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Quantum Chemical Studies on Zn_mO_n (m+n=2–8) Even Nanocluster's Stability

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Abstract: Present study shows a simple approach for constructing small computationally reasonable clusters and provides better understanding on structural motifs that stabilize the electronic structure of ZnO. The structural isomers of Zn_mO_n for m+n = (2-8), only even number, are optimized using Gaussian 09 program package with a B3LYP/LANL2DZ level basis set. In addition to this, other properties related to experimental data such as equilibrium geometry, point group symmetry, binding energy (BE), highest-occupied and lowest-unoccupied molecular orbital (HOMO–LUMO) gap, density of states (DOS), vibrational frequencies, infrared intensities (IR Int.) and Raman scattering activitieshave been computed for Zn_mO_n (m+n=2–8) nanoclusters using DFT theory. Our results show that the existence of the most stable configurations of the various ZnO nanoclusters depend on final binding energy (FBE) and the nonlinear structured nanoclusters are most stable. Also, the variation of HOMO–LUMO gap is decreasing and final binding energy (FEB) is increasing with clusters size. Finally, result would be very useful for new experimental studies on such significant nanoclusters.

Keywords: Nanoclusters, Final Binding Energy (FBE), ZnO, Density functional theory (DFT).

I. INTRODUCTION

Currently, when the world is surmounting on the pinnacle of technology, mostly on electronic equipment and thus creating quest to fabricate novel materials, which possess versatile properties. Semiconductors are very common material, which play very important role in the field of electronics and technology. Owing to need of speed and technology, many of the materials are being discovered and are using to serve the purpose. So there is requirement of such material to the world which possesses some unique properties such as larger band gap, higher electron mobility and higher breakdown field.

Zinc Oxide (ZnO) can be a better optional material. ZnO, II–VI group semiconductor, electronically play very important role due to the wide band gap. It has direct band gap energy of 3.37 eV and a large binding energy, 60 meV at the room temperature, very well satisfying the aforesaid properties [1]. ZnO is kind of semiconductor, which exhibit quantum confinement effect [2]. In recent time, ZnO-based low dimensional materials have produced great scientific interest because of their encouraging applications in the area of nanoscale optoelectronic devices, photo catalysis, photovoltaic solar cells, quantum devices, UV electronics, spintronic devices and sensor applications [3-10]. It has been commonly used in its polycrystalline form over hundred years in a wide range of applications and has emerged as a prominent material with potential optoelectronics, involve polycrystalline or nano structured ZnO [11-17].

The computational study may be a useful and dominant instrument for overcoming the existing disadvantages and predicting theoretical concept of such type of semiconductor material systems. Theoretical investigation of ZnO nano clusters will provide vital information for understanding the growth mechanisms of geometry and stability of ZnO nanoclusters having lowest energy of formation. Density functional theory (DFT) is a reliable theoretical method to study nanoclusters, particularly prediction of the structures that lie between molecular and bulk. This allows for much possible geometry and it is challenging to find a true global minimum energy structure. Though, there are a number of theoretical studies performed to investigate the properties of ZnO clusters [18–20],to best of our knowledge no precise quantum calculations have been performed, for considered nanoclusters using density function theory (DFT) calculations and basis set.

Therefore, the theoretical study of these systems is required. In present paper, ZnO nanocluster is get stabilized up to m+n=2-8, only for even nanoclusters for different structures and their structural stability, dipole moment, HOMO-LUMO energy gap, binding energy per atom, DOS, Ionization potential, Electron affinity and vibrational behaviour of these nanoclusters have been calculated and discussed.

II. COMPUTATIONAL TECHNIQUES

For optimization of ZnO nanocluster and to calculate their ground and excited state properties, we have used density functional theory. Structural optimizations (i.e. the geometrical parameters) have been done with no constraints imposed on the nanocluster structures during the optimization. We have constructed various possible structures for each ZnO cluster. For geometry optimization and vibrational analysis, B3LYP level of DFT method, Beck's three parameters with correlation function (Lee-Yang-Parr), and relativistic effective core potential with

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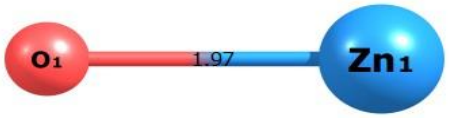
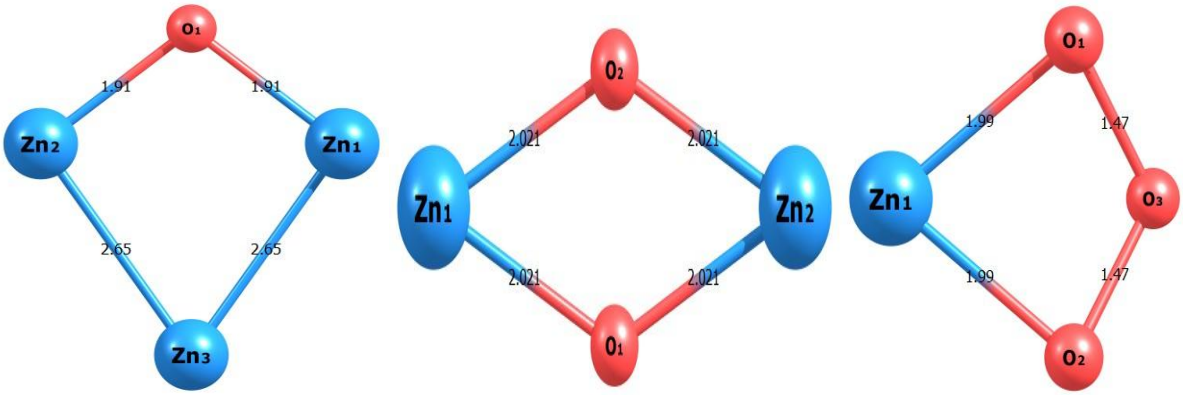
Vol. 2, Issue 11, November 2015

double zeta basis set, LANL2DZ as implemented in Gaussian 09 programme suit [21] are used. DFT is one of the promising and efficient methods to investigate electronic, optical and structural stability of nanoclusters. Also, Gauss Sum 3.0 [22] has been used for the evaluation of density of states (DOS) spectrum.

