene Nano surface, density functional theory method

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Abstract

The project is comparing four types of calculation derived graphene. That two of these derivatives of graphene carbon nitrite connection created the difference is only in the state of Para and meta carbons connectivity state. But other derivatives first silicon-carbon alternatives in the meta and para position, then nitrite is added to the silicon. To evaluate the effect of silicon element to absorb energy and other thermodynamic parameters in the derivatives compared with them.

Keywords: nitrite, Graphene, silicon, thermodynamic parameters, Temperature

1 Introduction

Nano Structure Graphene has a single layer. Due to the extraordinary material properties and electrical conductivity thermal conductivity, high density, optical conductivity and mechanical properties of the material has become unique. The new solid-state system by these extraordinary properties as good candidates to replace silicon in the next generation of photonic and electronic segment is considered and hence the unprecedented attention in basic and applied research has attracted. Band gap energy range is said to be occupied by electrons and is important for electronic applications. Create a band gap in graphene electron energy range an essential prerequisite for the use of graphene transistors. the project to replace silicon in place of carbon in graphene are looking at changes, the removal of nitrite as a water pollutants is of unique importance enjoys, in this research project nitrite ion absorption by the nanostructured graphene impact on the absorption of silicon element is checked. In this research nitrite ion absorption by the nanostructured graphene impact on the absorption of silicon element is checked and then by replacing silicon instead of carbon in graphene in the same position again NO_2 molecules on silicon surface in two meta and para-connected mode, Different scenarios to optimize the geometry and the calculation of the energy consumption in order to calculate thermochemistry parameters were performed on them. The thermal energy of the cases studied, enthalpy, entropy, Gibbs free energy and thermal energy in the calculation of carbon and silicon case, and were compared. In this study, density functional theory and calculation method of calculating the level B3lyp / 6-31g and in the gas phase is done.
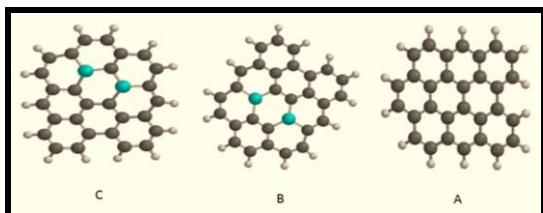

Figure 1. A: Ger B: Ger Si_2 Para C: Ger Si_2 Meta. Gray ball: C atom, Blue ball: Si atom

2 Research stage

To make the project easily be checked, four-derived graphene and abbreviations are defined separately.

A) First compound that is formed from 2 Nitrite is absorbed on the surface of Graphene (Ger) (Figure. 1) In the Para position relative to each other, with the Latin letter P is displayed

B) Second compound which consists of 2 Nitrite is absorbed on the surface of Graphene (Ger) (Figure. 1) In the meta position relative to each other , with the Latin letter M is displayed.

C) The third compound that consists of 2 Nitrite is absorbed on the surface of Ger Si_2 P (Figure. 1) In the meta position relative to each other ,with the Latin letter P* is displayed.

D) Fourth compound that consists of 2 Nitrite is absorbed on the surface of Ger Si_2 M (Figure. 1) In the meta position relative to each other , with the Latin letter M* is displayed Figure 2.
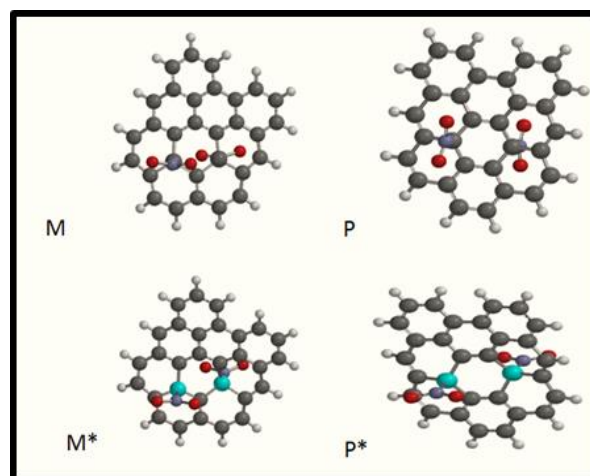

