



Original Research article

The AIM, RDG, NBO, Quantum and Structural Study of Adsorption of Phosgene Gas on the Surface of Pristine and Al, P Doped Ga₁₂N₁₂ Nano Cluster: A DFT Method



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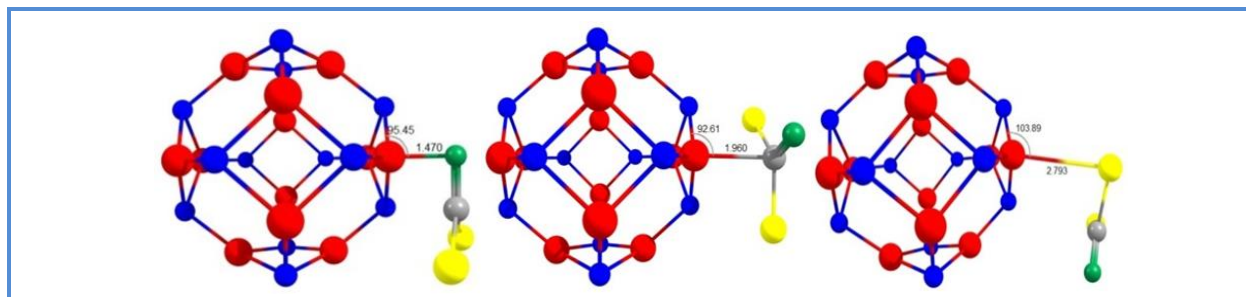
ABSTRACT

The main objective of this work is to study the sensitivity of pristine, Al, P and Al & P doped Ga₁₂N₁₂ to adsorb phosgene (COCl₂) molecule. The interaction of COCl₂ from O, C and Cl sites on the surface of Ga₁₂N₁₂ is investigated by applying the density functional theory (DFT) at the cam-B3LYP/6-31G(d) level of theory. The geometrical and electrical structures, quantum descriptive, thermodynamic parameters, solvent effect, atom in molecule theory (AIM), natural bond orbital (NBO), and the reduced density gradient (RDG) are calculated at the above level of theory. The calculated results indicate that the adsorption of COCl₂ on the surface of pristine and Al, P and Al & P doped Ga₁₂N₁₂ is exothermic, as well as Al-doped Ga₁₂N₁₂ is more favorable than P and Al & P doped. The recovery time results for adsorption of COCl₂ from O site on the surface of Ga₁₂N₁₂, Al-Ga₁₁N₁₂, Ga₁₂N₁₁P and Al-Ga₁₁N₁₁P are 0.103, 4.69×10⁻⁷, 3.81×10⁻¹² and 4.31×10⁻⁷ respectively. As a result, these nanoclusters can be used as sensor devices toward COCl₂ molecule.

The deformation energy results reveal that the structural change of Ga₁₂N₁₂ and COCl₂ at all adsorption states are not significant. The AIM, RDG and NBO results demonstrate that the intermolecular interaction from O site of COCl₂ on the surface of pristine, Al, P and Al & P doped Ga₁₂N₁₂ is stronger than C and Cl atoms sites of COCl₂ as it is an electrostatic attractive type.

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Graphical Abstract



Introduction

Phosgene (COCl_2) is a colorless and nonflammable gas. It is a very reactive and highly toxic gas, its odor resembles freshly cut grass. Phosgene is used as an industrial reagent in the synthesis of organic compounds, pharmaceuticals, chemical weapon, and intermediate in the production of isocyanates, carbamoyl chlorides, carbazates, chloroformates, thiochloroformates, carbamates, urethanes, azo dyes, oxazolidinediones and other compounds [1–3]. In the industrial manufacture, small amounts of phosgene were produced from combustion and breakdown organochlorine compounds. COCl_2 vapors are strongly poisonous and cause disease in eye and breathe system such as coughing, chest tightness, choking, and coughing [4]. In addition, COCl_2 reacts with enzymes and proteins in biological systems and cause formation of covalent adducts in molecular functions and so the activity of enzymes decreases and may lead to loss cellular function and cell death [5]. The computational results of Raissi *et al.*, [6] showed that COCl_2 molecule adsorbed on the pristine AlNNTs through weak van der Waals interaction means that the adsorption is physisorption process.

Due to the environmental pollution, effective and inexpensive systems such as novel nanomaterial are used for detection and absorption of toxic and dangerous compounds from environmental system. The novel nanomaterial, which is made from third and fifth elements of the periodic table, attracted the attention of many scientists for this means [7–18]. One of them is gallium nitride nanotube. The single-crystal GaN nanotubes (GaNNTs) were successfully synthesized in 2003 using epitaxial casting approach [19]. Theoretical studies have shown that the band gap of GaNNTs is about 2 eV and independent of their chirality [20–21]. Yang *et al.*, using DFT, found a band gap of 1.72 eV for zigzag GaNNTs with 5.35 Å diameter, and this study indicated that the band gap of GaNNTs increases with the diameter size [22]. Khaddeo *et al.*, [23] reported that single atomic layer GaNNTs have smaller band gap than multi atomic layers. In recent years, much attention has been focused on the physical and chemical absorption of materials on the surface of GaN nanotube

[24–26]. Recent research results showed that adsorption of oxygen, hydrogen, NH₃, NO₂, and Si on the surface of GaNNTs is more favorable than other nanotubes; this nanotube can be a good adsorbent for these compounds [27–31]. In the previous work we studied the interaction of isoniazid drug with the pristine and Ni-doped of (4, 4) armchair GaNNTs [32]. The results of our study demonstrated that Ni-doped GaNNTs decrease adsorption strength of isoniazid drug on the surface of nanotube. After our previous studied [33–35], in the current project we decided to investigate the interaction of phosgene gas on the surface of pristine and Al and P doped GaN nanocluster (Ga₁₂N₁₂) using density functional theory. At the first step, we considered various different positions for adsorbing COCl₂ molecule on the surface of GaN nanotube. After full optimization of all considered models, the stable structures without any imaginary frequency are selected. By using the selected structures the electrical and geometrical properties of COCl₂/Ga₁₂N₁₂ are investigated. The results of this project may be useful for finding and making novel adsorbent or sensor for phosgene molecule.

