



Adsorption Properties of O₂ on Cr₅ Nanostructures: A DFT Study

MOHAMMAD T. BAEI*, ALI KAZEMI BABAHEYDARI and PARVIZ TORABI[§]

*Department of Chemistry, Azadshahr Branch
Islamic Azad University, Azadshahr, Golestan, Iran

Department of Chemistry, Sharekord Branch
Islamic Azad University, Sharekord, Iran

[§]Department of Chemistry, Mahshahr Branch
Islamic Azad University, Mahshahr, Iran

baei52@yahoo.com

Received 3 July 2010; Revised 3 September 2010; Accepted 6 November 2010

Abstract: Based on the density functional theory (DFT) adsorption properties of oxygen molecule on Cr₅ nanostructures at various positions (top, bridge and central sites) were investigated. Geometry optimizations and vibrational frequencies of them were carried out at B₃LYP level of theory with LANL2DZ and 6-31G* basis sets using Gaussian 98 suites of program. Their thermodynamic properties were estimated. We have also investigated the total electronic properties, HOMO, LUMO and energy gap for Cr₅ nanostructures with O₂. The result showed that the adsorption of O₂ on Cr₅ nanocluster in horizontal bridge site is the most stable state of adsorption and its binding energy is strong, -145.88 kcal/mol.

Keywords: Nanocluster, Adsorption, DFT, Energy gap, Frequency

Introduction

Oxide transition metal clusters and nanocomponents have attracted significant attention due to their important role as components of model-catalysts¹⁻⁶, sensors⁷, solar-cells⁸ and magnetic recording devices⁹. The adsorption of oxygen on transition metal surface has been studied using a wide range of techniques and methods because of its interest for both basic and applied problems in surface science in the past several decades¹⁰. Wen, Kaichen *et al.*¹¹ explained the results of O₂ adsorption and dissociation on CuCr₂O₄ surface and Masahiro Katoh *et al.*¹² studied adsorption properties of gases on chromium silicate¹².

In this work, we report the most favorable site of adsorption of oxygen on Cr₅ nanostructures and the vibrational frequencies, thermodynamic changes, HOMO, LUMO and the electronic properties of Cr₅ by O₂ adsorption.

Computational details

All calculations have been carried out by using the Gaussian 98 suite of programs¹³. The density functional theoretical method with the B₃LYP functional was used for all the calculations. Cr₅ nanostructures is considered as a doublet molecules with partitioning of the basis sets, for O₂ molecule described by the standard 6-31G* basis set, but for chromium the standard LANL2DZ basis set was used. Adsorptions energies, the vibrational frequencies, thermodynamic properties, HOMO, LUMO and density of state (DOS) have been carried out at B₃LYP level of theory with LANL2DZ and 6-31G* basis sets.

Results and Discussion

DFT calculations on adsorption of O₂ molecule on Cr₅ nanocluster

Chromium has the body - centered cubic structure with a lattice constant of 2.88Å and every metal layer contains five Cr atoms as shown in Figure 1a. The interaction of the O₂ molecule with the surface of Cr₅ nanocluster was studied by performing single point energy (SPE) calculation for several orientations on the molecule. Three possible configurations, named top, bridge and center site with vertical and horizontal orientations, were selected for the approach of O₂ molecule to the nanocluster: (Top site) directly on top of a Cr atom (Figure 1b and 1c), (Bridge site) on the middle of two nearest neighbor Cr atom (Figure 1d and 1e) and (Center site) in the center of the smallest unit structures of the surface (Figure 1f and 1g).