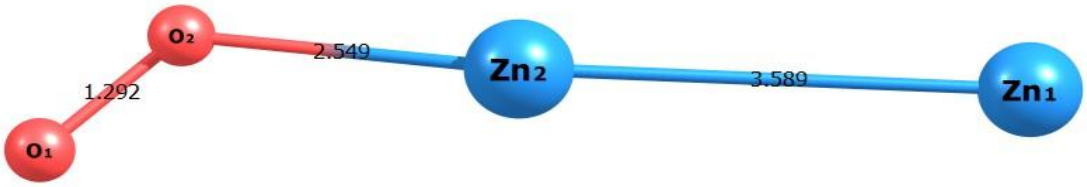


(Zn_1O_1**)**Linear

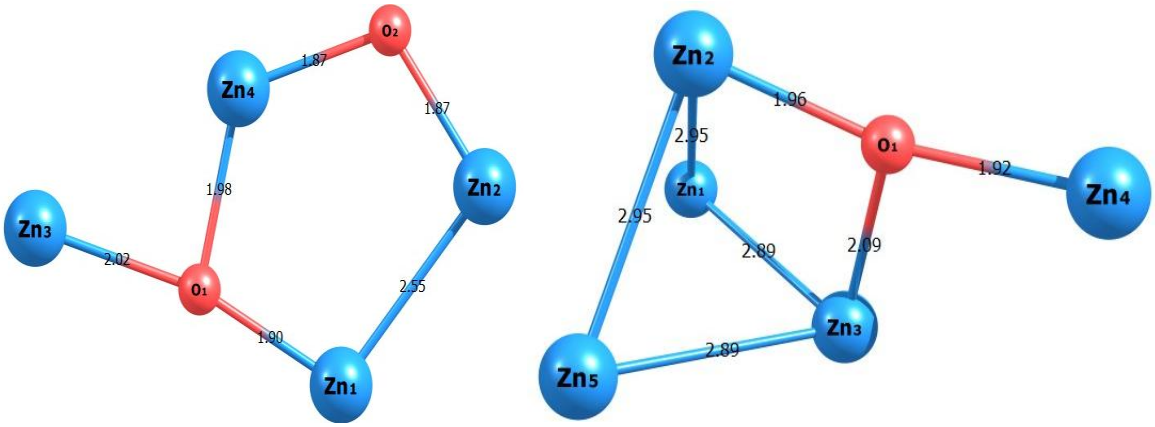
(Zn_3O_1**)**Linear



(Zn_3O_1**)**Rhomboidal **(**Zn_1O_3**)**$Rhomboidal_1$**(**Zn_2O_2**)**$Rhomboidal_2$



(Zn_2O_2**)**Bent



(Zn_4O_2**)**Planer (Zn_5O_1) Triangular bipyramidal

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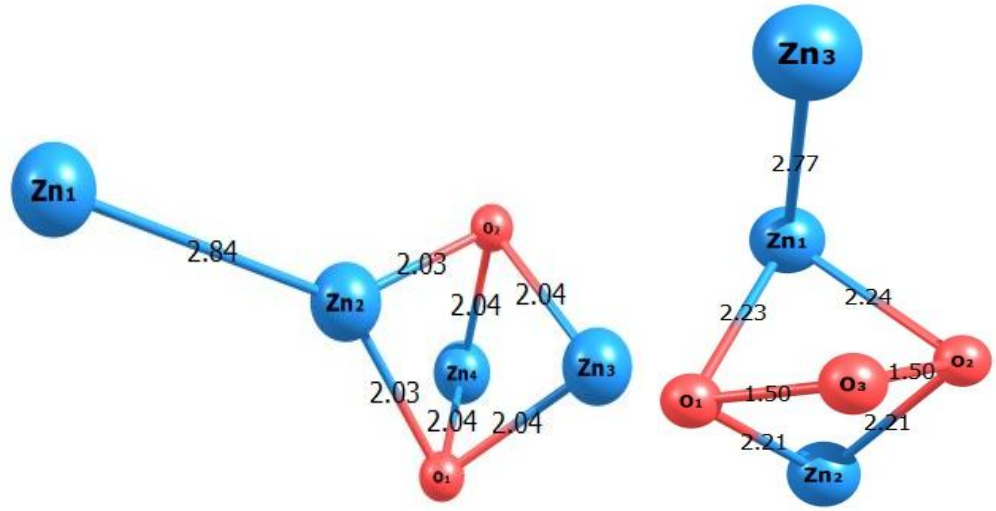
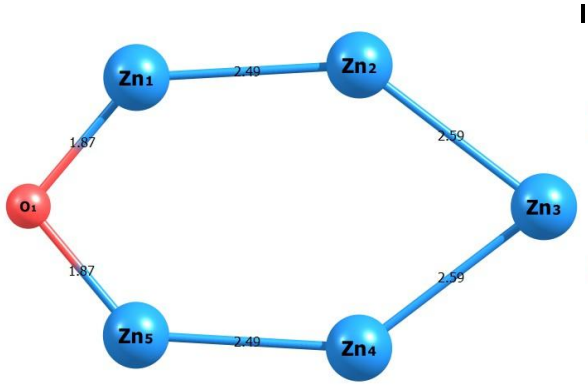
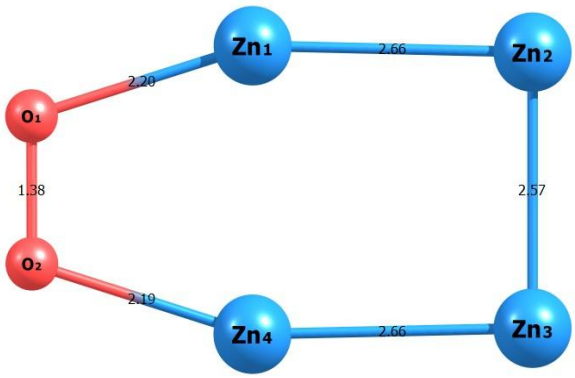