Material and methods

Computational aspects

In this work, for simplicity of our study, at the first step the indexes **a**, **b** and **c** are applied for determining COCl₂ molecule adsorption orientation from O, C and Cl atoms respectively (see Figure 1). The pristine and Al, P and Al&P doped Ga₁₂N₁₂ nano cluster is denoted by A, B, C and D models (see Figure 2). All adsorption models (A-a, A-b, A-c, B-a, B-b, B-c, C-a, C-b, C-c, D-a, D-b and D-c) are optimized using density functional theory (DFT) at B3LYP [36–37] and coulomb-attenuating method (CAM-B3LYP) level of theory [38] at the 6-31G* basis set with performing the Gaussian 09 suite of programs [39]. All adsorption models are optimized with optimization criteria (Max force=0.000014, RMS force=0.000003, Max displacement=0.00072 and RMS displacement=0.000093) and confirmed that all the stationary points correspond to true minima on the potential energy. From the optimized structures, the adsorption energy (E_{ads}) of COCl₂ on the Ga₁₂N₁₂, Al Ga₁₁N₁₂, Ga₁₂N₁₁P, and Al Ga₁₁N₁₁P clusters is determined by:

$$E_{ads} = E_{Nanocluster/COCl_2} - E_{Nanocluster} - E_{COCl_2} + BSSE \quad (1)$$

where $E_{Nanocluster/COCl_2}$, $E_{Nanocluster}$ and E_{COCl_2} are total energies of COCl₂/(Ga₁₂N₁₂, Al Ga₁₁N₁₂, Ga₁₂N₁₁P, Al Ga₁₁N₁₁P) complex, pure nanocluster and COCl₂, respectively. The adsorption energies of all studied models are corrected by the basis set superposition error (BSSE) based on the counterpoise correction [40].

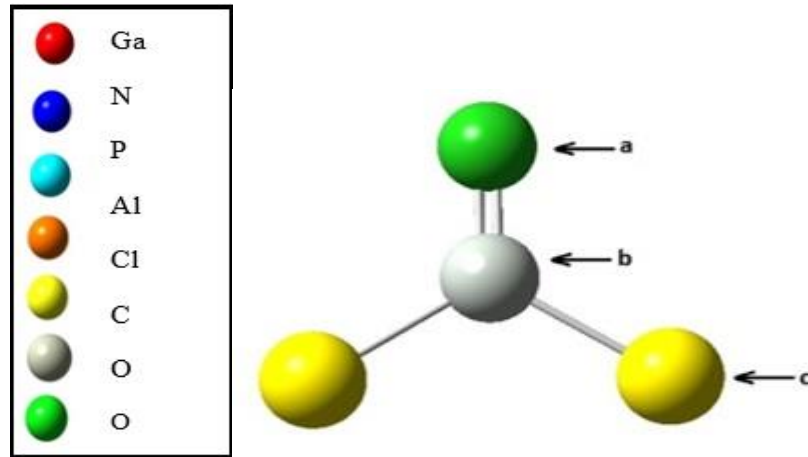


Figure 1. The adsorption positions of COCl_2 molecule on the surface of $\text{Ga}_{12}\text{N}_{12}$ nano cluster

The deformation energy (E_{def}) contributions [41], which are occurred during the adsorption process for nanocluster, COCl_2 and the $\text{COCl}_2/\text{nanocluster}$ complex are calculated by Eqs. (2-5):

$$E_{\text{def Ga}_{12}\text{N}_{12}} = E_{\text{Ga}_{12}\text{N}_{12}\text{ free}} - E_{\text{Ga}_{12}\text{N}_{12}\text{ in complex}} \quad (2)$$

$$E_{\text{def COCl}_2} = E_{\text{COCl}_2\text{ free}} - E_{\text{COCl}_2\text{ in complex}} \quad (3)$$

$$E_{\text{int}} = E_{\text{Ga}_{12}\text{N}_{12}/\text{COCl}_2} - (E_{\text{Ga}_{12}\text{N}_{12}\text{ in complex}} + E_{\text{COCl}_2\text{ in complex}}) \quad (4)$$

$$E_{\text{def /complex}} = E_{\text{ads}} - E_{\text{int}} \quad (5)$$

where $E_{\text{Ga}_{12}\text{N}_{12}\text{ in complex}}$ and $E_{\text{COCl}_2\text{ in complex}}$ is the total energy of $\text{Ga}_{12}\text{N}_{12}$ and COCl_2 in the $\text{COCl}_2/\text{Ga}_{12}\text{N}_{12}$ complex. The $E_{\text{def Ga}_{12}\text{N}_{12}}$, $E_{\text{def COCl}_2}$, and $E_{\text{def complex}}$ are the deformation energy of $\text{Ga}_{12}\text{N}_{12}$, COCl_2 and $\text{COCl}_2/\text{nanocluster}$ complex in its optimized geometry.

The HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) are performed for study the electrical properties of $\text{COCl}_2/\text{nanocluster}$ complex. From HOMO and LUMO energies the physical properties such as gap energy, electrochemical potential (μ), chemical hardness (η), and maximum amount of electronic charge ΔN [42–44] are calculated by Eqs. (6-9)

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (6)$$

$$\mu = (E_{\text{LUMO}} + E_{\text{HOMO}}) / 2 \quad (7)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (8)$$

$$\Delta N = -\mu / \eta \quad (9)$$

The thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) and Gibbs free energy solution (ΔG_{sol}) are calculated by Eq. 10:

$$\Delta Q = Q_{\text{Nanocluster}/\text{COCl}_2} - Q_{\text{Nanocluster}} - Q_{\text{COCl}_2} \quad Q : G, H, S \quad (10)$$

Here $Q_{\text{nanocluster}/\text{COCl}_2}$, $Q_{\text{nanocluster}}$ and Q_{COCl_2} are the total thermodynamic parameters of $\text{COCl}_2/\text{nanocluster}$ complex, free nanocluster and free COCl_2 molecule respectively.