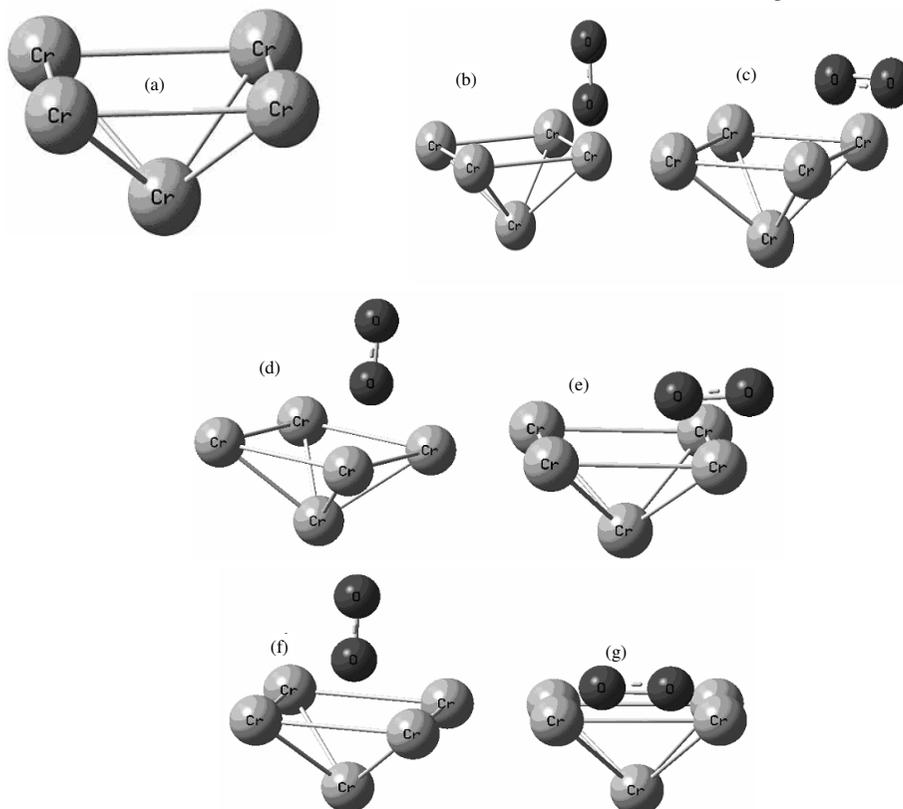


Figure 1. Atomistic configurations of adsorption of O₂ molecule with vertical and horizontal orientations in top, bridge and center sites

The adsorption energy ($E_{\text{adsorption}}$) of one O₂ molecule on the Cr₅ nanocluster can be calculated as follows:

$$E(\text{ads}) = E_{\text{O}_2/\text{Cr}_5} - [E_{\text{O}_2} + E_{\text{Cr}_5}] \quad (1)$$

In equation (1), the first term is the SPE of the O₂/Cr₅ surface super molecule, E_{Cr_5} is the SPE of separated fragment and E_{O_2} is the energy of an optimized O₂ molecule. The adsorption energies in the three cases are plotted in Figure 2 and the adsorption energy with the equilibrium distance in each case is summarized in Table 1.