(Zn_4O_2) Triangular bipyramidal$_1$ (Zn_3O_3) Triangular bipyramidal$_2$

(Zn_5O_1**)**Linear

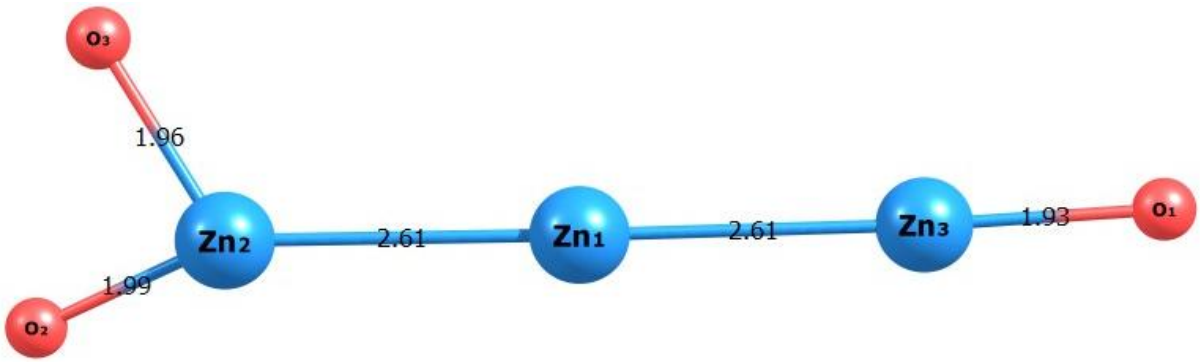


(Zn_5O_1**)**Hexagon



(Zn_5O_2**)**Hexagon$_1$

(Zn_4O_2**)**Linear



(Zn_3O_3**)**Linear

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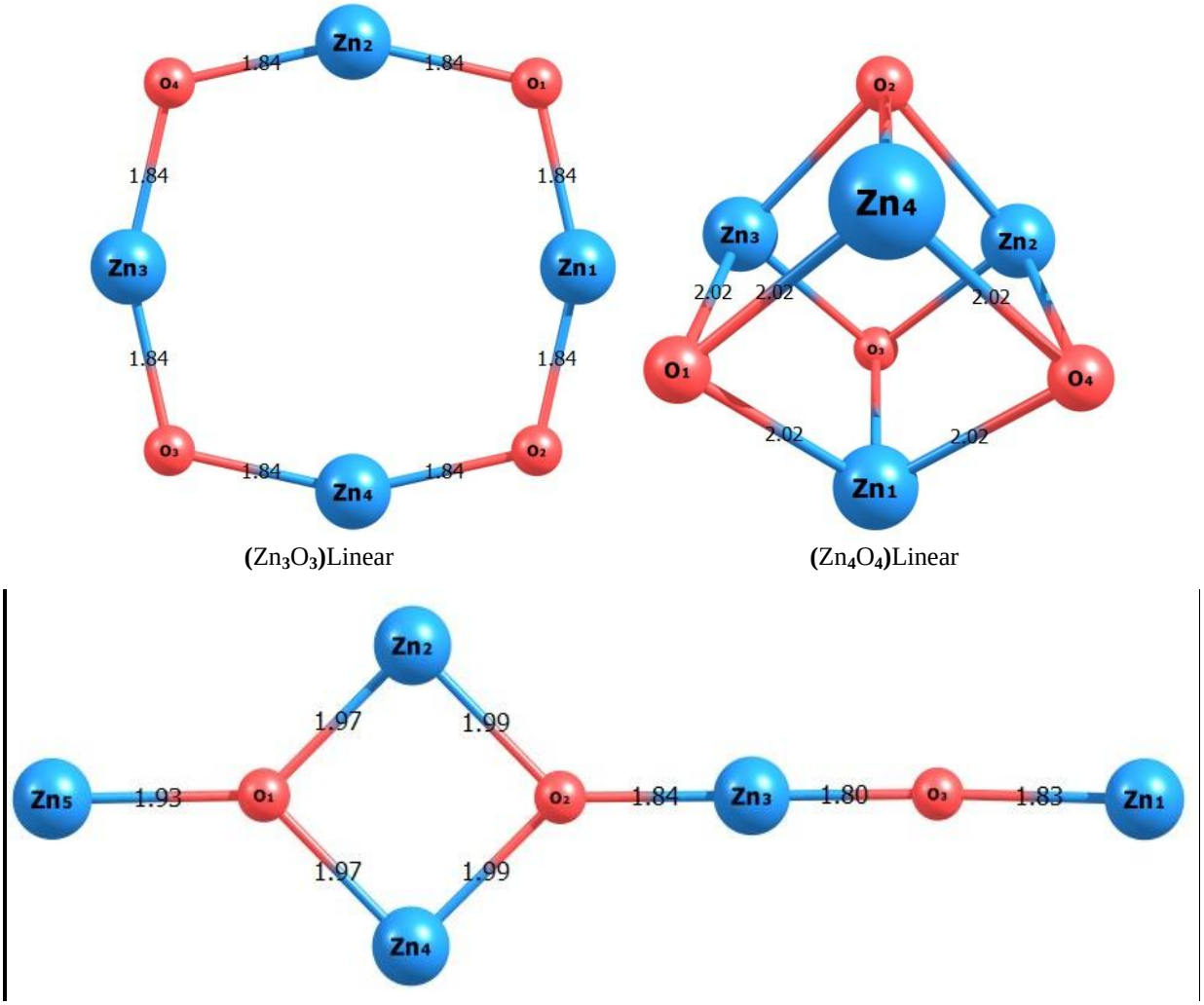