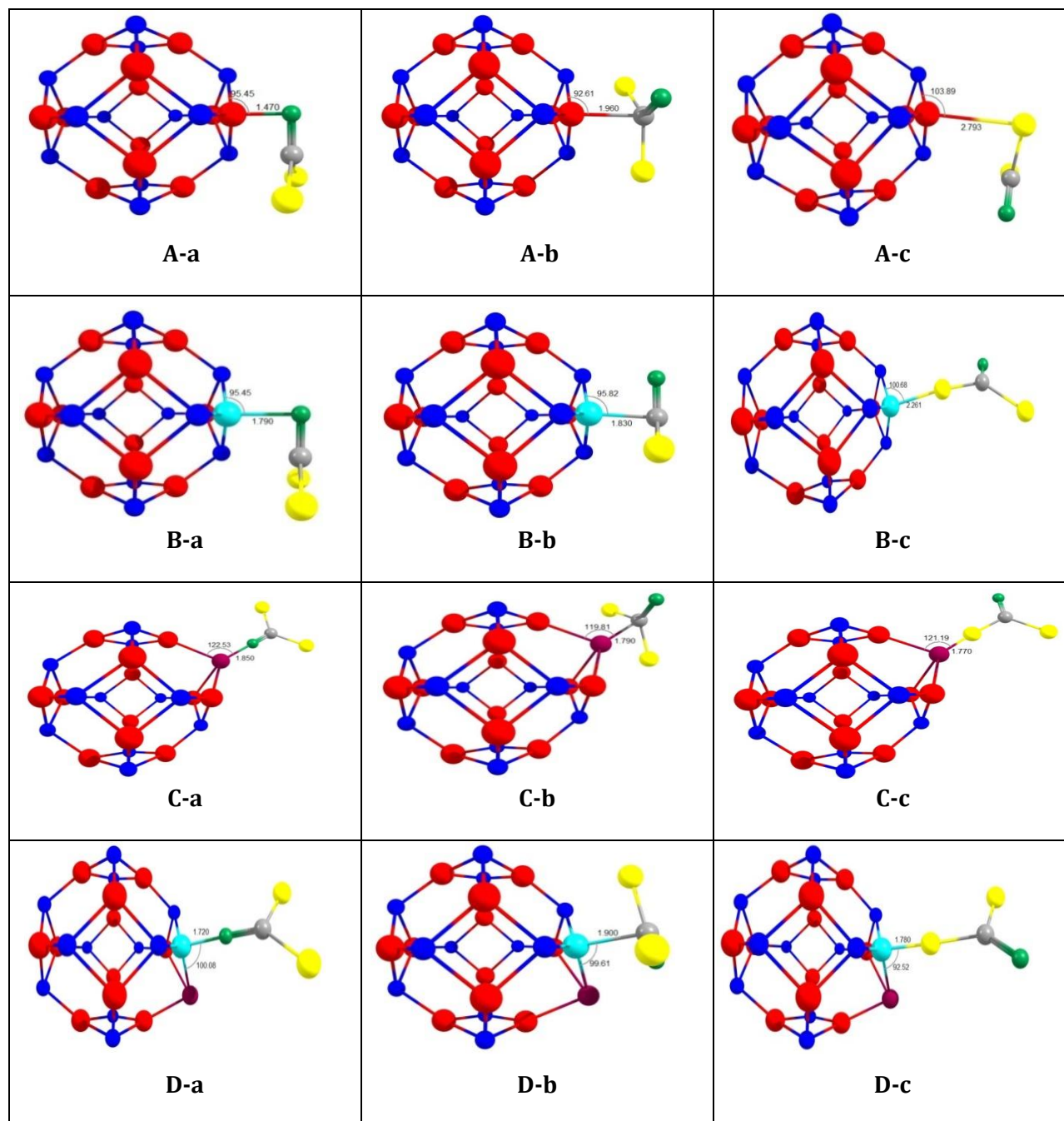


Figure 2. 2D views of COCl_2 molecule adsorption on the surface of pristine, Al, P and Al&P doped Ga₁₂N₁₂ for A-a to D-c adsorption models

Results and discussion

The structural geometry and energetics properties

The optimized structure of the A-a to D-c adsorption models are shown in Figure 2. According to the calculated geometrical properties, the average Ga–N bond length in six tetragonal and eight hexagonal GaN ring around doping site in the pristine, Al Ga11N12, Ga12N11P and Al Ga11N11P are (1.92, 1.85), (1.85, 1.79), (2.38, 1.85), and (2.39, 1.79) respectively (see the Figures S1-S2 in supplementary data). This result is in agreement with other reports [24–28, 32].

The dipole moment of the pristine, Al Ga11N12, Ga12N11P and Al Ga11N11P are 0.0085, 0.5138, 0.3257 and 0.7112 Debye respectively. The average Ga–N bond length in six tetragonal and eight hexagonal GaN ring in the A-a, B-a, C-a and D-a models are (1.94 and 1.86 Å), (1.87, 1.81), (2.35, 1.85) and (2.43, 1.81) respectively (see the Figures S1-S2 in supplementary data). The dipole moment of A-a, B-a, C-a and D-a models are 4.098, 6.449, 4.966 and 7.344 Debye respectively. From NBO results, it is found that the NBO charges of Ga and N atoms in pristine Ga12N12 are 1.627 and -1.627 |e| respectively, the hybridization of Ga atom in the Ga–N bonds is $SP^{4.46}$. In the Al doped model the NBO charge of Ga, N and Al atoms in doping position Al Ga11N12 are 1.627, -1.701 and 1.871 |e| respectively, the hybridization of Ga atom in the Ga–N bonds is $SP^{1.29}$. In the pdoped model the NBO charge of Ga, N and P-doped in Ga12N11P are 1.371, -1.645 and -0.774 |e| respectively, the hybridization of Ga atom in the Ga–N bonds is $SP^{1.96}$. In the Al & P doped the NBO charge of Ga, N and Al & P-doped in Al Ga11N11P are 1.353, -1.748 , 1.660 and -0.876 |e| respectively, the hybridization of Ga atom in the Ga–N bonds is $SP^{5.25}$. Comparison results indicate the NBO charge of Ga and N atoms in the P doped state is lower than pristine and Al doped, because the electronegativity of P (2.19) atom is more than Al (1.61) atom.

On the other hand with adsorbing $COCl_2$ molecule, the NBO outcomes for A-a, B-a, C-a and D-a models reveal that the NBO charge of Ga and N atoms in $COCl_2/Ga12N12$ complex are (1.635 and -1.677), (1.610, -1.714), (1.328, -1.680) and (1.631, -1.758) |e| respectively. The hybridization of Ga atom in the Ga–N bonds in the A-a, B-a, C-a and D-a models in the adsorption position are $SP^{4.37}$, $SP^{1.98}$, $SP^{1.75}$ and $SP^{5.12}$ respectively. These results indicate that the NBO charge of Ga and N atoms of pristine and doped Ga12N12 nanocluster after adsorbing $COCl_2$ alter slightly from unadsorbed structure.

According to calculated results of the A-a to D-c adsorption model (Figure 2) the bond distance between $COCl_2$ and nanocluster in the **a**, **b** and **c** orientation of $COCl_2$ (Figure 1) are in order:

C-a (1.85 Å)>B-a (1.79 Å)>D-a (1.72Å)>A-a (1.47Å); A-b (1.96 Å)>D-b (1.90Å)>B-b (1.83Å)>C-b (1.79Å); A-c (2.79Å)> B-c (2.26Å)> D-c (1.78Å)> C-a (1.77Å). On other hand, based on the results of Table 1, the dipole moment is in order: D-a>B-a>C-a>A-a; D-b>B-b>A-b>C-b; B-c>D-b>A-c>C-c. Comparison results indicate that the dipole moment of the D-a model is more than other models and the C-c model is lower than other models.

The calculated adsorption energy and deformation energy of A-a to D-c models are tabulated in Table 1. The calculated results indicate that the adsorption energy values of all adsorption models are negative and exothermic. It is notable that the adsorption energy of B-a model (-17.71 Kcal/mol) is more than other models whereas the adsorption energy of C-a model (-0.97 Kcal/mol) is lower than other models. The order of adsorption energy in the **c** orientation of COCl₂ is: B-c (-17.38 Kcal/mol)>A-c (-17.01Kcal/mol)>C-c (-15.26 Kcal/mol)>D-c (-12.72 Kcal/mol). This result reveals that the adsorption of COCl₂ on the surface of Al doped Ga₁₂N₁₂ nanocluster is more favorable than P and Al & P doped. To further understand the sensivity of pristine and doped Ga₁₂N₁₂ toward COCl₂ molecule as a sensor device, the recovery time ($\tau = \nu^{-1} \exp^{(-E_{ads}/kT)}$) at 298.15 K is calculated. The calculated results for adsorption of COCl₂ at the A-a, B-a, C-a and D-a models are 0.103, 4.69×10^{-7} , 3.81×10^{-12} and 4.31×10^{-7} . These results confirm that pristine, Al, P and Al & P doped Ga₁₂N₁₂ are a good candidate to making sensor device toward COCl₂ molecule.