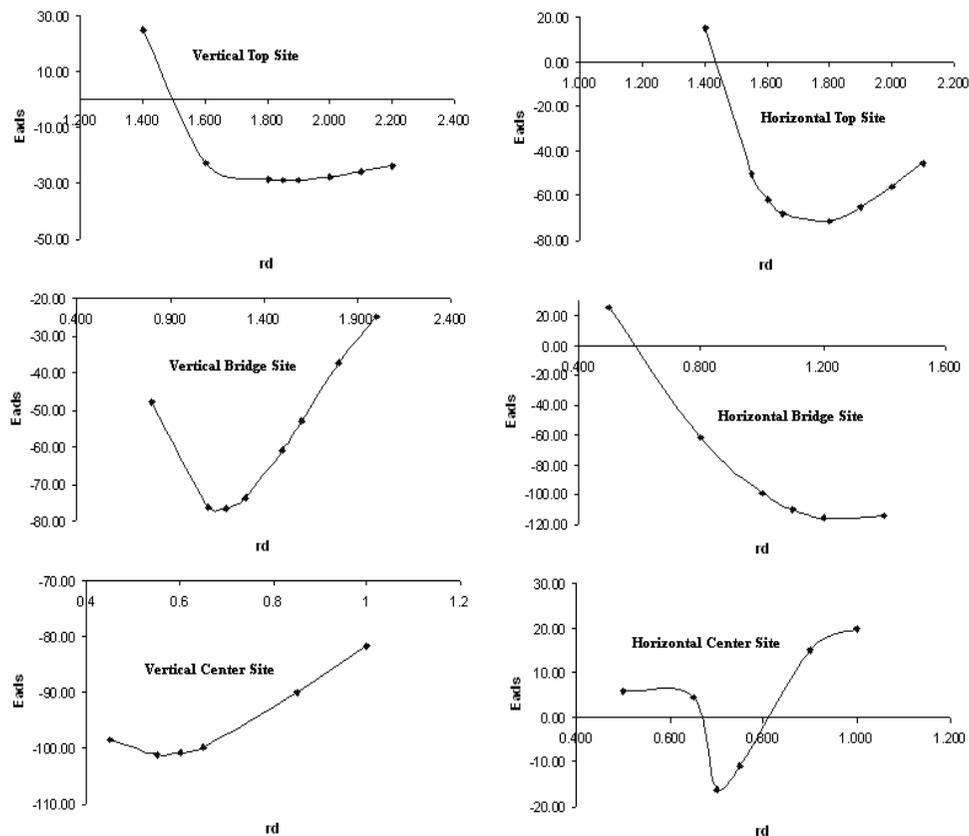


Figure 2. Interaction energy curves of an O₂ molecule adsorbed on the Cr₅ nanocluster, obtained by the SPE calculation in which the O=O and all the Cr-Cr bond lengths are kept constant and only the distance between the oxygen molecule and the Cr₅ surface is varied (rd).

Table 1. Adsorption energy (kcal/mol) and equilibrium distance (Å) of an O₂ molecule on the Cr₅ surface (O=O band length is 1.21 Å).

	Vertical top	Horizontal top	vertical bridge	horizontal bridge	vertical center	Horizontal center
Adsorption energy	-24.99	-67.49	-72.92	-111.85	-97.36	-14.33
Distance (rd) of O ₂ from the Cr ₅	1.85	1.80	1.20	1.20	0.55	0.70

The calculations showed that the obtained adsorption energies depend on orientations and locations of O₂ molecule. The most stable configuration of O₂ is horizontal bridge site; the current calculation showed that the adsorption energy for horizontal bridge site is -111.85 kcal/mol. In the next step, the adsorption energies in the equilibrium distance for the three cases were calculated with the increase of distance between oxygen atoms (Figure 3).