(Zn_3O_3**)**Linear **(**Zn_4O_4**)**Linear

(Zn_5O_3**)**Linear

Fig.1. Optimized Structures of Zn_mO_n (m+n=2-8) Nanoclusters.

III. RESULTS AND DISCUSSION

(Geometries and stability of ZnO nanoclusters**)**

This section deals with structural stability of ZnO nanoclusters. We have applied first principal calculation for various ZnO cluster to get the stable isomer in each size. For stability of nanocluster, we have defined binding energy of the nanocluster by the equation-

$$BE = [mE(Zn) + nE(O) – E(Zn_mO_n)]/(m+n)$$

Where, E(Zn), E(O), and $E(Zn_mO_n)$ are the total energy of isolated atoms ZnO and Zn_mO_n clusters, respectively, and m+n is the total number of Zn and O atoms. This is termed as the binding energy (BE) per atom. For more precise reckoningof binding energy of a system, the zero point vibrational energy (ZPE) is subtracted from the previous calculated binding energy value.

Calculated value of final binding energy, HOMO-LUMO gap and dipole moment are shown in the table1. In the following section, most sable nanoclusters of each even sized cluster have been discussed. Zn_mO_n (**m+n=2**) nanocluster contains only linear possible structure having bond length 1.97 A^0 and final binding energy is 0.10 Hartree.

Ground state multiplicity of ZnO is triplet and dipole moment is 2.71 Debye. For this linear ZnO molecule, theoretical bond length, 1.73 and 1.71 Å, is reported by A. Jain at. al. [23] and B. L. Wang et al. [24] which is slightly lower than the calculated results.

For the nanocluster size (**m+n=4**) of Zn_mO_n, we considered five geometries including trigonal, linear, bent and rhomboidal, are optimized wherein ZnO_3 $rhomboidal_1$ nanocluster has maximum final binding energy of 0.13 Hartree. So it will be the most stable structure among these five nanocluster structures. The bond length between Zn-O and O-O are 1.99 Å and-1.47 Å respectively, and bond angle between Zn-O-O is 85.84°. However, ZnO_3 has singlet ground state multiplicity and dipole moment 5.84 Debye. For Zn_mO_n (**m+n=6**), we optimized nine structures which possess the different geometry including linear, planer, triangular bipyramidal and hexagon. Out of these nine, Zn_4O_2 having planer geometry is found to be most stable because it has maximum final binding energy. The bond length between Zn_4-O_2 and O_2-Zn_2 is 1.87 Å, which is similar while between Zn_3-O_1 and O_1-Zn_4 is different. The angel between Zn_3-O_1-Zn_4 and Zn_1-O_1-Zn_4 is 86.52° and 105.39° respectively.

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TABLE1. The Symmetry, multiplicity of ground state (G.S), binding energy (B.E), Homo-Lumo gap and Dipole moment for ZnmOn (m+n=2-8) nanoclusters.

Nanocluster (No. of atoms)	**Configuration**	**Symmetry**	**Multiplicity**	**FBE (E_h)**	**Homo-Lumo Gap(E_h)**	**Dipole Moment(D)**
ZnO_(2)	**Linear**	**C*V**	**Singlet**	**0.10**	**0.09**	**2.71**
Zn_3O_(4)	Linear	CS	Singlet	0.04	0.07	11.94
Zn_2O_2	Bent	C1	Triplet	0.11	0.07	1.64
Zn_3O	Rhomboidal	C1	Singlet	0.05	0.04	2.62
ZnO_3	**$Rhomboidal_1$**	**CS**	**Singlet**	**0.13**	**0.08**	**5.84**
Zn_2O_2	$Rhomboidal_2$	C2V	Triplet	0.12	0.05	0.29
Zn_4O_2_(6)	**Planer**	**C1**	**Singlet**	**0.50**	**0.07**	**3.87**
Zn_5O	Triangular Bipyramidal	C1	Singlet	0.15	0.07	0.60
Zn_4O_2	$Triangular\ Bipyramidal_1$	C1	Singlet	0.06	0.07	3.03
Zn_3O_3	$Triangular\ Bipyramidal_2$	C1	Singlet	0.04	0.07	1.84
Zn_5O	Hexagon	C1	Singlet	0.01	0.01	2.31
Zn_4O_2	$Hexagon_1$	C1	Triplet	0.12	0.01	3.96
Zn_5O	Linear	CS	Singlet	0.02	0.07	14.74
Zn_4O_2	$Linear_1$	CS	Triplet	0.12	0.05	0.14
Zn_3O_3	$Linear_2$	C1	Triplet	0.10	0.08	2.04
Zn_4O_4 (8)	Ring	C1	Singlet	1.08	0.15	0.00
Zn_4O_4	Cube	C_2H	Singlet	1.06	0.11	0.00
Zn_5O_3	**Linear**	**C1**	**Triplet**	**1.24**	**0.03**	2.08

The ground state multiplicity of Zn_4O_2 is singlet and FBE is 0.50 E_h. Dipole moment is 3.87 Debye.