Based on the calculated results of Table 1, the deformation energy values of Ga₁₂N₁₂, COCl₂, for all adsorption models are negative. This result confirms that the curvature of structure of COCl₂ and nanocluster is spontaneously from original state. The deformation energy of Ga₁₂N₁₂ is in range -0.24 to -1.85 Kcal/mol and for COCl₂ is in range -0.15 to -1.65 Kcal/mol. Inspection of deformation energy results reveal that the structural deformation amount of Ga₁₂N₁₂ and COCl₂ is not significant. The total deformation energy of Ga₁₂N₁₂/COCl₂ complex at the all adsorption models are positive and are in range 0.25 to 3.48 Kcal/mol, and the interaction energy (E_{bin}) for all adsorption models are negative in range -1.23 to -20.53 Kcal/mol. Comparison results show that the structural deformation of COCl₂ and Ga₁₂N₁₂ and interaction energy (E_{bin}) in the C-c models is lower than other models.

The thermodynamic parameters and solvent effect of all adsorption models are calculated based on the cam-B3LYP level of theory at the 6-31 G(d) base set and the results are listed in Table 2.

Close inspection of results indicate that the enthalpy (ΔH) and entropy (ΔS) of all adsorption models are negative and exothermic. The values of the standard enthalpy indicate that formation of COCl₂/ Ga₁₂N₁₂ complexes in all adsorption models is enthalpically favored (exothermic).

Table 1. Adsorption, deformation energies of GaNNTs, COCl₂ and total complex; and binding energy for A-a to D-c adsorption models

μ (dipole) Debye	E _{ads}	E _{def tot}	E _{Bin}	E _{def COCl₂}	E _{def Ga_{12N}₁₂}	property
4.09	-14.97	1.87	-16.84	-0.96	-0.90	A-a
5.66	-10.62	2.53	-18.69	-1.18	-1.35	A-b
2.16	-17.01	1.12	-11.66	-0.71	-0.40	A-c
6.49	-17.71	3.50	-20.51	-1.65	-1.84	B-a
6.50	-16.98	3.48	-20.53	-1.65	-1.85	B-b
2.98	-17.38	1.76	-9.48	-1.23	-0.53	B-c
4.96	-0.97	1.98	-14.96	-0.91	-1.07	C-a
4.81	-11.94	1.43	-10.81	-1.29	-1.13	C-b
1.31	-15.26	0.25	-1.23	-0.15	-0.24	C-c
7.39	-7.66	2.61	-14.55	-0.99	-1.62	D-a
6.59	-10.82	3.17	-18.44	-1.52	-1.65	D-b
2.69	-12.72	1.37	-9.04	-1.06	-0.30	D-c

Table 2. Thermodynamic parameters and solvent energy for A-a to D-c adsorption models

	ΔG_{sol} (kcal/mol)	ΔS (cal/mol-K)	ΔG (kcal/mol)	ΔH (kcal/mol)
A-a	-13.78	-4.11	-34.27	4.27
A-b	-14.85	-4.02	-36.30	3.55
A-c	-9.40	0.68	-33.82	0.63
B-a	-15.79	-4.86	-36.56	3.89
B-b	-15.79	-4.89	-36.55	3.89
B-c	-13.74	-3.74	-33.52	-1.87
C-a	-11.73	-1.29	-34.99	1.16
C-b	-16.27	-6.38	-33.18	5.43
C-c	-5.41	2.21	-25.65	-7.09
D-a	-11.93	1.44	-44.84	-3.36
D-b	-14.03	-2.90	-37.03	1.83
D-c	-6.60	3.63	-34.34	-2.49

The Gibbs free energy (ΔG) of the A-c, C-c, D-a and D-c models in gas phase are positive and so the adsorption of COCl₂ on the surface of Ga_{12N}₁₂ are unspontaneous in thermodynamic approach. Whereas the Gibbs free energy (ΔG) of other adsorption models in gas phase is negative and spontaneous. On the other hand the solvent Gibbs free energy (ΔG_{sol}) in the aqueous phase of the B-c, C-c, D-a and D-c models are negative, and at the other adsorption models are positive. The positive amounts of ΔG_{sol} indicate that the adsorption process of COCl₂ on the surface of Ga_{12N}₁₂ in aqueous phase is unspontaneous in thermodynamic view of point.

From thermodynamic results the infrared (IR) spectrum for A-a to D-c adsorption models are determined, the calculated results are shown in Figure S3 in supplementary material. According to IR spectrum in Figure S3, at the frequencies 750, 850 and 1900 cm⁻¹, three peaks with maximum intensity are observed, so that with doping of Al, P, Al & P atoms, the numbers of peaks of system change significantly from original states.