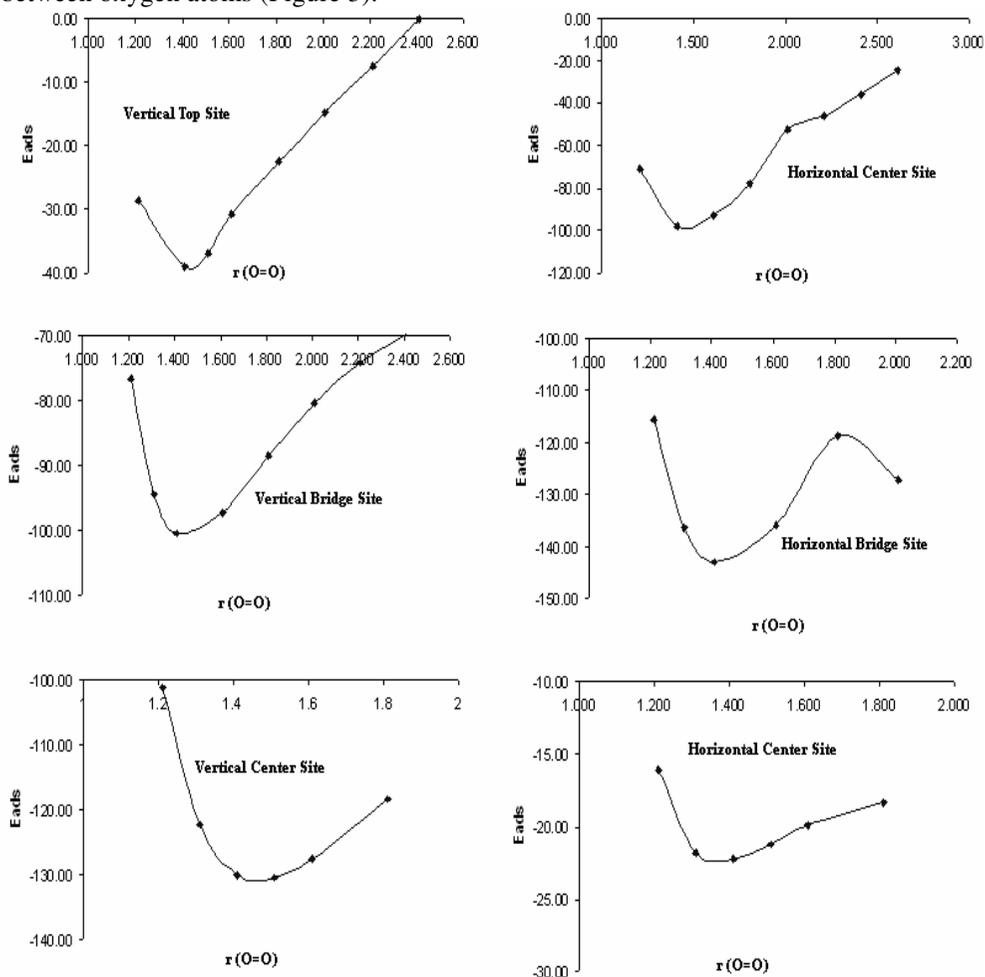


Figure 3. Interaction energy curves of an O₂ molecule adsorbed on the Cr₅ nanocluster, obtained by the SPE calculation, the O₂ bond length r(O=O) is varied and the equilibrium distance between the oxygen molecule and the Cr₅ surface is kept constant.

In this step, r(O=O) for the most stable state in all of the cases is 1.41 Å (Figure 3), then with r(O=O) = 1.41 Å, the adsorption energies for all of states were calculated by increasing the distance between O₂ and Cr₅ surface (r_d). The calculations showed that the adsorption of O₂ on Cr₅ nanocluster in horizontal bridge site is the most stable state of adsorption and its binding energy is strong, -145.88 kcal/mol in r_d = 1.25 (Figure 4 and Table 2).

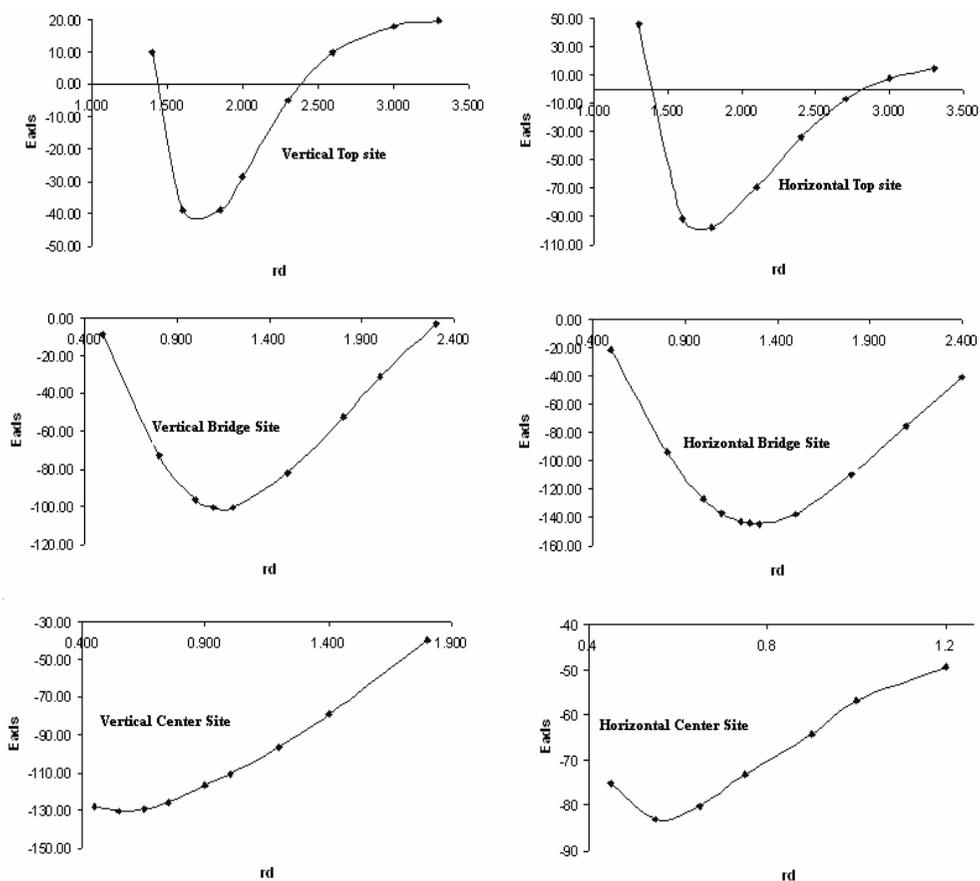


Figure 4. Interaction energy curves of an O₂ molecule adsorbed on the Cr₅ nanocluster, obtained by the SPE calculation, the O₂ bond length, $r(\text{O}=\text{O})$ is 1.41 Å and only the distance between the oxygen molecule and the Cr₅ surface is varied (rd).

