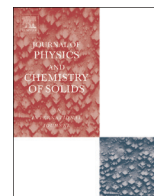




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Effect of oxygen content and charge on the structure, stability and optoelectronic properties of yttrium oxide clusters



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ABSTRACT

The electronic and geometrical structures of neutral and charged YOn ($n=2-12$) clusters have been investigated using density functional theory (DFT) with generalized gradient approximation. The oxygen atom in YOn has been found to be in oxo, peroxy and in superoxy forms. The geometrical structures and topologies of small size anionic clusters resemble that of neutral clusters. Yttrium showed higher coordination number than scandium. Computed results reveal the existence of YO_{10} cluster to have a pentaperoxy oxygen with a homoleptic $Y(\eta^2-O_2)_5$ geometrical configuration. The HOMO–LUMO gaps decrease with increasing n due to the increase in $2p$ orbital population of oxygen atoms. It has been shown that in these clusters bonding are predominantly ionic in nature and anions are thermodynamically more stable, due to the charge delocalization between the metal atom and oxygen ligands. YO_{10}^+ and YO_{12}^+ were found to be highly exothermic to release one and two oxygen molecules, while YO_{11}^+ dissociates through the ozonide dissociation channel. Computed absorption spectra of small clusters are mainly contributed by yttrium metal d and s valence orbitals. The absorbance spectra, shifts towards lower energy with cluster size increase, while charge has no substantial effect on the absorption spectrum.

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1. Introduction

Oxides of transition metals do play an important role in various catalytic and biological processes and consequently are the subject of numerous experimental and theoretical studies [1–3]. The transition metal atom with incomplete filled d -shell were able to form diverse oxide clusters, as dioxygen can bind to the metal centers in various ways such as side-on, end-on, or split to individual atoms, leading to the formation of peroxy-, superoxy-, oxoperoxy and oxosuperoxy forms [4,5]. The coordination number of oxygen atoms is an important property of an oxide cluster, which has a close relationship with the structural compactness and bonding character. It provides a clue to understand the microstructure of bulk oxide materials by methods such as NMR. There exist many studies on first row transition metal oxides. However, only little attention has been paid to heavy transition metal oxides [6].

Yttrium oxide is the most familiar yttrium compound which is also one of the most creep resistance oxides. Furthermore, yttrium oxide is a component of ceramic materials such as yttrium aluminum garnet (YAG) finds applications in optical sensors, is used

as X-ray detection material and in high temperature ceramic composites [7]. Besides the above, yttrium oxide materials have low-thermal expansion, high optical transparency, low acoustic loss, high threshold for optical damage, hardness, and general stability against chemical and mechanical interactions. The oxide a high temperature infrared (IR) and electronic material, and it has many attractive applications [8]. Moreover, yttrium oxide has been widely investigated as a host material for rare-earth ion doping, used in optical applications due to its excellent chemical stability, high optical transparency in the far-IR region and high band gap [9]. For the above pointed reasons, several studies have been carried out on the optical properties of lanthanides doped on the Y_2O_3 crystals.

The optical constants, namely the refractive index and extinction coefficient (k), of Y_2O_3 play a critical role in designing optical and electro-optic devices [10]. Specifically, significant efforts were directed to enhance the refractive index, which is expected to lead the optical transmission enhancement. However, refractive index and extinction coefficient profiles of real Y_2O_3 films are highly dependent on their microstructure [11]. Recent studies have shown that the increase in the oxygen flow during the preparation of Y_2O_3 films, results in structure transforms from cubic to polycrystalline and then to amorphous states [12]. Furthermore, the disordered structure of Y_2O_3 film facilitates the acquirement of low values of refractive index values [13]. Hence, the ability to tailor the properties and optimize performance requires a detailed

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understanding of the relationship between electronic and geometric structure, particularly at the nanoscale level.

Among the oxides clusters of group 3 elements, scandium oxides are well studied; however little information is known about yttrium oxides [14–18]. Knickelbein probed the ionization potentials (IPs) of Y_n and Y_nO clusters in a size range from 2 to 31 atoms [19]. Matrix isolated infrared spectroscopic studies of yttrium monoxide shows the formation of complexes with a coordination of multiple noble gas atoms [20]. Further, under oxygen rich condition, the initially formed yttrium dioxide molecule interacts spontaneously with additional O_2 molecules to form the oxygen-rich superoxo bisozonide complex [21]. A study on laser-ablated Y and La atom reactions with molecular oxygen showed the formation of metal oxides, which were absorbed on matrix [22]. The IR spectra for the matrix absorbed YO molecule showed a 12.1 cm^{-1} red-shift from the gas-phase value. In addition, Wu and Wang carried out vibrationally resolved photodetachment studies on YOn ($n=1-5$) clusters. The photoelectron spectra of yttrium oxide cluster anions were studied by Nakajima and coworkers [23]. The threshold energies of the photoelectron spectra were found to shift to higher binding energies with the cluster size increase. Ducan and Reed carried out a photodissociation studies on yttrium oxide cluster cations [24]. Photodissociation occurs by a sequential process, with the loss of Y_2O_3 with the predominant formation of $Y_6O_8^+$ cluster.

