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Theoretical Structures Study of Indium Oxide (In_2O_3) Cluster Using DFT Calculations

Rashed T. Rasheed✉

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ABSTRACT

The structural, geometric and electronic prosperities of most stable indium oxide (In_2O_3) shapes in the neutral state and in both open and close forms are studied and investigated using density function theory (DFT). The ball shape structure in neutral quintet is preferred over all the other possible structures for the neutral shape. The lowest energy geometric prefers the Y shape arrangement in triplet state. The energy gap (E_{gap}) of the most stable indium oxide shapes as a function to the shapes is also discussed.

KEYWORDS

Indium oxide, theoretical study, DFT.

INTRODUCTION

Indium oxide (In_2O_3), an important *n*-type semiconductor, with wider band gap (≈ 3.6 eV). Single crystal In_2O_3 has cubic bixebyte structure (also called as c-type rare-earth oxide structure) with lattice parameter of 10.117 Å [1,2]. The electronic properties of the material makes it suitable for various solid state devices such as solar cells [3], sensors [4], electrocatalyst [5,6] and nanoscale transistors [7], *etc*. There is a variety of synthesis techniques (routes) for preparation of indium oxide nanoparticles such as sol-gel, pulsed laser deposition and chemical vapor deposition [8]. Small clusters of indium oxide provide the prototype model to understand the physics and chemistry of the formed nanostructures. To understand structure, optical and electronic properties of indium oxide many efforts have been made. It is noted that the doped indium oxide has been a focus of recent theoretical [9] and experimental studies [10,11].

There are many theoretical study calculations and experimental observations of electronic properties, vibrations and equilibrium structures of indium oxide, based on discrete variation of In_2O_3 ascertained that In-O bond is predominating in In_2O_3 molecule [12,13]. In this work, density function theory (DFT) at B3LYP level of In_2O_3 clusters such as shape structures, stability of structure as a function to HOMO (higher occupied molecular orbital) in three states (singlet, triplet and quantet), total energy, energy gap (E_{gap}) and symmetry of molecules are calculated.

Author affiliations:

Applied Chemistry Division, Applied Sciences Department, University of Technology, Baghdad, Iraq

✉To whom correspondence to be addressed:

E-mail: r_awsy@yahoo.com

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COMPUTATIONAL METHOD

By using density funiction theory (DFT) through correlation function B3LYP level [14,15], the calculation of geometrical optimization and the electronic structure on indium oxide clusters were calculated using the Gaussian 03 code [16]. B3LYP method is applicable for theoretical study of indium oxide clusters [17]. Los Alamos National Laboratory (LanL2DZ) basis sets [18], were used for both indium and oxygen atoms in all these calculations. The stability of all clusters analyzed in this work were corresponding to lowest energy configuration leading to true minima.

RESULTS AND DISCUSSION

Through DFT calculations, several configurations (liear, non-linear, planar and non-planar) of pentaatomic of indium oxide clustures were calculated. The shapes and names as we suggested are shown in Fig. 1.

The energies of the clusters are computed in the singlet, triplet and quintet electronic states and the calculated results found that the triplet electronic state in both (Y and fish) shapes have the higher value in the ground state configuration HOMO (the highest occupied molecular orbital). While quintet electronic state in ball shape has the highest energy gap (E_{gap}) value. All the lowest energy structures (HOMO) exhibit low spin electronic state with the exception of the shapes (Y and fish), which have spin triplet electronic state; their geometric and energetic properties are collected in Table-1.

Electronic stability: Both HOMO and LUMO parameters are very important to charcterize the electronic stabilities of In_2O_3 clusters. According to the Koopmans theory, the hardness corresponds to the gap between the HOMO and LUMO orbitals (HOMO-LUMO = E_{gap}). The HOMO energy level is associated with molecule ability of losing its electrons (ionization potential), while the LUMO energy level equals to the ability to obtaining the electrons (electron affinity potential). Hence, the principle of maximum hardness confirms the results which show that the stability of clusters depends on energy gap. The larger the energy gap of the harder molecule. The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles. E_{gap} determined the energy required by an electron jumping from the occupied orbital (HOMO) to unoccupied orbital (LUMO).

