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Study of electrostatic potential surface and molecular orbitals of O_4 nano cluster by first principles

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Abstract

Study of properties of nanoclusters are important from various fundamental and applications point of view. The study of frontier orbitals, molecular electrostatic potential surface of O_4 oxygen nano cluster in the puckered square (O_{4A}) and the pinwheel (O_{4B}) geometry has been carried out using the first principles. The MEP surface has been used to predict the active sites for electrophilic and nucleophilic interactions in both the O_4 cluster geometries.

Key Words: Frontier orbitals, Nano cluster, MEP, Cluster energy.

Introduction

A molecular cluster of oxygen, the tetraoxygen cluster O_4, known as "oxozone" was predicted in 1924 by Gilbert N. Lewis as an explanation for magnetism of oxygen O_2 molecule, nevertheless metastable O_4 cluster has been recently observed in mass spectroscopy experiments [1]. Devina and others have proposed an adsorption model for molecular oxygen on reduced TiO_2(110) and have studied the formation of tetraoxygen (O_4) [2]. Since its discovery, O_4 cluster has been a subject of interest from both experimental as well as theoretical point of view [3-6], because of its potential, being more powerful oxidizer than O_2 or O_3 and therefore may also be used as rocket fuel in future [1].

In the present communication a complete systematic study of structural, energetic properties of O_4 cluster has been carried out using the first principles. With the optimized geometry, the frontier orbitals, electron density and molecular electrostatic potential surfaces of the cluster have been generated with further analysis leading to prediction of stability and activity of the cluster.

Results and Discussion

The tetraoxyen was proposed as an explanation for the failure of liquid oxygen to obey curie law [13]. Computer simulations have indicated that O_2 molecules associate in pair and form O_4 cluster [14]. The two different geometries: a puckered square (O_{4A}) and a pinwheel (O_{4B}) in case O_4 [15,16] have been the starting point for the present calculations. The equilibrium geometry optimization of the nano cluster in ground state has been achieved by energy minimization, using DFT/ B3LYP functional with 6-31++G(d,p), cc PVQZ and AUG cc PVQZ basis sets. The optimized molecular structures thus obtained together with the numbering scheme of the atoms is shown in the Fig. 1. and the optimized parameters are given in table 1. The ground state energy of the optimized structure of O_{4A} and O_{4B} at different basis sets are given in table 2.

Figure 1: Optimized Geometries of Tetra - Oxygen Cluster

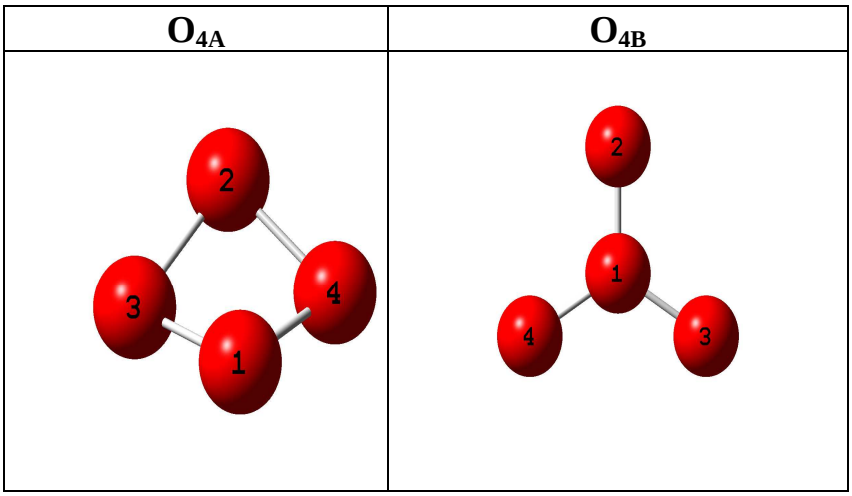


Table 1: Optimized Bond Lengths, Angles and Dihedrals of O_4 Cluster

O_{4A}		O_{4B}	
R(1,3)	1.5305	R(1,2)	1.2905
R(1,4)	1.5305	R(1,3)	1.2905
R(2,3)	1.5305	R(1,4)	1.2905
R(2,4)	1.5305	A(2,1,3)	120.0
A(3,1,4)	86.7742	A(2,1,4)	120.0
A(3,2,4)	86.7743	A(3,1,4)	120.0
A(1,3,2)	86.7743	L(2,1,3,4,-2)	180.0
A(1,4,2)	86.7743		
D(4,1,3,2)	-26.6893		
D(3,1,4,2)	26.6893		
D(4,2,3,1)	26.6893		
D(3,2,4,1)	-26.6893		

Note: Bond lengths are in Å, angles and dihedrals are in degrees.

Table 2 : Optimized ground state energies of O_{4A} and O_{4B} cluster in Hartree

Functional/Basis Set	O_{4A}	O_{4B}
B3LYP/ 6-31++G(d,p)	-300.4893	-300.4737
B3LYP/ cc- PVQZ	-300.6220	-300.6078
B3LYP/ aug-cc-PVQZ	-300.6243	-300.6103

According to second derivative analysis, the calculated vibrational spectra for the cluster has no imaginary frequency, therefore the optimized geometry is confirmed to be located at the local minima on potential energy surface (table 3). The intramolecular bond lengths in the O_{4A} and O_{4B} are calculated to be 1.5305 A^0 and 1.2905 A^0. It is interesting to note that the calculated intramolecular bond length is found to be larger in case of puckered square O_{4A} structure and shows the single bond character, whereas the corresponding bond length in case of pinwheel structured O_{4B} cluster reflects a partial double bond character, as its value is closer to the standard O=O bond length (1.210 A^0). It has been observed theoretically that the ground state energy of the tetra-oxygen cluster decreases with an increase in dimensionality of the basis set. The binding energy and the bond energy of oxygen cluster are reported in the table 4 at the Aug-cc-PVQZ basis sets. Although the ground state energy of O_{4A} and O_{4B} are almost same but the pinwheel shaped O_{4B} cluster seems to be thermally more stable than puckered squared shaped O_{4A} cluster, as the calculated bond energy is smaller in later. It is also interesting to note the order of the calculated bond energy for O_4 cluster is Eb O_{4B} > Eb O_{4A} (refer to Table 4).