For Zn_mO_n (**m+n=8**), we optimized only three structures which are shown by figure1. The structural geometry-including linear, ring, and cube, are optimized. Out of these three structures, Zn_5O_3 rhomboidal linear is found to be most stable because it has maximum final binding energy of 1.24 E_h.The bond lengths between O_1-Zn_2, O_1-Zn_4 andZn_2-O_2, O_2-Zn_4 are 1.97 Å and 1.99 Å respectively while between Zn_5-O_1, O_2-Zn_3, Zn_3-O_2 and O_3-Zn_1 are 1.93 Å, 1.84 Å, 1.80 Å and 1.83 Å respectively. Bond angle between Zn_2-O_1-Zn_4 and Zn_2-O_1-Zn_4 is 90.37° and 89.23°. The ground state multiplicity of Zn_2O is singlet and dipole moment is 0.00 Debye. All the most stable configurations of ZnO nanoclusters are shown boldly in the Table 1, while structures are depicted by fig 1. The variation of final binding energy (FBE) of most stable structures with the cluster size is shown by figure 2. From the figure, it is clear that the binding energy is increasing with increasing the number of atoms in the clusters. Binding energy is minimum for Zn_mO_n (m=1, n=1) configuration and maximum for Zn_mO_n (m=5, n=3). On the basis of binding energy, we can say that Zn_5O_3 linear structure is most stable among all considered nanocluster.

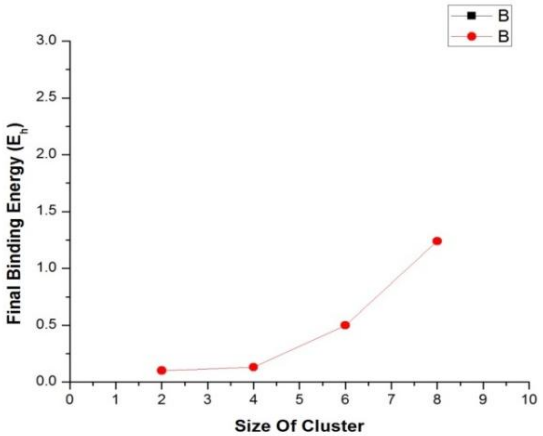

Fig.2. Final binding energy vs cluster size of ZnmOn

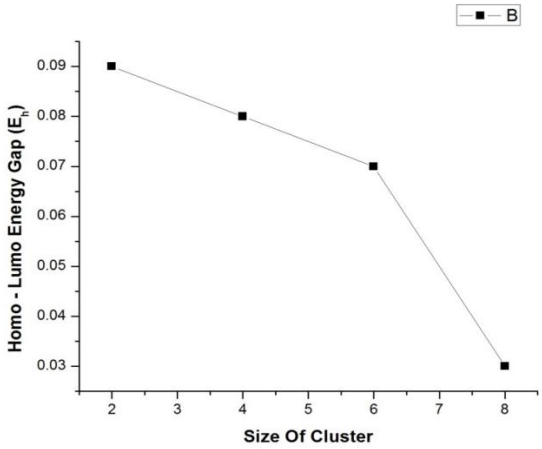

Fig.3. HOMO-LUMO gap vs cluster size of ZnmOn.

IV. ELECTRONIC PROPERTY: HOMO-LUMO GAP AND DOS OF ZNO NANOCLUSTERS

The HOMO–LUMO gap is defined as the energy difference between heighest occupiedand lowest unoccupied molecular orbitals. It depends upon the chemical reaction between atoms and molecules and structurel geometry.

The calculated energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) i.e. HOMO–LUMO gap for all the studied nanostructures is shown in Table 1whereas for the most stable structures it is shown bolded in the table.

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International Advanced Research Journal in Science, Engineering and Technology
Vol. 2, Issue 11, November 2015

Further, the graph is plotted between the total no. of atoms in nanocluster i.e. size of cluster and HOMO-LUMO energy gap for the most stable configuration of Zn_mO_n on the basis of lower binding energy.Figure 3 shows calculated energy gap as a function of cluster size.

It is evident from the figure 3 that with the increase of cluster size, the Homo-Lumo gap is decreasing. For Zn_mO_n (m=1, n=1) and Zn_mO_n (m=5, n=3) , we found it maximum and minimum which are 0.09 and 0.03 Hartree respectively. With the help of values of HOMO-LUMO, the information about the electronic properties of ZnO nanocluster can be known. High value of energy gap reveals that the electrons in the valance band needed more energy to go the conduction band.