Table 2. Adsorption energy (kcal/mol) and equilibrium distance (Å) of O₂ molecule on the Cr₅ surface (O=O band length is 1.41 Å).

	Vertical top	Horizontal top	vertical bridge	horizontal bridge	vertical center	Horizontal center
Adsorption energy	-35.79	-99.28	-94.92	-145.88	-127.57	-83.10
Distance (rd) of O ₂ from the Cr ₅	1.65	1.80	1.15	1.25	0.55	0.70

Vibration frequencies

The vibrational frequencies have been calculated at the B₃LYP level of theory with LANL2DZ and 6-31G* basis sets. Vibrational frequencies are used to simulate the IR spectra (Figure 5) for all of the states. Figure 5 simulated IR spectra for the configurations of adsorption of O₂ molecule with vertical and horizontal orientations in top, bridge and center sites. IR spectrum scaled by 1.000000.

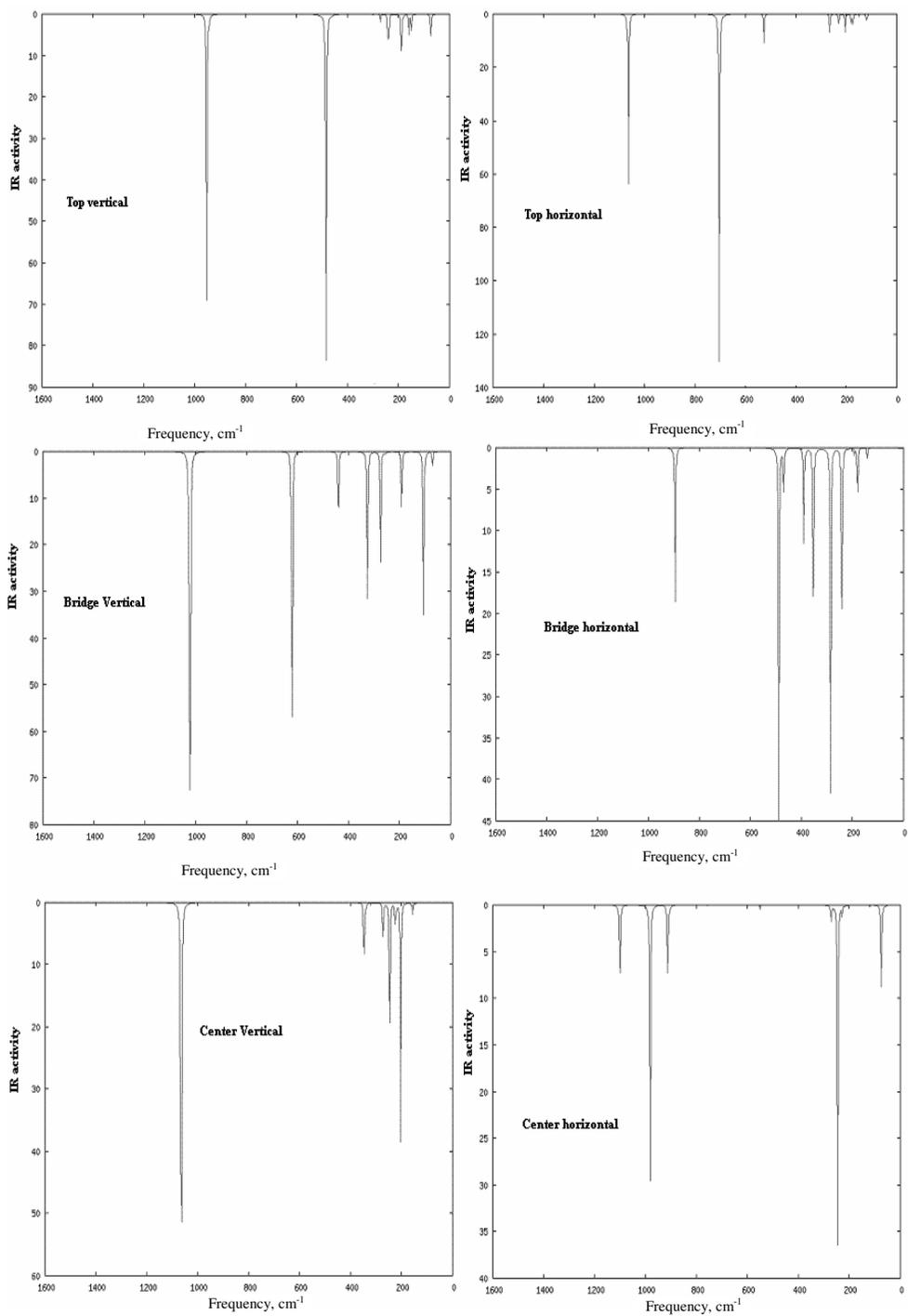


Figure 5. Simulated IR spectra for the configurations of adsorption of O_2 molecule with vertical and horizontal orientations in top, bridge and center sites IR spectrum scaled by 1.000000