Table 3 : Harmonic Frequencies of O_{4A} and O_{4B} cluster in cm^{-1}

S.No.	**O_{4A}**	**S.No.**	**O_{4B}**
1.	397	1.	601
2.	804	2.	601
3.	804	3.	668
4.	861	4.	894
5.	923	5.	1060
6.	1000	6.	1060

Table 4 : Cluster Energy, Binding Energy and Bond Energy of O_{4A} and O_{4B} at B3LYP/ AUG-cc-PVQZ

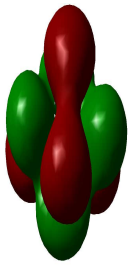
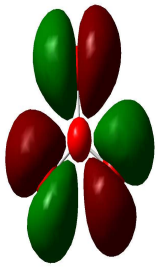
S.No.	Parameter	**O_{4A}**	**O_{4B}**
1.	Cluster Energy(eV)	-17.2058	-16.82481
2.	Binding Energy (eV/ atom)	-4.3014	-5.6082
3.	Bond Energy (Kcal/mol)	99.1935	129.3297

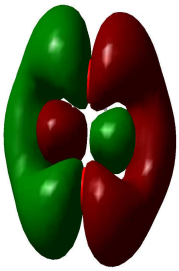
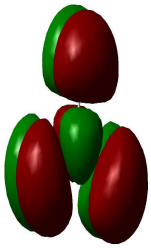
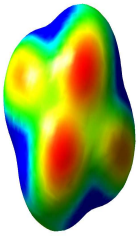
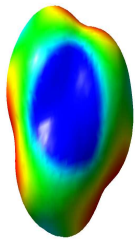
Electronic properties

The basic electronic parameters related to the frontier orbitals in a molecule are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their resulting energy gap. These orbitals not only determine the way the molecule interacts with other species, but their energy gap (frontier orbital gap) help in characterizing the chemical reactivity and kinetic stability of the molecule. The 3D plots of the HOMO, LUMO, Total Electron Density (TED) and electrostatic potential surface mapped on isodensity surface (MEP) for both the structure of O_4 cluster are shown in fig. 2. The calculated value of frontier orbital energy gap of O_4 having 0.1764 Hartree and 0.1322 Hartree for puckered square and pinwheel shaped structures respectively, is calculated at the same level of theory and the same basis sets. The high frontier orbital gap is associated with a low chemical reactivity and high kinetic stability [17].

The electrostatic potential is a physical property of a molecule related to how a molecule is first "seen" or "felt" by another approaching species. A portion of a molecule that has a negative electrostatic potential is susceptible to electrophilic attack – the more negative the better. The molecular electro-static potential (MEP) map as shown in fig.2., is an important parameter which is related to the electronegativity and the partial charges on the different atoms of the molecule along with the TED. Its study leads to the better

Figure 2 : Frontier Orbitals, Total Electron Density and MEP of Tetra - Oxygen Cluster

CLUSTER SURFACES	**O_{4A}**	**O_{4B}**
HOMO		

LUMO		
TOTAL ELECTRON DENSITY		
MEP		

understanding of complex processes involving the charge-dipole, dipole-dipole, and quadrupole-dipole interactions. The red and blue regions in the MEP map refers to the regions of negative and positive potential and correspond to the electron-rich and electron-poor regions respectively whereas the green colour signifies the neutral electrostatic potential. The MEP surface provides necessary information about the reactive sites. The MEP of O_4 reveals some interesting features that in case of puckered square O_{4A} cluster there are four centres (represented by blue colour) for nucleophillic attack, whereas in spinwheel case there are only two centres for nucleophillic attack, one above and the other below the plane of the tetra-oxygen cluster in O_{4B} geometry .

Materials and methods

The *ab initio* calculations reported here, have been carried out using the Gaussian 03, suite of program [7-12] employing density functional theory to investigate the oxygen nano cluster O_4. The reported geometry, molecular properties such as equilibrium energy, HOMO-LUMO band

gap, dipole moment have also been used to understand the O_4 cluster under investigation. After the geometry optimization, the vibrational frequencies were also calculated. The stability of cluster has been discussed in terms of the total interaction energy Vcluster, the binding energy B.E. and the bond energy Eb defined as following:

$$\text{Vcluster} = [E_n - nE_1],\ \text{B.E.} = \text{V cluster}/\ n \text{ and } \text{Eb} = \text{Vcluster}/\ m$$

Where n is the number of Oxygen atoms and m is the number of O-O bonds in the cluster, E_n is the cluster energy of O_n and E_1 refers to the atomic ground state energy.

Conclusion

The equilibrium geometries of the oxygen cluster O_4 were determined and analyzed at DFT level using B3LYP functional employing 6-31++G(d,p) and cc-PVQZ and AUG-cc-PVQZ basis sets. The harmonic frequencies were determined at AUG- cc-PVQZ basis set. The binding energy, bond energy and frontier orbital energy gap data suggest that the spinwheel structure is kinetically more stable than other puckered squared O_4 cluster under study. The MEP has been used to understand the characteristics of oxygen cluster O_4. The present quantum chemical study predicts reasonably well the geometric parameters as well as electronic properties and might play an important role in better understanding of the tetra-oxygen cluster.

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