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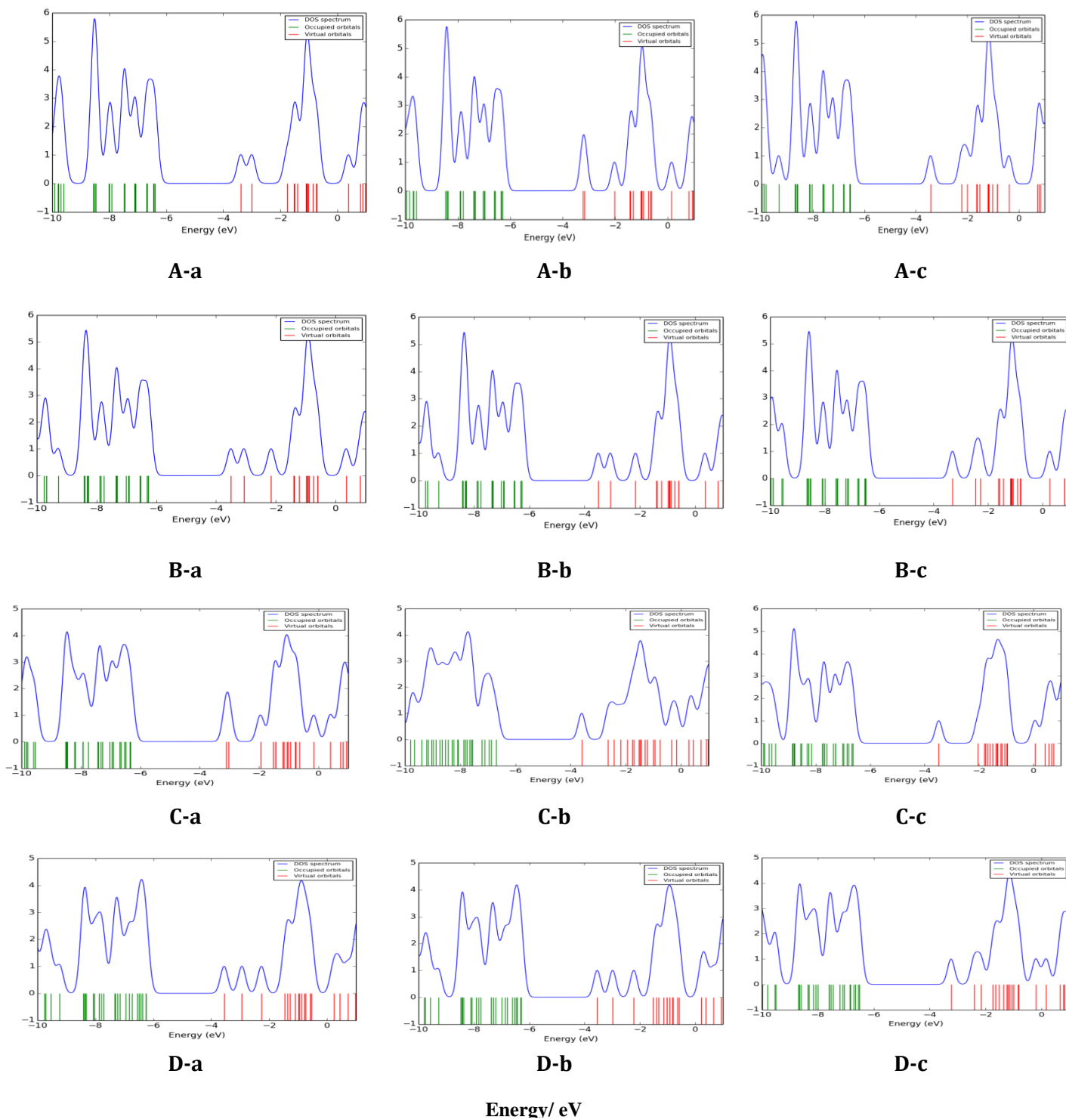


Figure 3. The DOS plots of COCl2 molecule adsorption on the surface of pristine, Al, P and Al&P doped Ga12N12 for A-a to D-c adsorption models

Quantum parameters

To further study the electronic nature of the interaction between COCl_2 and pristine, Al, P, and Al & P doped Ga12N12 nano cluster, the HOMO and LUMO orbitals of all adsorption models are calculated, and the results are shown in Figure S4 in supplementary material.

Comparison results of all adsorption models indicate that the most density of HOMO orbital are localized around nano cluster surface and the most density of LUMO orbital are distributed around COCl_2 molecule and the adsorption position. For this means, the surface of nanocluster is a good surface for attraction electrophilic compound.

By using HOMO and LUMO energies the gap energy, electrochemical potential (μ), chemical hardness (η), electrophilicity (ω), and maximum amount of electronic charge ΔN are calculated by Eqs. (6-11) and the calculated results are listed in Table 3. One the significant parameter to determine the chemical activity of Ga12N12 nanocluster in presence of COCl_2 is gap energy. It is well known that a large gap indicates high stability and low chemical reactivity and a small gap shows low stability and high chemical reactivity [45–47]. According to calculated gap energy, it can be seen the gap energy of the **a** orientation (O head of COCl_2) at the all adsorption models are smaller than the **c** orientation (Cl head of COCl_2). In addition, with doping Al atom the gap energy of $\text{COCl}_2/\text{Ga12N12}$ complex decrease significantly from pristine and P doped Ga12N12, and so according to $\sigma \propto A \exp^{(-E_{\text{gap}}/kT)}$ the reactivity and electrical conductance of Al doped Ga12N12 is more than other states.

The global hardness of system is a measure of the resistance of a system to change its electronic configuration, while electronic chemical potential is a measure of escaping tendency of an electron cloud [48–49]. The global hardness and electronic chemical potential values of all adsorption models are in range (1.34 to 1.64 eV) and (–4.71 to –5.14 eV). These results indicate that similar to gap energy the global hardness of adsorption of COCl_2 on the surface of Al-doped Ga12N12 is lower than other models and so the change of electronic properties of this system more than other models. The negative values of chemical potential reveal that the structures of $\text{COCl}_2/\text{Ga12N12}$ nanocluster are stable. The electron transfer parameters (ΔN) is used to explain the rate of interaction and stability of system. For a special interaction, the value of (ΔN) is useful to determine the donor-acceptor systems, and the direction of spontaneous electron flow. According to our results, the numerical value of ΔN for all adsorption models (A-a to D-c models) are positive in range 3.06 to 6.68. The positive values of ΔN indicate that the COCl_2 acts as an electron donor. It is notable that the values of ΔN for adsorption of COCl_2 on the surface P-doped Ga12N12 (C-a to C-c

models) are larger than other models, and so the donor properties of COCl_2 at these models are more than other adsorption models.