The simulated IR spectra could be used as evidence to identify the Cr/O₂ nanocluster. Here we discuss several vibrational bands in the IR intensities of the all of the configurations to be compared with future experimental identification; (1) for vertical top site: the stronger IR spectroscopic signals with IR intensities 84.55 and 72.49 are determined at the frequencies 485.65 and 952.57 cm⁻¹ respectively, (2) for horizontal top site: two strong modes are observed at the frequencies 1064.08 and 702.99 cm⁻¹ with IR intensities of 63.72 and 139.89 km mol⁻¹ respectively, (3) for vertical bridge: four strong modes are observed at the frequencies 105.88, 326.55, 622.64 and 1023.72 cm⁻¹ with IR intensities of 42.11, 48.33, 60.94 and 129.37 km mol⁻¹ respectively, (4) for horizontal bridge site: five strong modes are observed at the frequencies 242.35, 286.26, 353.29, 489.60 and 896.48 cm⁻¹ with IR intensities of 20.32, 50.52, 33.93, 47.73 and 22.48 km mol⁻¹ respectively, (5) for vertical center site: three strong modes are observed at the frequencies 204.19, 247.67 and 1065.46 cm⁻¹ with IR intensities of 39.17, 31.08 and 92.01 km mol⁻¹ respectively, (6) for horizontal center site: five strong modes are observed at the frequencies 74.10, 246.22, 912.56, 982.56 and 1101.59 with IR intensities of 13.01, 37.56, 12.32, 31.64 and 13.48 km mol⁻¹ respectively.

Thermodynamic changes

In this study thermodynamic changes for all of the configurations were estimated using total energies obtained by the B₃LYP level of theory with LANL2DZ and 6-31G* basis sets. The thermodynamic properties were calculated from the standard statistical mechanical equations which include the finite-temperature translational, rotational and vibrational energies¹⁴. For example, the enthalpy (H) was calculated as follows:

$$H = E_{\text{elec}} + E_{\text{vib}}(T=0) + E_{\text{vib}}(T) + E_{\text{rot}}(T) + E_{\text{tra}}(T) + PV \quad (1)$$

Where E_{elec} is the total electronic energy at 0 K, $E_{\text{vib}}(T = 0)$ is the zero-point vibrational energy which is a linear sum of the basic harmonic frequencies, and $E_{\text{vib}}(T)$, $E_{\text{rot}}(T)$ and $E_{\text{tra}}(T)$ are vibrational, rotational and translational contributions, respectively. Also, the entropy (S) of molecules can also be calculated from a standard formula:

$$S = S_{\text{elec}} + S_{\text{vib}} + S_{\text{rot}} + S_{\text{tra}} \quad (2)$$

Where, S_{elec} , S_{vib} , S_{rot} and S_{tra} are the electronic, vibrational, rotational and translational terms. The change in the standard Gibbs free energy is given by

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

The thermodynamic properties with the equilibrium distance (Table 2) in each case were calculated. For this cases ΔH , ΔS and ΔG were calculated at the B₃LYP level of theory with LANL2DZ and 6-31G* basis sets and ΔH of O₂ on Cr₅ nanocluster in horizontal bridge site is more than another cases (Table 3). Also $\Delta H < 0$ show that this process is exothermic.

Table 3. The ΔH , ΔS and ΔG in kcal/mole for all of the configurations in B₃LYP level of theory with LANL2DZ and 6-31G* basis sets.

Model(the most stable states)	ΔH	$T\Delta S$	ΔG
Vertical top site	-24.41	-12.35	-12.06
Horizontal top site	-88.97	-13.00	-75.97
Vertical bridge site	-84.75	-12.83	-71.92
Horizontal bridge site	-135.15	-13.37	-121.79
Vertical center site	-116.38	-11.92	-104.46
Horizontal center site	-70.46	-13.77	-56.69

Electronic properties

Finally, we studied the influence the electronic properties of Cr_5 nanocluster by oxygen molecule adsorption. The most stable states for adsorption of the configurations (Table 2), the total densities of states (DOS) of these clusters are shown in Figure 6, where the Fermi energy set to 0 eV. The HOMO and LUMO energies and their energy gaps are listed in Table 4, the calculated band gap of the Cr_5 is -4.81 eV (Table 4).

