

## Structural, vibrational and electronic properties of small group IV oxide clusters in lower and higher spin state: a DFT study

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**Abstract.** Structural, vibrational and electronic properties of the zirconium oxide clusters [ $n=1-6$ ] are calculated to investigate the changes in, lower and higher state by Density functional theory with the B3LYP exchange-correlation functional using LANL2DZ as the basis set. We optimize several isomers for each size in order to obtain the lowest energy structures and to understand the growth behavior. In the next step, these optimized geometries are used to calculate the binding energy and HOMO-LUMO gap (band gap) of the clusters. In all cases ring type structures are found to be most favorable but for  $n=3-6$ , the ring structures are not planar suggesting that the bonding nature in these cluster has some covalent character.

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**Key words:** density functional theory, zirconium oxide clusters, HOMO-LUMO

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## 1 Introduction

In the past two decades small and medium sized semiconductor clusters have been extensively studied due to their extremely important role in the physical and chemical processes taking place at the metal-semiconductor interface [1–5]. Zirconia assumes importance because of its high melting point, low thermal conduction and high ionic conductivity. The cubic phase of zirconia also has a very low thermal conductivity, which has led to its use as a thermal barrier coating or TBC in jet and diesel engines to allow operation at higher temperatures. A great deal of research is being carried out to improve the quality and durability of these coatings. It is used as a refractory material, in insulation, abrasives, enamels and ceramic glazes. Stabilized zirconia is used in oxygen sensors and fuel cell membranes because it has the ability to allow oxygen ions to move freely through the crystal structure at high temperatures. This high

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ionic conductivity (and a low electronic conductivity) makes it one of the most useful electroceramics. Zirconia is also an important high-k dielectric material that is being investigated for potential applications as an insulator in transistors in future nanoelectronic devices [6]. Its durability permits its use as a container for the safe disposal of high-level nuclear waste [7]. Small clusters of zirconium oxide can be taken as model geometries /models to understand the basic physics and chemistry of structures at nanolevel. Since the nanoclusters can be seen as intermediate between single atom/molecule and bulk materials the physical properties of material are dimension dependent and hence are scalable with respect to the amount of atoms in the material so effectively, that at nanoscale these properties vary with every change in the number of atoms.

Therefore, the studies on ZrO and its clusters assumes importance and in this communication we investigate the electronic, structural and vibrational properties of ZrO clusters with an increase in size in lower and higher state both. From the applications point of view, it shall be fully justified if we try to know the competing isomers as well as their properties such as the stability, HOMO-LUMO gaps, bonding nature etc.

## 2 Computational methods

The theoretical methods used in this study were based on the density functional theory [8] using the three-parameter hybrid functional B3LYP [9, 10] and LANL2DZ [11] as the basis set. The standard LanL2DZ basis as effective core potential with no symmetry constraint is employed here. This basis set provides an effective way to solve two-electron integrals even in case of heavy elements. The previous calculations as revealed in the literature [12–15] have shown that LanL2DZ basis sets of the effective core potential theory were found to be reliable for the geometries, stabilities, and electronic properties of transition metal clusters. The vibrational frequencies under the harmonic approximation, with analytical force constants were calculated. Harmonic vibrational analysis was performed for each system not only to obtain the vibrational frequencies, but also to characterize the nature of the structure obtained in the potential energy surface (PES). All calculations were performed using the Gaussian 09 software package [16].

## 3 Results and discussion

The optimized structures of different isomers are shown in Fig. 1. Isomers marked with 'a' are in lower state and those marked 'b' are in higher state. The details of the structures and the properties of the most stable isomers are given in Tables 1 and 2 for the lower and the higher states. The binding energy per ZrO molecule is calculated from the following equation

$$E_B = \frac{nE_{Zr} + nE_O - E_{ZrO}^n}{n},$$

where  $n$  is the number of ZrO molecules in the cluster. The variation of binding energies and HOMO-LUMO gap of the most favourable structures are shown in Figs. 2 and 3 for the lower