Theoretical study of transition metal oxide clusters (TM$_n$O$_m$) [(TM- Pd, Rh, Ru) and (n, m =1, 2)]

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Abstract. Structural, vibrational and electronic properties of the transition metal oxide clusters (PdO, RhO, and RuO) are calculated to investigate the changes, when an electron is either added or removed from the corresponding neutral clusters by Density functional theory with the B3LYP exchange-correlation functional using LANL2DZ as the basis set. In the first place, geometrical optimization of the nanoclusters have been carried out. In the next step, these optimized geometries are used to calculate the binding energy and HOMO-LUMO gap (band gap) of the clusters. The calculated results tell that the addition of an electron to the neutral clusters induces appreciable structural changes relative to the case when an electron is removed. The changes in vibrational properties can be explained in terms of the variation of the interatomic distances upon removing or adding the electron.

1 Introduction

There has been a considerable interest in the study of chemical, materials, and surface sciences because of their diverse physicochemical properties and technological applications [1]. Because of the wide applications in many areas, such as high temperature chemistry, nanotechnology, material science, microelectronics and heterogeneous catalysts or catalysis supports in the chemical industry, transition metal clusters, especially transition metal oxide clusters, have attracted a lot of attention in the recent past from both theory and experiment [2-6] point of view. Transition metal oxides, among them pure V-O, Mo-O oxides and mixed V-O-X (X = P, Mg), Mo-O-X (X = Co, Bi, Sb) systems represent an important class of materials due to their technological and commercial applications. They play a crucial role in catalysis and environmental protection; their properties form

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a platform for totally new devices and technologies [7-10]. Because of the inability of experimental methods to probe a system precisely, the computer mimicking is fast becoming increasingly useful to explore the physics and chemistry at the atomic level.The main thrust of this study is to investigate the structural, electronic, vibrational and chemical reactivity of small transition metal oxide clusters and possibly use them for predicting and fine tuning of materials properties.

2   Computational methods

The first principle calculations used the B3LYP functional with Lanl2dz basis set for both transition metal and oxygen atom. The study of neutral, cationic and anionic transition metal oxide clusters has been carried out by the density functional theory (DFT) using the Gaussian 09 code [11]. The gradient-corrected B3LYP functional form (i.e. Becke's 3-parameter hybrid exchange functional [12] and Lee, Yang, and Parr correlation functional [13]) was employed in the calculations. The previous calculations [15-18] revealed that LanL2DZ basis set of the effective core potential theory were proven to be reliable for the geometry, stability, and electronic properties of transition metal clusters. To determine the ground state structures of these TM_nO_m clusters, we constructed as many initial structures as possible. The geometry optimizations were carried out with no symmetry constraint.

2.1   Results and discussion

2.1.1   Structural analysis (Clusters like TMO, TMO_2, TM_2O and TM_2O_2)

The calculated spectroscopic constants, i.e., bond length (R_e), vibrational frequency (ω), and binding energy (D_e), dipole moment and band gap of the transition metal oxide monomers are listed in Table 1. The calculated spectroscopic constants, i.e., bond length (R_e), and binding energy (D_e), and band gap of the transition metal oxide clusters like TMO_2 and TM_2O are collected in Table 2. The initial bent structure [(O-TM-O) and (TM-O-TM)] with the C_{2v} symmetry is found to be the most stable in all states. All the possible structures of TM_2O_2 which have been considered are shown in Fig. 1. The bond lengths and binding energy of the most stable structure of the neutral as well as the ionic clusters can be found in Table 3.

2.1.2   Neutral state

The calculated bond length (R_e) for neutral PdO, RhO and RuO is 1.83, 1.78 and 1.73 Å, respectively, and the corresponding vibrational frequencies (ω) are 711, 802 and 917 cm^{-1}, respectively. The value of bond length increases when we go from left to right (Ru$\rightarrow$ Pd) in a periodic table due to the increase in atomic size. The calculated bond length (R_e) for neutral PdO_2, RhO_2 and RuO_2 is 1.76, 1.72 and 1.71 Å, respectively. The calculated bond length (R_e) for neutral Pd_2O, Rh_2O and Ru_2O is 1.94, 1.96 and 1.99 Å,