Figure 2. Derivatives investigated in this study P: Ger (NO2) 2 para, M: Ger (NO2) 2Meta, P*: Ger Si2 (NO2) 2 Para, M*: Ger Si2 (NO2) 2 Meta. Gray ball: C atom, Blue ball: Si atom

3 Calculation and Results:

3.1.Reviews the Energy Gap, Chemical potential, Chemical hardness, Electrophilicity and ΔN_{MAX}:

The calculations NBO, energy occupied the highest level (EHOMO) and the lowest unoccupied level (ELOMO)extract, and using mathematical equations, Chemical potential, Chemical hardness, Electrophilicity, ΔN_{MAX} and Energy Gap values is obtained.

The formula (1) in order to obtain chemical hardness (ŋ)was used.

$$\eta = \frac{E\,LOMO - E\,HOMO}{2} \qquad (1)$$

II. Meanwhile, using the formula (2) chemical potential(μ) of the compounds were calculated.

$$\mu = \frac{E\,LOMO + E\,HOMO}{2} \qquad (2)$$

III. The formula for calculate electrophilicity:

$$\omega = \frac{\mu 2}{\eta \times 2} \qquad (3)$$

IIII. The energy gap or distance between the level of HOMO and LUMO obtained from the following equation.

$$\mathbf{HLG = E_{HOMO} - E_{LUMO}} \qquad (4)$$

V. The rate of electron transfer reactions in the equation using the following equation can be obtained ΔN_{MAX}.

$$\Delta \mathbf{N_{MAX} = - (\mu/\eta)} \qquad (5)$$

HOMO and LUMO energy level values of the compounds tested are given in the table .1. HOMO and LUMO energy levels in Graphene in a meta-level connectivity silicon nitrite to show significant decline.

Table 1: amounts of HOMO and LOMO of derivatives investigated in this study calculated by DFT method

Compounds	E_{LOMO} (a.u)	E_{HOMO} (a.u)
P	0.139	-0.213
M	0.139	-0.213
P*	0.133	0.224
M*	0.035	0.145

Amounts of gap energy, chemical hardness, chemical potential, electrophilicity, dipole moment and ΔN_{MAX} in different connection with carbon and silicon nitrite graphene surface is given in the table 2.

Table 2: compares the energy gap, chemical hardness, chemical potential, electrophilicity, dipole moment and ΔN_{MAX} of derivatives investigated in this study calculated by DFT method

Compounds	P	M	P*	M*
ΔN_{MAX}	0.2102	0.2102	0.5098	0.611
dipole moment	1.0061	1.352	10.46	10.0522
electrophilicity	0.00389	0.00389	0.02319	0.0168
chemical potential	-0.037	-0.037	-0.091	-0.055
chemical hardness (a.u)	0.176	0.176	0.179	0.09
gap energy (a.u)	0.352	0.352	0.357	0.18

3.2 Review the amount of energy gap

Comparing the values of the energy gap so that, Energy gap in the compound P * (nitrite in Para state is connected to silicon graphene surface) than the rest, then in the case of P (technical connection to the graphene surface crane in Para state) and M (connection nitrite to carbon graphene level meta state) energy Gap equal value and in the case of M * (nitrite in meta silicon graphene surface is connected) has the lowest energy Gap, the difference between HOMO and less LUMO and electron transfer from the HOMO to LUMO will be easier than others.

The values show the following trends:

P* > (P = M) > M

The values obtained from the chemical hardness, with the same amount of energy gap.