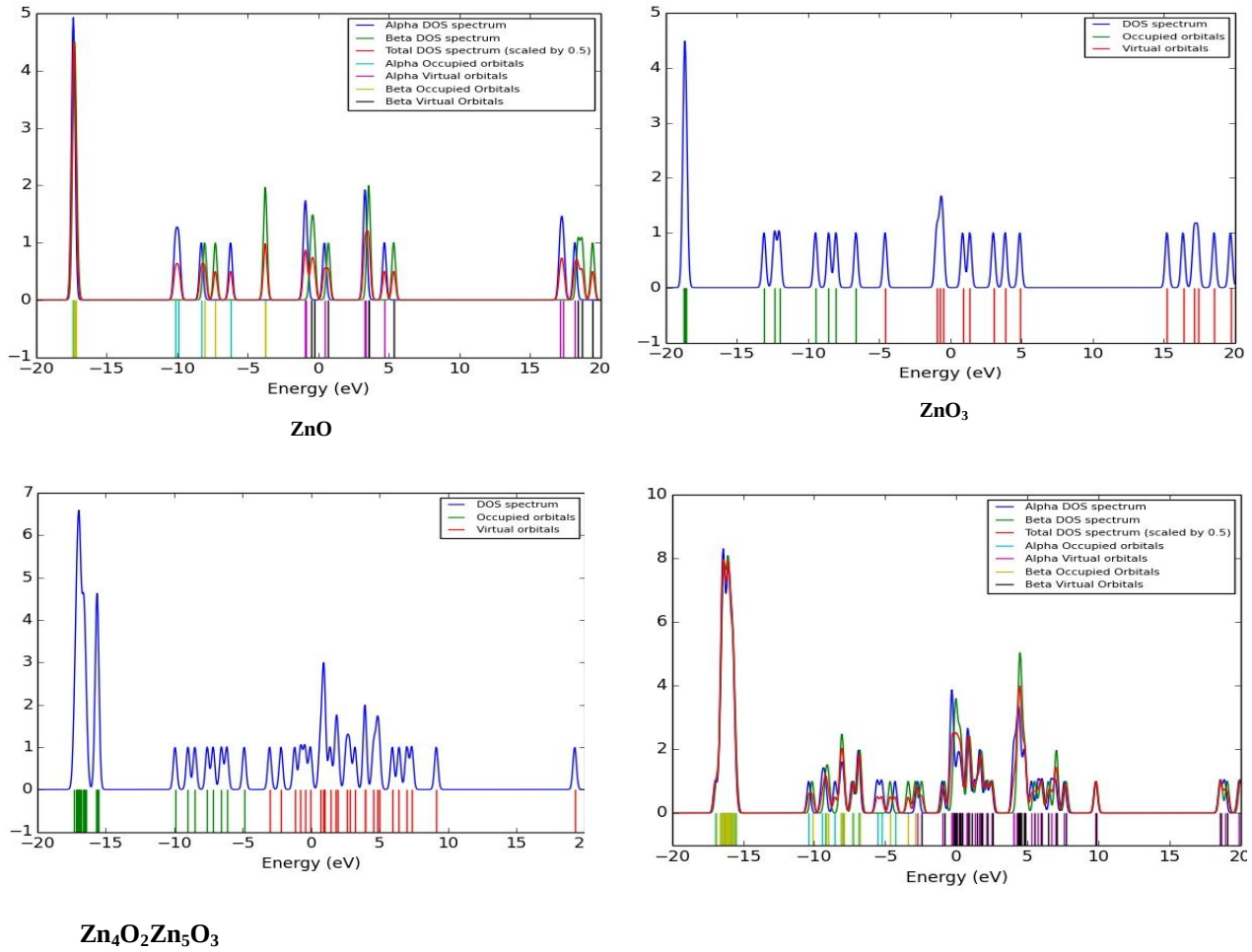

Fig.4. DOS, HOMO-LUMO energy diagram.

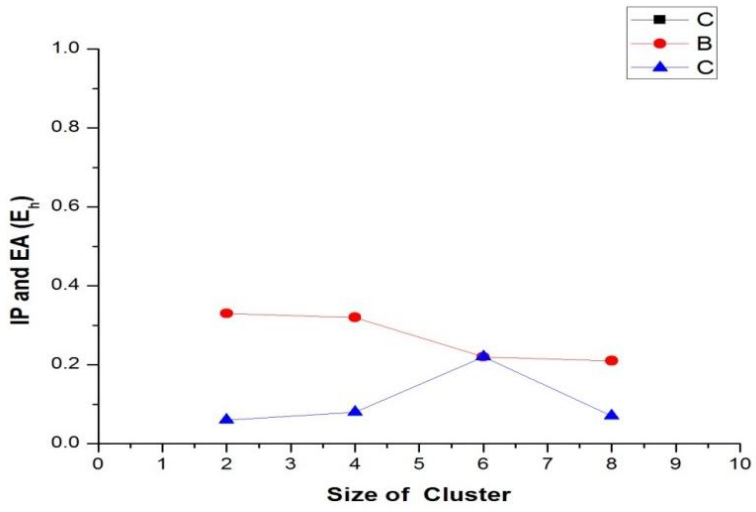

Fig.5. Inoization Potential and Electron Affinity gap vs cluster size of $Zn_mO_n$of most stable Zn_mO_n(m+n=2-8) nanoclusters**.**

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Density of state is much more depending on the geometry and number of the atoms present in the nanocluster. Figure 4, reveals that the ZnO and Zn_5O_3 both contain spin up and down electron because alpha and beta molecular orbital are presented in DOS diagram. In the case of ZnO_3 and Zn_4O_2 only alpha molecular orbital exists in particular range of energy which is clear from the figure. HOMO-LUMO energy visualization for all the most stable configuration of the Zn_mO_n (m+n=2-8) nanoclusters are displayed in figure 4.

V. IONIZATION POTENTIAL AND ELECTRON AFFINITY

From the theoretical point of view, ionization potential (IP) and the electron affinity (EA) of a nanocluster are very important properties. They are experimentally accessible and provide a direct measure for the type of bonding involved in a cluster. The ionization potential (IP) is well-defined as the amount of energy required to remove an electron from a nanocluster. In the present study, adiabatic ionization potential (AIP) has been calculated by taking the energy difference between the neutral and the ionized nanoclusters after finding the most stable structure for the ionized nanoclusters using the optimization procedure.