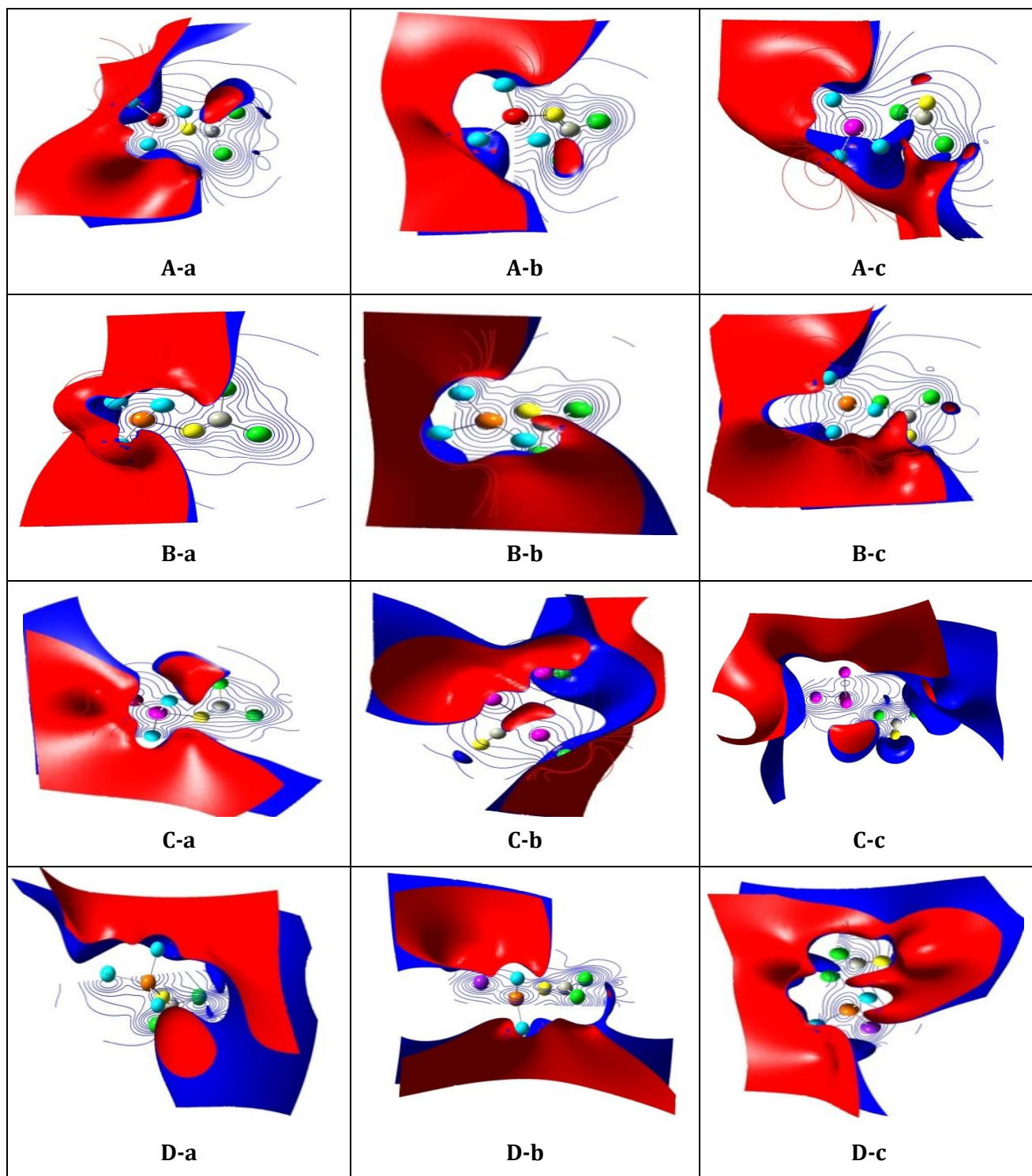


Figure 4. The MEP Plots of COCl_2 molecule adsorption on the surface of pristine, Al, P and Al&P doped $\text{Ga}_{12}\text{N}_{12}$ for A-a to D-c adsorption models

These results are in a good agreement with the positive values of NBO and Mulliken charge of COCl_2 . Moreover, these results confirm that the charge transfer occurs from COCl_2 toward to nanocluster surface.

In order to investigate the electronic properties of $\text{COCl}_2/\text{Ga}_{12}\text{N}_{12}$ complex, the densities of states (DOS) of complex have been calculated and presented in Figure 4. The results of DOS plots indicate that the conduction levels of Al-doped $\text{Ga}_{12}\text{N}_{12}$ in the B-a and B-b models shift toward lower energies compared to those of the pristine and P-doped $\text{Ga}_{12}\text{N}_{12}$. According to DOS plots, at the all adsorption models in the HOMO and LUMO region it can be seen 6 peaks. In the C-a, C-b and C-c models with doping P atoms the scheme and altitude of DOS peaks change significantly from pristine models, whereas the scheme and altitude of DOS peaks at the Al-doped alter slightly from original states. These results display the high sensitivity of electronic properties of P-doped $\text{Ga}_{12}\text{N}_{12}$ nano cluster towards the adsorbed COCl_2 . Therefore, the presence of the COCl_2 molecule can be detected by calculating the conductivity change of the nanocluster before and after the COCl_2 adsorption.

Table 3. Quantum parameters, NBO and Mulliken charge of COCl_2 for A-a to D-c adsorption models

	D-c	D-b	D-a	C-c	C-b	C-a	B-c	B-b	B-a	A-c	A-b	A-a
E(HOMO)/ev	-6.39	-6.29	-6.54	-6.26	-6.26	-6.49	-6.32	-6.68	-6.63	-6.24	-6.29	-6.51
E(LUMO)/ev	-3.38	-3.21	-3.42	-3.50	-3.50	-3.30	-3.11	-3.59	-3.37	-3.55	-3.54	-3.23
E(gap)\ev	3.00	3.07	3.11	2.75	2.75	3.18	3.21	3.09	3.26	2.69	2.75	3.28
μ / eV	-4.89	-4.75	-4.98	-4.88	-4.88	-4.89	-4.71	-5.14	-5.05	-4.89	-4.91	-4.87
η /eV	1.49	1.53	1.55	1.37	1.37	1.59	1.60	1.54	1.58	1.34	1.37	1.64
ΔN /eV	3.26	3.09	3.19	3.53	3.54	3.07	6.32	6.68	6.63	6.24	6.29	6.51
NBO/ e	0.10	0.13	0.12	0.13	0.13	0.13	0.25	0.19	0.18	0.12	0.13	0.12
Mulliken/ e	0.11	0.13	0.12	0.16	0.16	0.13	0.22	0.34	0.22	0.16	0.16	0.18

Natural bond orbital (NBO) population analysis

To investigate intra and intermolecular bonding and interaction among bonds, charge transfer or conjugative interaction in molecular systems, the natural bond orbital (NBO) [50] parameters for all adsorption models are calculated at the cam-B3LYP level of DFT theory and the calculated results are tabulated in Table 4.

For this means the stabilization energy ($E^{(2)}$) associated with the donor orbital (i) and acceptor orbital (j) is calculated by Eq.:

$$E^{(2)} = q_i \frac{F_{ij}^2}{\epsilon_j - \epsilon_i} \quad (11)$$

Here, ε_i and ε_j are orbital energies, F_{ij} is the off-diagonal NBO Fock matrix element and q_i is donor orbital occupancy. The value of $E^{(2)}$ illustrates the nature of interaction between donor orbital electron and acceptor orbital electron, and the greater the extent of conjugation of the whole system. Inspection of calculated results in Table 4 indicates that the strongest intermolecular interaction in the A-a and B-a model occurs in the $\sigma N_1-Ga_1 \rightarrow \sigma^* N_8-Ga_2$ with $E^{(2)}$ values 5.75 and 7.69 Kcal/mol respectively. Wherein the strongest intermolecular interaction for the C-a model occurs in the $\sigma N_1-Ga_1 \rightarrow \sigma^* N_2-Ga_1$ with $E^{(2)}$ value 7.40 Kcal/mol, and for the D-a model occurs in the $\sigma N_1-Ga_2 \rightarrow \sigma^* N_1-Ga_1$ with $E^{(2)}$ value 4.38 Kcal/mol. Whereas the lowest intermolecular interaction occurs for A-b and B-b models in the $\sigma N_1-Ga_2 \rightarrow \sigma^* N_1-Ga_2$ with 1.24 and 1.81 Kcal/mol and the $E^{(2)}$ value for C-b model in the $\sigma N_1-Ga_2 \rightarrow \sigma^* N_1-Ga_2$ is 0.27 Kcal/mol. In addition, the $E^{(2)}$ value for D-b model in the $\sigma N_1-Ga_2 \rightarrow \sigma^* N_2-Ga_2$ is 2.43 Kcal/mol. These results demonstrate that the intermolecular interaction from O site of $COCl_2$ on the surface of pristine, Al, P and Al & P doped Ga12N12 is stronger than C and Cl atoms site of $COCl_2$. Noticeably, the adsorption and interaction of $COCl_2$ on the surface of Al doped Ga12N12 is more suitable than other models; this result is in a good agreement with adsorption and thermodynamic energies.