When energy gaps (E_{gap}) is large that means there is a higher energy required to aggravate the electron structure. A shape with bigger energy gap (Table-1), is more stable and this shape possesses a weaker chemical activity, as shown in Fig. 2. The energy gap of the most stable indium oxide shapes are shown in Fig. 2(b). These changes due to the different shape and atomic coordinations. The energy gap of the most stable shape configurations varies from 3.733 to 5.640 eV. Most appeared peaks are seen of both ball and Y shapes to be at 5.640 eV and 5.272 eV, respectively. This indicate these shapes are more stable than other shape. While another study [19], which used DFT (B3LYP) method with 3-21G basis set, found the fish shape is more stable. Accordingly, it can be

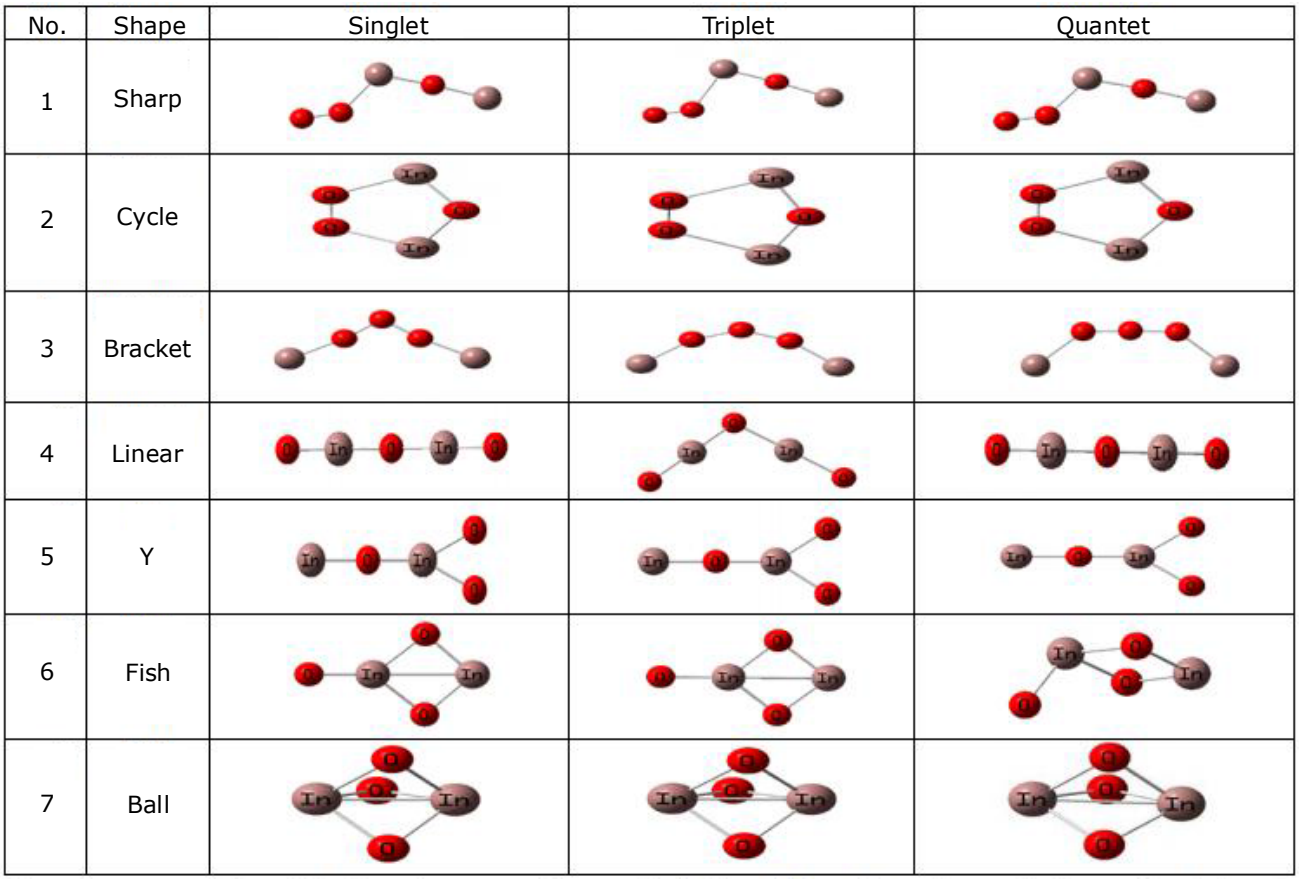

Fig. 1. Schematic representation of the lowest energy and energetically favourable configurations of indium oxide clusters in and quinter states. The violet solid circles represent indium atoms and the red solid circles denote oxygen atoms