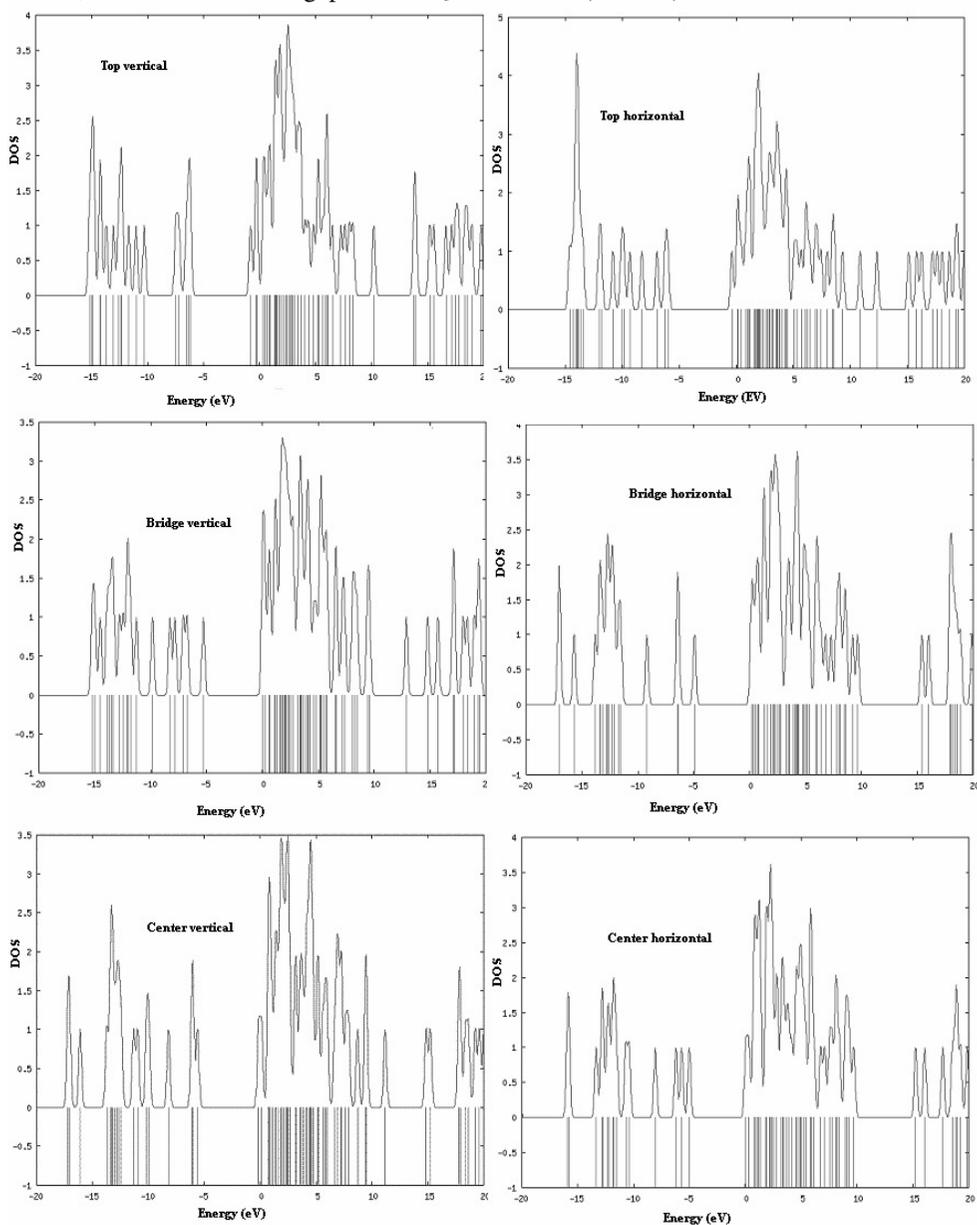


Figure 6. Electronic density of states for the most favorable states of adsorption of O_2 molecule with vertical and horizontal orientations in top, bridge and center sites

The effects of oxygen molecule on adsorption energies in Cr₅ are related to their electronic structure. When oxygen molecule is adsorbed on the Cr₅, the interaction between them is strong, their electronic properties changes obviously. It is clear that the presence of O₂ molecule increases the energy-gap of Cr₅ nanocluster (Table 4) and reduces its electronic conductance. The TDOS for the (O₂/Cr) systems are presented in Figure 6. For these systems, significant changes in the DOS are observed near the Fermi level. However, the adsorption of O₂ molecule in horizontal top site further increases the energy gap of Cr₅ nanocluster (-5.63 eV).