Xiong and Yang carried out DFT study to understand the structural, electronic and magnetic properties of yttrium clusters with oxygen atom [25]. The magnetic moments of the yttrium clusters were quenched by the introduction of oxygen atom. The introduction of dioxygen atom near the yttrium clusters showed that the oxygen molecule undergoes dissociative addition on clusters, while the O_2 absorbed structures were unstable [26]. Further, the Y_3O_2 anion was found to be more stable compared to other clusters. In addition, the magnetic moment of the clusters were very small, and it is mainly due to the 4d and 5s electrons of Y atom. The low lying electronic state of YO_2^- molecules were computed by Mok and coworkers [27]. The Franck–Condon spectra computed using the coupled-cluster with single and double and perturbed triple excitations (CCSD(T)) method are in excellent agreement with the photodetachment spectrum obtained at the 355 nm excitation. In the recent DFT study made on the small yttrium trioxide clusters, it was indicated that the neutral and anion have similar geometry [28]. Among the trioxides, Y_4O_3 was found to have higher stability with zero magnetic moment, while its anion has $3\text{ }\mu\text{B}$ magnetic moment. Recently, Deshpande and coworkers carried out DFT studies on neutral and charged Y_2O_3 clusters to understand their growth pattern [29]. They observed the increase of the charge transfer from Y atom with the increase in cluster size and the clusters preference for the lowest spin state.

The oxidation number of Y is the same as that of Sc as both the elements belong to the same group three in the periodic table. As yttrium atom is bigger in size has more lanthanide character and has higher electron affinity: can yttrium atom bind more oxygen atoms than scandium? Unfortunately there are no experimental or theoretical data on the structure of YOn for $n > 4$. The present paper is aimed at systematic search of the geometrically stable YOn isomers for $n=2$ to 12 using the density functional theory (DFT). Next we have performed extensive calculations to identify the effect of oxygen content on the stability and electronic properties of neutral and charged YOn clusters. We also computed the optical properties using the Time-Dependent Density Functional Theory (TD-DFT) of the lowest energy neutral, cationic and anionic species to understand how the optical properties are altered by the charge and oxygen content. In Section 2, we outline our theoretical procedures followed. Section 3 describes the changes in the yttrium oxide structure when changing the oxygen content

and the charge. We discuss the properties of the neutral and charged species in terms of their thermal stability, ionization potential and electron affinity. We also present the TD-DFT results for the lowest energy geometries of the neutral and charged YOn clusters and discuss how the oxygen content changes its optical properties. In Section 4, the conclusion drawn from the above work is presented.

2. Computational details

All the density functional theory calculations were performed with the Gaussian 09 program package [30]. Since the growth motifs of YOn clusters are unclear, we have made an extensive search to find the lowest energy structures in two ways (i) by considering the possible structures reported for the first row transition metal oxides and (2) by considering different trial geometries, where oxygen atoms are bound to the yttrium atom molecularly, dissociatively and in the ozonide form [31–34]. All spin multiplicities from singlet to undecet were tried in order to determine the total spin of the ground state, and the default convergence threshold were used during the calculations. The structural optimizations were carried without symmetry constraints using the hybrid B3LYP [35], PBE0 [36] and the pure functional BPW91 [37]. In our previous study, the use of pure functional has provided accurate prediction on the bond parameters, ionization energy and frequencies for the yttrium alloy clusters [38]. In order to induce the scalar relativistic effect for the heavy element yttrium, it was treated with effective core potentials, the Los Alamos set of double-zeta type (Lanl2DZ) basis set [39] and polarized Quadruple- ζ basis set def2-QZVP [40], while the all electron basis set is used for oxygen.

In order to gain insight in to the performance of the different methods, calibration calculations are performed using B3LYP, PBE0 and BPW91 methods with Lanl2DZ and def2-QZVP basis sets. Table 1 provides the bond length, vibrational frequency and vertical electron affinity (VEA) and vertical ionization potentials (VIP) for the neutral and charged YO dimer clusters. All the tested methods predict the ground state geometry, similar to those predicted in the previous works. Furthermore, in all the methods the spin contaminations was found to be low and are close to the theoretical values. The BPW91 method was able to predict vibrational frequencies, VIP, VEA and dissociation energy closer to the experimental values, as compared to the other methods tested. Furthermore, the use of def2-QZVP basis set was essential to predict the stretching frequencies accurately for these clusters. Thus the choice of BPW91/def2-QZVP for DFT calculations is justified as a compromise between reliable results and reasonable computational cost. It should be mentioned that the BPW91 functional has been preferred in the study of transition metal oxides. Since the pure generalized gradient approximation (GGA) functional such as BPW91 usually lead to high symmetry structures, B3LYP calculations are also employed [41]. The first five low lying energy states for all the oxygen compositions were re-optimized using the B3LYP functional with symmetry constraints and the energy discrepancy by different functional was verified. In order to confirm the proper converges to minima, the vibrational frequencies were computed at the BPW91/def2-QZVP level of theory and negative frequency absence was confirmed.

The adiabatic electron affinity (EA_{ad}) is calculated as the energy difference between total energies and the corresponding anion energy at their respective ground state geometries and the adiabatic ionization energy is computed as the energy difference between total energies of a cation and corresponding neutral species at their respective ground state cation energy and corresponding neutral species at their respective ground state spin multiplicity

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