TABLE-1
SOME PHYSICAL PROPERTIES OF INDIUM OXIDE CLUSTERS

No.	Shape	HOMO (eV)	LUMO (eV)	E_{gap} (eV)	Total energy (a.u.)	Sym.
1	Sharp					
	Singlet	-5.801	-3.985	1.816	-229.377597178	C_1
	Triplet	-5.847	-1.405	4.442	-229.405707266	C_1
	Quintet	-5.801	-3.984	1.816	-229.377597201	C_1
2	Cycle					
	Singlet	-6.282	-4.632	1.658	-229.390770984	C_{2V}
	Triplet	-6.097	-1.433	4.664	-229.408104946	C_{2V}
	Quintet	-3.089	-2.198	0.891	-229.280782798	C_{2V}
3	Bracket					
	Singlet	-5.517	-1.387	4.130	-229.340948463	C_1
	Triplet	-5.419	-1.465	3.954	-229.289647892	C_{2V}
	Quintet	-2.977	-2.408	0.569	-229.178732753	C_{2V}
4	Linear					
	Singlet	-7.199	-3.466	3.733	-229.422686362	D*H
	Triplet	-6.317	-4.074	2.243	-229.290136094	C_{2V}
	Quintet	-4.755	-1.833	2.922	-229.251307073	D*H
5	Y					
	Singlet	-5.833	-2.181	3.652	-229.409915514	C_1
	Triplet	-7.214	-1.942	5.272	-229.397049595	C_1
	Quintet	-3.852	-2.449	1.403	-229.267941387	C_1
6	Fish					
	Singlet	-6.760	-5.998	0.762	-229.384728221	Cs
	Triplet	-6.970	-1.941	5.029	-229.428706896	Cs
	Quintet	-5.572	-1.991	3.581	-229.363403552	C_1
7	Ball					
	Singlet	-6.746	-5.697	1.048	-229.335002946	Cs
	Triplet	-6.612	-4.623	1.989	-229.382188499	Cs
	Quintet	-6.294	-0.654	5.640	-229.377694606	Cs

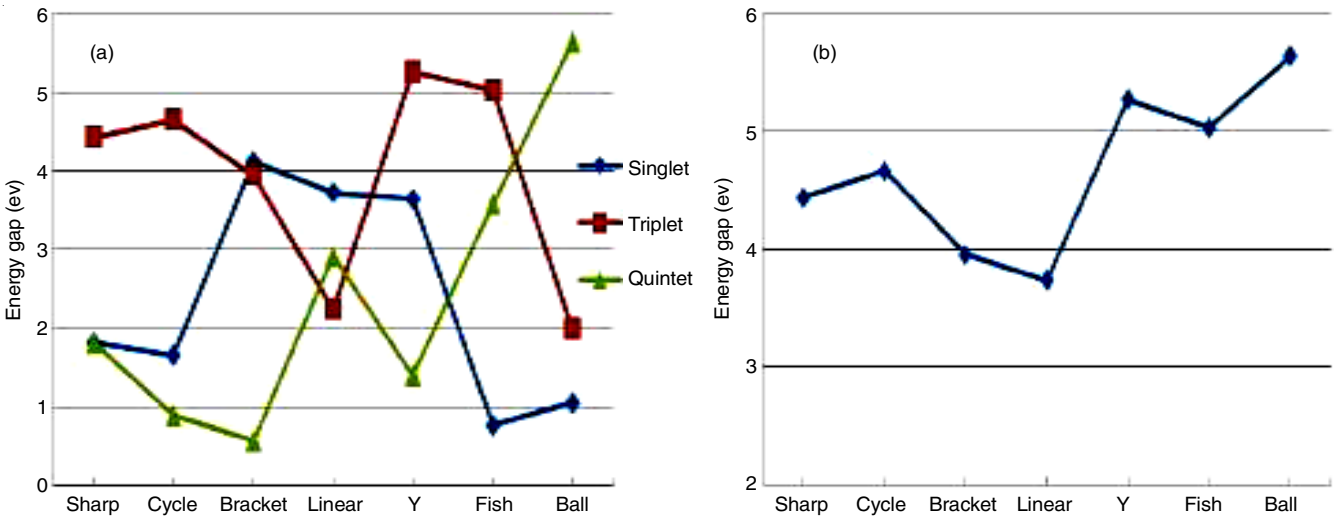

Fig. 2. Energy gaps (in eV) of (a) all stable configurations of indium oxide clusters and (b) the most stable configurations

said that ball shape should have the lowest energy among the other shapes. This may be due to the charge transfer from In atom to O atom (metal ligand charge transfer) resultion in increase stability of In-O bond.

Conclusion

The calculations in present our study using DFT through corre-lation function B3LYP level, Los Alamos National Laboratory (LanL2DZ) basis sets find that the ball configurations are preferred over all other possible ones for all the neutral indium oxide shape clusturs considered. The energy gap (E_{gap}) is found to depend on the structure of the shapes. Our results predict that the ball shape in quintet form has the most stable one for In_2O_3 shaped (the highest E_{gap}) among all the initial configu-rations, this maybe due to all oxygen atoms (three) have two angles bending with two neighbouring indium ions.

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