The electron affinity (EA) is defined as the energy evolved when an electron is added to a neutral cluster. In the current study, we have evaluated AEA by finding the energy difference between the neutral and the anionic nanocluster. The anionic nanocluster is relaxed to its most stable state. The graph is drawn for the most stable nanoclusters, between IP, EA and cluster size as shown in figure5. To the best of our knowledge, experimental data and earlier calculation is available very scarcely for comparison of IP and EA of considered configuration of Zn_mO_n nanoclusters.

Graph B represent the value of ionization potential and C represent the value of electron affinity. From graph it is clear that value of ionization potential is greater than electron affinity. The value of IP is decreasing with size of cluster. It is maximum for ZnO linear (0.33) and minimum for Zn5O3 linear (0.21) structure. Behaviour of electron affinity with size of cluster is zigzag. The value of EA is increasing from m+n = 2 to 6 and after then it is decreasing up to m+n = 8. The maximum and minimum value of EA are 0.22 and 0.06 Hartree for m+n = 6 and 2 nanocluster, respectively.

VI. VIBRATIONAL ANALYSIS

Analysis of vibrational frequencies is very significant parameter in exploring the local minimum in structures. It is observed that even for a small number of atoms in a cluster there are plenty of possible structures which may represent local minima on the energy hyper surface.In the present investigation, the displacement is found out and the obtained above calculated physical quantities for the most stable nanoclusters are listed in table2. The above physical properties have not been reported by any other worker for the considered nanocluster. We discuss the above properties for each most stable nanocluster in the following section:

For ZnO, we obtain the stretching mode frequency of 441.64 cm^{-1} which is both IR and Raman active. The values of IR intensity and Raman Activity at this frequency are 3.63 km mol^{-1} and 61.4472 A^4/amu found. Our IR value is slightly lower than the value 4.74 [25] reported by Xuelie et al. For ZnO_3 rhomboidal$_1$ structure, we obtain the frequencies 277.01 cm^{-1}, 312.00 cm^{-1},401.25 cm^{-1}, 651.09 cm^{-1}, 651.09 $cm^{-}1$, 795.47 $cm^{-}1$ and 856.97 cm^{-1} wherein the highest frequency of 856.97 cm^{-1} corresponds to the Zn–O stretching vibration.

TABLE2.The calculated vibrational frequencies (cm-1), infrared intensities (IR Int. in km mol-1), and Raman scattering activities (Raman activity in A4/amu) of most stable ZnmOn(m+n=2-8) nanoclusters.

Nanocluster	Configuration	Properties	Values
ZnO	Linear	Frequency IR Int. Raman activity	441.64 3.63 61.4472
ZnO_3	Rhomboidal$_1$	Frequency IR Int. Raman activity	277.01, 312.00, 401.25, 651.09, 795.47, 856.97 35.93, 23.34, 4.97, 0.12, 38.68, 139.10 29.93, 24.31, 6.82, 16.60, 2.59, 4.83
Zn_4O_2	Planer	Frequency IR Int. Raman activity	7.89, 71.25, 91.23, 112.76, 115.06, 144.49, 185.13, 210.23, 413.72, 491.33, 595.33, 632.29 0.02, 7.41, 2.08, 7.30, 7.08, 17.07, 2.48, 1.09, 3.87, 60.78, 35.55, 132.74 0.95, 143.96, 14.93, 12.77, 43.56, 0.44, 135.20, 1.00, 16.46, 21.98, 337.28, 1629.18
Zn_5O_3	Linear	Frequency IR Int. Raman activity	12.05, 17.34, 38.81, 45.29, 66.87, 91.79, 116.72, 121.68, 150.08, 201.93, 210.69, 243.49, 249.76, 331.97, 393.12, 617.29, 746.32, 880.54 0.68, 0.01, 1.25, 0.36, 17.93, 11.49, 1.57, 8.13, 3.75, 7.12, 33.122, 276.14, 102.41, 3.27, 10.82, 3.93, 21.76, 229.86, 8.27, 9.55, 16.82, 48.10, 316.44, 62.83, 495.56, 98.46, 9.19, 181.42, 12.58, 5597.79, 3099.41, 2407.19, 127.51, 4570.13, 10653.4546, 36930.5561

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Vol. 2, Issue 11, November 2015

In this case frequency 856.97 cm^{-1} is found to highly IR reactive in comparison to others. The value of IR intensity at this frequency is 139.10 km-mol^{-1}.The lowest frequency for this configuration is 7.89cm^{-1} and the value of IR intensities at this frequency is 0.02 km-mol^{-1}.In case of Zn_5O_3 linear structure18 mode of vibrational frequencies are exist and each mode of frequency is IR and Raman active. The frequencies are 12.05, 17.34, 38.81, 45.29, 66.87, 91.79, 116.72, 121.68, 150.08, 201.93, 210.69, 243.49, 249.76, 331.97, 393.12, 617.29, 746.32, 880.54cm^{-1}. At the highest frequency asymmetrical starching exist between Atom O_2, Zn_3, O_3 and Zn_1. The values of IR and Raman activity at this frequency are 229.86km mol^{-1} and 36930.5561A^4/amu respectively.

VII. CONCLUSIONS

In summary, DFT methods were used for the optimization of the most stable structures of the Zn_mO_n Nanoclusters. The calculated properties include bond lengths, multiplicity, point group symmetry, binding energy, Homo-Lumo energy gap and dipole moments, Ionization potential and Electron Affinity for the Zn_mO_n nanoclusters. Our results reveal that the existence of the most stable configurations of various Zn_mO_n nanoclusters depend on final binding energy and the nanocluster Zn_5O_3 (m+n = 8) with linear structure is most stable among all considered nanoclusters.