Molecular electrostatic potential (MEP)

The molecular electrostatic potential is a useful method to investigate the total charge distribution of the molecule. This property is used to display molecular size, shape as well as positive, negative, and neutral electrostatic potential regions in terms of color grading and physiochemical property system [51]. The calculated MEP plots for all adsorption models are shown in Figure 4. In the Figure 4, the red color represents regions of most negative electrostatic potential and blue color represents regions of most positive electrostatic potential. It is clearly observed that at all adsorption models (A-a to D-c model) the most negative charge (red color) is localized around Ga12N12 nano cluster and the most positive charge (blue color) is distributed around $COCl_2$ molecule. This result indicates that the highest electron transfer occurs between Ga12N12 nanocluster and $COCl_2$ molecule, resulting in a strong interaction between $COCl_2$ and nanocluster. The charge transfer occurring in the Al doped Ga12N12 nano cluster is more than other models specially at the orientation of O site of $COCl_2$

molecule. It can be concluded that the electron rich O atom of COCl_2 strongly tends to interact with nanocluster.

Table 4. The perturbation second order energy for donor and acceptor orbital, for A-a to D-c adsorption models

	F(i, j)	E(j)-E(i)	E ² (kcal/mol)	Acceptor	Donor
A-a	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	5.75	0.63	0.054
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	1.76	0.60	0.029
A-b	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	4.47	0.63	0.048
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	1.24	0.61	0.025
A-c	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	0.52	0.54	0.015
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	2.60	0.56	0.035
B-a	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	7.69	0.65	0.063
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	1.83	0.79	0.034
B-b	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	7.65	0.65	0.063
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	1.81	0.79	0.034
B-c	$\delta N_1 Ga_1$	$\delta^* N_8 Ga_2$	8.61	0.63	0.066
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_2$	2.37	0.77	0.038
C-a	$\delta N_1 Ga_1$	$\delta^* N_2 Ga_1$	7.40	0.48	0.054
	$\delta N_1 Ga_1$	$\delta^* N_3 Ga_1$	5.54	0.49	0.047
C-b	$\delta N_1 Ga_1$	$\delta^* N_2 Ga_1$	1.30	0.80	0.030
	$\delta N_1 Ga_1$	$\delta^* N_3 Ga_1$	0.27	0.82	0.014
C-c	$\delta N_1 Ga_1$	$\delta^* N_2 Ga_1$	6.14	0.48	0.057
	$\delta N_1 Ga_1$	$\delta^* N_3 Ga_1$	5.12	0.49	0.045
D-a	$\delta N_1 Ga_2$	$\delta^* N_2 Ga_2$	2.53	0.56	0.034
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_1$	4.38	0.48	0.042
D-b	$\delta N_1 Ga_2$	$\delta^* N_2 Ga_2$	2.43	0.56	0.033
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_1$	4.57	0.48	0.034
D-c	$\delta N_1 Ga_2$	$\delta^* N_2 Ga_2$	4.17	0.53	0.042
	$\delta N_1 Ga_2$	$\delta^* N_1 Ga_1$	4.43	0.49	0.042

Quantum theory of atom in molecule (QTAIM) and reduced density gradient (RDG)

One of the powerful methods to study the nature of interactions between two compounds is atom in molecule [52]. Nature of chemical bonds and other valuable information about chemical bonding can be described by analysis of total electronic density, ρ_{BCP} , and Laplacian of electron, densities ($\nabla^2\rho$) at bond critical point (BCP), the potential energy (V_{BCP}), the total electronic energy (H_{BCP}), and the kinetic energy (G_{BCP}) of the bond in critical points are calculated and listed in Table 5. According to Bader [52] theory, the negative values of $\nabla^2\rho$ and H_{BCP} indicate the strong interaction (strong covalent bond), the positive values of $\nabla^2\rho$ and H_{BCP} values denote the weak covalent interactions (strong electrostatic bond) and the positive value of $\nabla^2\rho$ and negative value of H_{BCP} define medium

strength as partially covalent bond. For this means, the values of $\nabla^2\rho$ and H_{BCP} for the (A-c, B-a, B-b, B-c, C-c and D-a models) are positive and refers to the weak covalent interactions (strong electrostatic bond) between COCl_2 . Ga12N12 complex. Wherein the values of $\nabla^2\rho$ and H_{BCP} for the (A-a, A-b, C-a, C-b, D-b and D-c models) are positive and negative respectively and define medium strength as partially covalent bond between COCl_2 . Ga12N12 complex.

To identify the weak inter molecular interaction between the COCl_2 and pristine, Al, P and Al & P doped Ga12N12 nanocluster, we calculate non-covalent interaction (NCI) index [53]. The scatter plot of reduced-density gradient (RDG) as function of sign (λ_2) $\rho(r)$ (product between electron density $\rho(r)$ and the sign of the second lowest eigenvalues of electron density hessian matrix (λ_2)) is determined by multiwfn program [54] and result is shown in Figure 5. In the RDG scatter, graph red color circle shows the bonded interactions ($\lambda_2 < 0$), blue color circle denotes nonbonding interactions ($\lambda_2 > 0$) and green circle implies low electron density, corresponding to Van der Waals interactions ($\lambda_2 = 0$). Comparison RDG scatter graph Figure 5 demonstrate that the reduced density gradient of the B-a, B-b, D-a and D-b models in $\lambda_2 < 0$ region is more than other models and so attractive interaction between COCl_2 . Ga12N12 complex in these models is more than other models. And so doping of Al atom increase the adsorption of COCl_2 and the surface of Ga12N12 nanocluster. This result is in agreement with the more values of adsorption energy of these models. On the other hand, the attractive interaction from O atom of COCl_2 on the surface of Ga12N12 nanocluster is stronger than C and Cl atoms of COCl_2 . The broad inter molecular iso surface of RDG plot in the B-a, B-b and B-c models suggests that an attractive electrostatic type interaction is operative between O atom of COCl_2 gas and Ga12N12 nanocluster, and on the A-a, A-b, C-b, and D-b models, the number of peaks around $\lambda = 0$ is more than other models, which correspond to van der Waals interaction.