3.3 The trend Values the chemical potential of the compounds studied:

Compare the values of the chemical potential can be seen, Negative chemical potential is a symbol of stability, In other words, the chemical potential in P * (nitrite in Para state is connected to silicon Graphene surface) is less than the rest, in the case of M * (nitrite in meta attached to the Graphene surface silicon) compared to P * value chemical potential is great. After P (technical connection to the Graphene surface crane in Para state) and M (nitrite connection to the Graphene surface carbon in Meta) chemical potential equal value, although the value is greater than before, as well as modes the values show the following trends:

P= M > M* > P*

3.4. Reviews the values of the dipole moment of the substances studied:

The amount of dipole moment in the M * (2 nitrite ion in Meta position to one another connected to silicon graphene surface) more than P * (nitrite in Para state silicon graphene surface is connected) . In the M (connection 2nitrite ion to carbon in the graphene surface at Meta position to one another) and case of P (nitrite in para position connected to Carbon of graphene surface) has a dipole moment are low. And the values indicate the following trends:

M* >P > P* > M

Study of adsorption enthalpy of binding compounds resulting nanostructure with nitrite and resulting from the replacement of silicon element in the meta and para position with nitrite. First Derivatives investigated in this study P: Ger (NO$_2$) 2 para, M: Ger (NO$_2$) 2Meta, P*: Ger Si$_2$ (NO$_2$) $_2$ Para, M*: Ger Si$_2$ (NO$_2$) 2 Meta

were optimized, in order to calculate the enthalpy of absorption , IR calculations were carried out, all calculations in the B3lyp/6-31g computational level, 298 temperature and 1 atmospheric pressure were performed. for investigating below reactions:
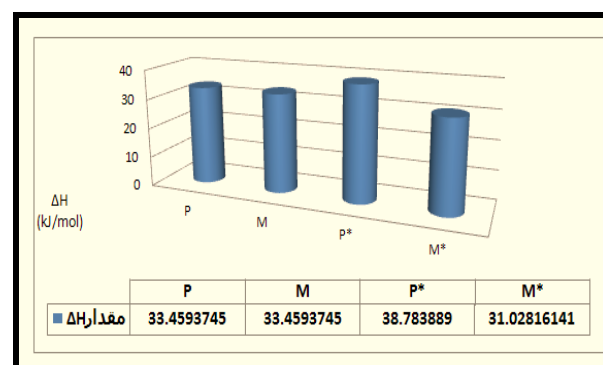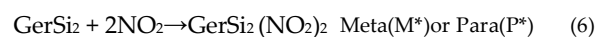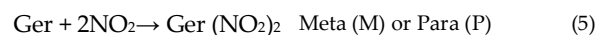
Ger + 2NO$_2$→ Ger (NO$_2$)$_2$ Meta (M) or Para (P)   (5)

GerSi$_2$ + 2NO$_2$→GerSi$_2$ (NO$_2$)$_2$ Meta(M*)or Para(P*)   (6)

	P	M	P*	M*
■ ΔH مقدار	33.4593745	33.4593745	38.783889	31.02816141

Chart table (1) compounds ΔH values P, M, P*and M*according kJ/mol

The values of ΔH indicates that the process of adsorption on Graphene reactions 5 and 6 , are the endothermic process Chart table (1).

4 The study of thermodynamic parameters at different temperatures

Using Spartan program, enthalpy, Entropy, heat capacity and Gibbs free energy values for Graphene (Ger), Ger (NO$_2$) $_2$ para (P), Ger (NO$_2$)$_2$ Meta (M), Ger Si$_2$(NO$_2$) $_2$ Para (P*), Ger Si$_2$ (NO$_2$) $_2$ Meta (M*) In the temperature range 300-400K Were calculated.

4.1 The first results of Enthalpy changes (H$^\circ$):

To evaluate the effect of temperature on thermodynamic parameters at first the enthalpy of compounds Case Study, In the temperature range 300-400K Were calculated and compared together. In all cases studied, Enthalpy values are increased with increasing temperature (table.3).

Table (3) Enthalpy (kJ/mol) values of Derivatives investigated in this study, calculated by DFT method.