Table 4. The HOMO and LUMO energies and their energy gaps for the most favorable states for adsorption of the configurations

Model(the most stable states)	HOMO	LUMO	Energy gap (eV)
Cr	-5.01	-0.2	-4.81
Vertical top site	-6.2	-0.81	-5.39
Horizontal top site	-6.01	-0.38	-5.63
Vertical bridge site	-5.29	-0.05	-5.24
Horizontal bridge site	-4.94	0.15	-5.09
Vertical center site	-5.61	-0.14	-5.47
Horizontal center site	-5.01	0.05	-5.06

Conclusion

We have theoretically studied the adsorptions of oxygen molecule on Cr₅ nanocluster through the DFT calculations. According to our calculations, it seems that the Cr₅ can be used as an oxygen storage medium as long as oxygen is adsorbed on the surface of Cr₅ because of the strong binding energy. The vibrational frequencies have been calculated at the B₃LYP level of theory with LANL2DZ and 6-31G* basis sets. The thermodynamic properties for all of the configurations are calculated and ΔH of O₂ on Cr₅ nanocluster in horizontal bridge site is more than another the configurations and the process are exothermic. In this study the presence of O₂ molecule increases the energy-gap of Cr₅ nanocluster and reduces its electronic conductance.

References

1. Lambert R M and Pacchioni G, *Chemisorptions and Reactivity on Supported Clusters and Thin Films*; Kluwer, Ed., Dordrecht, Aten, Greece, 1997, 395-424.
2. Gronbeck H, *Topics in Catalysis*, 2004, **28**, 59.
3. Heiz U and Schneider W-D, in *Metal Clusters at Surfaces*, Meiwes Broer K H, Ed., Springer, Berlin, Germany, 2000, 237.
4. Becker C and Henry C R, *Surf Sci.*, 1996, **352**, 457.
5. Freund H J, *Adv Catal.*, 2000, **45**, 333.
6. Shaikhutdinov S H, Heemeier M, Hoffmann J, Meusel I, Richter B, Bäumer M, Kuhlbeck H, Libuda J, Freund H J, Oldman R, Jackson S D, Konvicka C, Schmid M and Varga P, *Surf Sci.*, 2002, **501(3)**, 270-281.
7. Mizei J, Voutilainen J, Saukko S and Lantto V, *Thin Solid Films*, 2001, **391**, 209.
8. Westphalen M, Kreibig U, Rostalski J, Luth H and Meissner D, *Sol Ener Mater Sol Cells*, 2000, **61**, 97.
9. Fukami S, Ohno A and Tanaka A, *Mater Trans.*, 2004, **45**, 2012.

10. Thomas J M and Thomas W J, Principles and Practice of Heterogeneous Catalysis, Weinheim, Germany, 1997, 246.
11. Xiang-Lan X, Wen-Kai C and Jun-qian Li, *J Molecular Structure: THEOCHEM*. 2008, **860**. 18-23
12. Masahiro K, Manabu S and Tahei T, *J Colloid Inter Sci.*, 2004, **277(2)**, 280-284.
13. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheese- man J R, Zakrzewski V G, Montgomery Jr J A, Stratmann R.E, Burant J C, Dapprich S, Millam J M, Daniels A D., Kudin K N, Strain M C, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson G A, Ayala P Y, Cui Q, Morokuma K, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Cioslowski J, Ortiz J V, Baboul A G, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin R L, Fox D J, Keith T, Al-Laham M A., Peng C Y, Nanayakkara A, Gonzalez C, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Andres J L, Gonzalez C, Head-Gordon M and Replogle E S, Pople J A, GAUSSIAN 98, Gaussian, Inc, Pittsburgh, PA, 1998.
14. Lay J E, Statistical Mechanics and Thermodynamics of Matter. 1st Ed., Harper & Row Publishers, New York, America, 1990, 210.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