Table 5. The topological parameters of AIM method for A-a to D-c adsorption models

	ρ	$\nabla^2\rho$	G	H	V
A-a	0.0513	0.2099	0.0597	-0.0073	-0.0670
A-b	0.0492	0.2050	0.0576	-0.0064	-0.0640
A-c	0.0123	0.0395	0.0086	0.0012	-0.0074
B-a	0.0388	0.2340	0.0544	0.0041	-0.0503
B-b	0.0389	0.2343	0.0545	0.0040	-0.0505
B-c	0.0120	0.0371	0.0081	0.0012	-0.0069
C-a	0.0435	0.1706	0.0478	-0.0052	-0.0530
C-b	0.0708	0.0393	0.0384	-0.0285	-0.0669
C-c	0.0073	0.0242	0.0047	0.0013	-0.0034
D-a	0.0349	0.2292	0.0512	0.0060	-0.0451
D-b	0.1049	0.4077	0.1337	-0.0318	-0.1656
D-c	0.0183	0.0263	0.0092	-0.0026	-0.0117

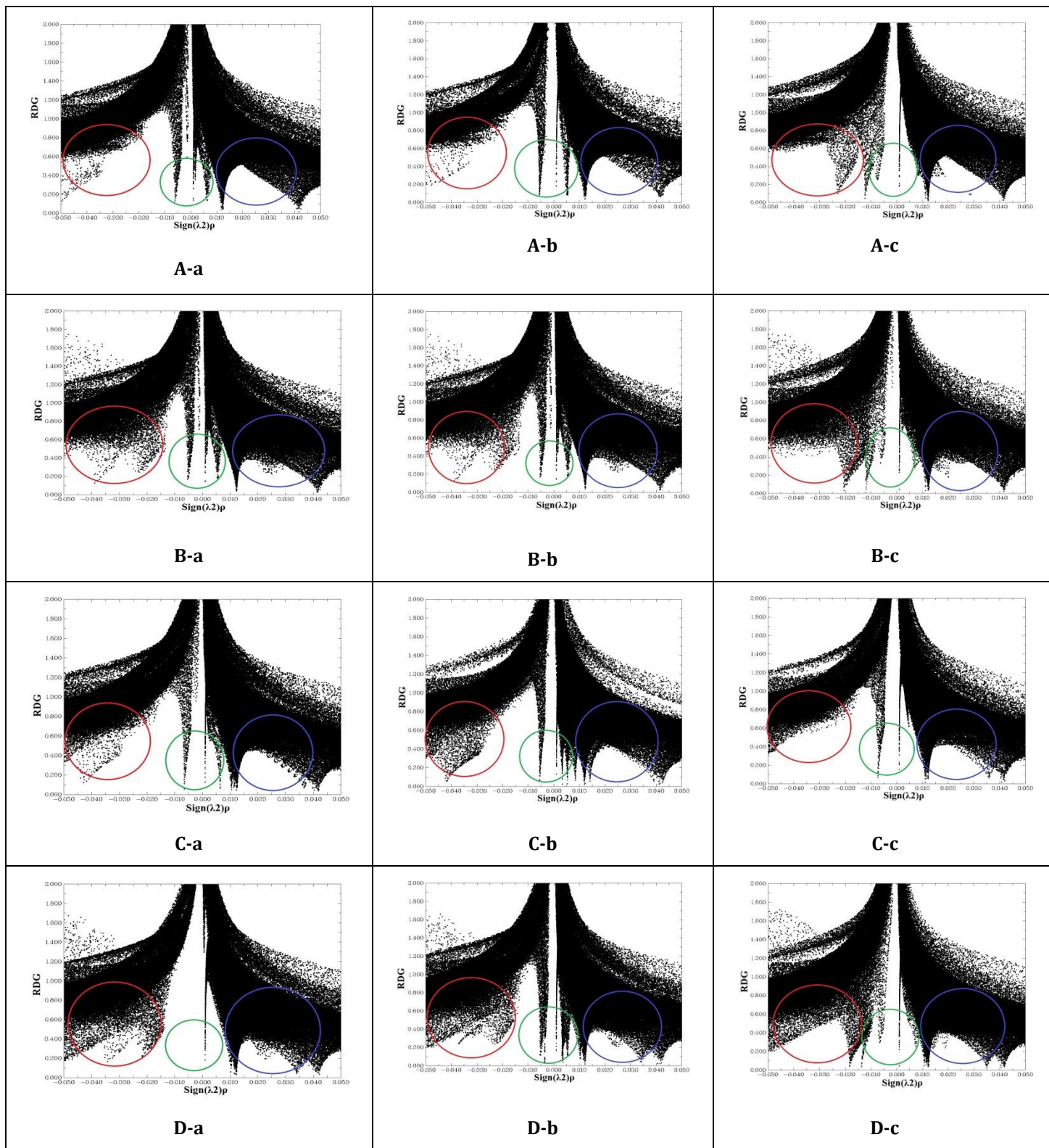


Figure 5. The RDGPlots of COCl_2 molecule adsorption on the surface of pristine, Al, P and Al&P doped Ga12N12 for A-a to D-c adsorption models

Conclusions

In this work, density functional theory at the cam-B3LYP level is applied to investigate the interaction and adsorption of COCl_2 molecule on the surface of pristine, Al, P and Al & P doped Ga₁₂N₁₂ nanocluster. The adsorption energy of COCl_2 from O, C and Cl sites on the surface of pristine, Al, P and Al & P doped Ga₁₂N₁₂ nanocluster are negative and exothermic. The order of adsorption energy in the c orientation of COCl_2 is: B-c (-17.38 kcal/mol) > A-c (-17.01 Kcal/mol) > C-c (-15.26 Kcal/mol) > D-c (-12.72 Kcal/mol). The Gibbs free energy (ΔG) of the A-c, C-c, D-a and D-c models in gas phase are positive and so the adsorption of COCl_2 on the surface of Ga₁₂N₁₂ are unspontaneous in thermodynamic approach. Whereas the Gibbs free energy (ΔG) of the other adsorption models in gas phase is negative and spontaneous. On the other hand, the solvent Gibbs free energy (ΔG_{sol}) in the aqueous phase of the B-c, C-c, D-a and D-c models are negative, and at the other adsorption models are positive. The gap energies of the A-a, B-a, C-a and D-a (O head of COCl_2) are smaller than other models. In addition, with doping Al atom the gap energy of $\text{COCl}_2/\text{Ga}_{12}\text{N}_{12}$ complex is decreased significantly from pristine and P doped Ga₁₂N₁₂. The global hardness of adsorption of COCl_2 on the surface of Al-doped Ga₁₂N₁₂ is lower than other models and so the change of electronic properties of system more than other models. The values of $\nabla^2\rho$ and H_{BCP} for the (A-c, B-a, B-b, B-c, C-c and D-a models) are positive and refer to the weak covalent interactions (strong electrostatic bond) between $\text{COCl}_2/\text{Ga}_{12}\text{N}_{12}$ complex.

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Supplementary data

Tables S1– S8 and Figures S1– S12 are given in supplementary data.

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