In general, nanoclusters with high BEs have large number of Zn atoms. It was observed that the value of HOMO–LUMO gap deceases with increase of cluster size. FBE is increasing with the increasing number of atoms i.e. size of cluster.The results of the present study should be useful in modelling and understanding the growth of Zinc-based clusters at the nano scale. The results should also motivate new experimental studies on this important discussion of clusters.

REFERENCES

[1] A. B. Djurišić, A.M. C. Ng, X.Y. Chen, "ZnO nanostructures for optoelectronics: Material properties and device applications", Progress in Quantum Electronics, Vol. 34, pp.191–159, 2010.
[2]CF Landes, S Link, MB Mohamed, B Nikoobakht, MA El-Sayed, "Some properties of spherical and rod-shaped semiconductor and metal nanocrystals", Pure and Applied Chemistry, vol. 74, pp. 1675-1692, 2002.
[3] G. Heiland, E. Mollwo, and F. Stockmann, "Electronic process in Zinc Oxide", Solid State Phys., Vol.8, pp. 193, 1959.
[4] J. R. Haynes, "Experimental observation of excitonic molecule", Phys. Rev. Lett., vol. 17 pp. 16, 1966.
[5] Y. Xia et al., "One dimensional nanostructures synthesis, characterization and application", Adv. Mater.Vol.15, pp. 353-388, 2003.
[6] B. Wen and R. Melnik, dynamics study of CdS "First principle molecular nanostructure temperature dependent phase stability", Appl. Phys. Lett., Vol. 92, pp. 261911, 2008.
[7] Ü. Özgür,a_ Ya. I. Alivov, C. Liu, A. Teke,b_ M. A. Reshchikov, S. Doğan,c_ V. Avrutin, S. J. Cho, and H. Morkoçd, "A comprehensive review of ZnO materials and devices", Journal Of Applied PhysicsVol. 98, pp. 041301, 2005.
[8] L. Ovsiannikova "Model and Properties of Fullerene-Like and Wurtzite-Like ZnO and Zn(Cd)O Clusters", Acta Physica Polonica A, Vol. 122, pp. 1062-1064, 2012.
[09] P. J. Sebastian and M. Ocampo, "A photo detector based on ZnCdS nanoparticles in a CdS matrix formed by screen printing and sintering of CdS and ZnCl2", Sol. Energy Mater. Sol. Cells, Vol. 44, pp. 1-10,1996.
[10] E. Corcoran, "Trends in Materials: Diminishing Dimensions", Sci. Am.Vol. 263, pp. 74, 1990.
[11] Z. L. Wang, "Nanostructures of zinc oxide",Mater. Today, vol. 7, pp. 26-33, 2004.
[12] X. Y. Kong, Y. Ding, R. Yang, Z. L. Wang, "Single-crystal nanorings formed by epitaxial self-coiling of polar Nanobelts", Science vol. 303 pp. 1348-1351, 2004.
[13]M. H. Zhao, Z.L. Wang, S.X. Mao, "Piezoelectriccharacterization on individual zinc oxide Nano belt under piezo response force microscope", Nano Lett., vol. 4, pp. 587-590, 2004.
[14] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A.Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, H. Morkoc, "A comprehensive review of ZnO materials and devices", J. Appl. Phys., vol. 98, pp. 041301, 2005.
[15] M. J. Spencer, "Gas sensing applications of 1D-nanostructured zinc oxide: Insights from density functional theory calculations" Prog. Mater.Sci., vol. 57, pp. 437-486, 2012.
[16] M. M. Brewster, X. Zhou, M. Y. Lu, S. Gradecak, "The interplay of structural and optical properties in individual ZnO nanostructures", Nanoscale vol. 4, pp. 1455–1462, 2012.
[17] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, "Exciton Spectrum of ZnO", Phys. Rev., vol. 143, pp. 512, 1966.
[18] X. Lü, X. Xu, N. Wang, Q. Zhang, M. Ehara, H. Nakatsuji, "Cluster modeling of metal oxides: How to cut out a cluster?", Chem. Phys. Lett., vol. 291, pp. 445–452, 1998.
[19] J. M. Matxain, J. E. Fowler, J. M. Ugalde, "Small clusters of II-VI materials: Zn_iO_i, i = 1-9", Phys. Rev. A vol. 62, pp. 053201–053211, 2000.
[20] J. Joswig, S. Roy, P. Sarkar, M. Springborg, "Stability and band gap of semiconductor clusters", Chem. Phys. Lett. Vol. 365, pp. 75-81, 2002.
[21] M. J. Frisch, G. W. Truck's, et-al, Gaussian, Inc., Wallingford CT, 2009.
[22] N. M. O. Boyle, A. L. Tenderholt, K. M Langner, Cclib a library for package-independent computational chemistry algorithms", J. Comp. Chem., vol. 29, pp. 839-845, 2008.
[23] A. Jain, V. Kumar, Y. Kawazoe, "Ring structures of small ZnO clusters", Comput. Mater.Sci. vol. 36, pp. 258-262, 2006.
[24] B. L. Wang, S. Nagase, J. J. Zhao, G. H. Wang, "Structural Growth Sequences and Electronic Properties of Zinc Oxide Clusters $(ZnO)_n$ (n=2-18)", J. Phys. Chem. C, vol. 111, pp. 4956-4963, 2007.
[25] Xueli Cheng, Feng Li and Yanyun Zhao, "A DFT investigation on ZnO clusters and nanostructures", Journal of Molecular Structure: Theochem,vol. 894, pp. 121–127, 2009.