Temperature	GER	M*	P*	M	P
300	1067.2885	1033.4139	1033.3604	1149.2798	1149.2745
310	1070.0561	1036.4249	1036.3759	1152.6715	1152.6665
320	1072.9363	1039.5439	1039.5059	1156.1694	1156.1644
330	1075.9289	1042.7515	1042.7142	1159.7923	1159.7873
340	1079.0337	1046.0718	1046.0074	1163.5394	1163.5344
350	1082.2449	1049.4658	1049.3899	1167.41	1167.4049
360	1085.5318	1052.9134	1052.8193	1171.4031	1171.398
370	1088.9048	1056.4441	1056.3105	1175.478	1175.4729
380	1092.386	1060.0441	1059.8815	1179.6119	1179.6092
390	1095.9287	1063.7217	1063.5575	1183.8051	1183.8029
400	1099.5593	1067.4959	1067.3375	1188.1138	1188.1116

2.3 The second results of Entropy (S°)

Then to evaluate the effect of temperature on entropy of compounds Case Study, In the temperature range 300-400K Were calculated and compared together. In all cases studied, Entropy values are increased with increasing temperature (table.4).

Table (4) Entropy values of Derivatives investigated in this study, calculated by DFT method

Temperature	Entropy(J/mol.K)				
	GER	M*	P*	M	P
300	480.5769	510.3413	504.852	564.6691	564.653
310	489.162	519.2591	513.7844	574.5534	574.537
320	497.6168	528.2573	522.7969	584.1512	584.136
330	506.1591	537.3293	531.8828	593.7354	593.72
340	514.7822	546.4685	541.0357	603.406	603.39
350	523.48	555.6688	550.2492	613.1554	613.14
360	532.1467	564.9241	559.5172	622.9765	622.961
370	540.7661	574.2285	568.8338	632.8195	632.807
380	549.4467	583.5764	578.1932	642.5602	642.548
390	558.1827	592.8071	587.517	652.3569	652.345
400	566.9685	602.0321	596.6278	662.2034	662.191

3.3 The third results of heat capacity (Cv)

To evaluate the effect of temperature on heat capacity of compounds Case Study, In the temperature range 300-400K Were calculated and compared together. In all cases studied, heat capacity values increase with increasing temperature (table.5).

Table (5) heat capacity values of derivatives investigated in this study, calculated by DFT method

Temperature	Cv(J/mol.K)				
	GER	M*	P*	M	P
300	289.0854	314.383	314.7937	376.1375	376.1359
310	300.528	325.9641	326.3851	388.9856	388.9842
320	311.9417	337.4878	337.9158	401.7662	401.7651
330	323.3117	348.9412	349.373	414.4663	414.4653
340	334.6241	360.312	360.7447	427.0731	427.0724
350	345.8658	371.5885	372.0197	439.5751	439.5746
360	357.0247	382.7598	383.1873	451.961	451.9607
370	368.0892	393.8158	394.2377	464.2206	464.2205
380	379.049	404.7472	405.1619	476.3445	476.3446
390	389.8945	415.5455	415.9516	488.3242	488.3244
400	400.617	426.2031	426.5995	500.1518	500.1522

4.3 The fourth results of Gibbs free energy(G°)

Then to evaluate the effect of temperature on entropy of compounds Case Study, In the temperature range 300-400K Were calculated and compared together in all cases studied, *the values of Gibbs free energy(G°) , are reduced with increasing temperature* (table.6).

Table (6) Gibbs free energy (G°) values of derivatives investigated in this study, calculated by DFT method

Temperature	G° (kJ/mol.K)				
	GER	M*	P*	M	P
300	923.1155	880.3115	881.9048	979.8791	979.8786
310	918.4159	875.4546	877.1027	974.5599	974.5601
320	913.6989	870.5015	872.2109	969.241	969.241
330	908.8965	865.4328	867.1928	963.8596	963.8598
340	904.0077	860.2725	862.0552	958.3814	958.3817
350	899.0269	854.9817	856.8027	952.8056	952.8061
360	893.959	849.5407	851.3931	947.1316	947.1322
370	888.8213	843.9795	845.842	941.3348	941.3343
380	883.5963	838.285	840.1681	935.439	935.4411
390	878.2374	832.527	834.4259	929.3859	929.3886
400	872.7719	826.6831	828.6864	923.2324	923.2352

5 Conclusion:

Compare enthalpy values for different scenarios studied indicate that the mode M* is more likely, the state P, M possible to achieve the same, P* is more difficult than others states. So adsorption on surface of composite Graphene-silicon (Meta) shows better adsorption than other derivatives investigated in this study.

6 Acknowledgments

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