

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

Apoorva Dwivedi and Neeraj Misra*

Department of Physics, Lucknow University, Lucknow 226007, India

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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.

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Key words: transition metaloxide, structure, stability, DFT

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

*Corresponding author. *Email address:* neerajmisra11@gmail.com (N. Misra)

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,

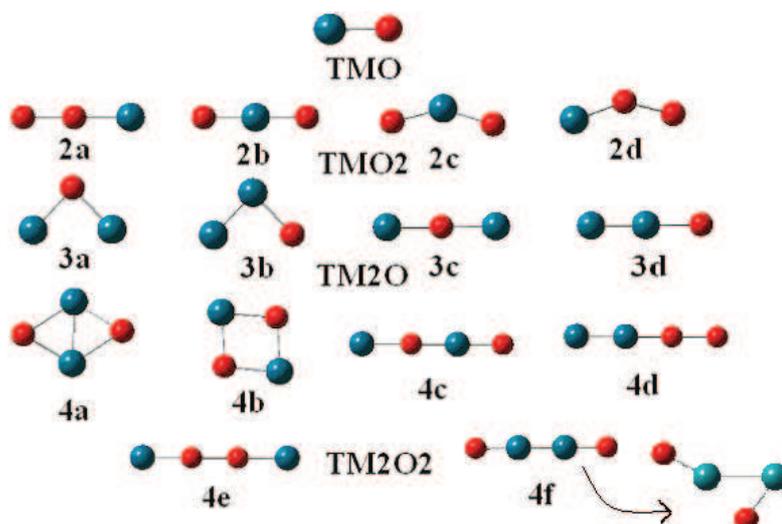


Figure 1: Different possible structures of Transition metal oxide clusters

respectively. Among all the initial configurations the square type structure is found to be the most stable one for Pd_2O_2 and Rh_2O_2 cluster, but Ru_2O_2 cluster was found stable in a distorted rhombic form. For Pd_2O_2 , The value of the Pd-O bond length is 1.98 Å. For

Table 1: Symmetry, bond lengths (Å), vibrational frequencies (cm^{-1}) and some other parameters of monomers.

Parameters	Symmetry	Bond length (Å)	Vibrational frequency (cm^{-1})	Binding energy (eV)	Dipole moment	Band gap
PdO	C_{infv}	1.83	711	1.92	4.82	1.32
PdO ⁺	C_{infv}	1.84	549	1.80	2.31	$\alpha = 2.88$ $\beta = 2.38$
PdO ⁻	C_{infv}	1.85	672	1.48	4.13	$\alpha = 2.31$ $\beta = 1.36$
RhO	C_{infv}	1.78	802	2.97	4.24	$\alpha = 2.05$ $\beta = 1.69$
RhO ⁺	C_{infv}	1.71	935	2.81	2.93	1.81
RhO ⁻	C_{infv}	1.81	756	1.72	4.33	0.84
RuO	C_{infv}	1.73	917	3.81	4.27	1.45
RuO ⁺	C_{infv}	1.66	917	3.32	3.27	$\alpha = 2.46$ $\beta = 2.48$
RuO ⁻	C_{infv}	1.77	851	3.41	1.36	$\alpha = 2.46$ $\beta = 2.29$

Rh_2O_2 , the value of the Rh-O bond length is 1.92 Å. For Ru_2O_2 , the value of Ru-O and Ru-Ru bond length is 1.91 Å and 2.46 Å respectively.

These calculated/predicted values can prove to be very helpful to the experimentalists.

Table 2: Symmetry, bond lengths (Å), binding energy and band gap for TMO_2 and TM_2O like clusters.

Parameters (Symmetry)	R(TM-TM) (Å)	R(TM-X) (Å)	R(X-X) (Å)	D_e (eV)	Band gap (eV)
PdO_2 (C_{2v})	-	1.76	-	2.91	1.86
PdO_2^+ (C_{2v})	-	1.75	-	2.06	$\alpha = 1.77$ $\beta = 1.45$
PdO_2^- (C_{2v})	-	1.81	-	3.18	$\alpha = 3.38$ $\beta = 2.32$
PdO_2 (C_{2v})	-	1.72	-	4.12	$\alpha = 1.85$ $\beta = 1.96$
PdO_2^+ (C_{2v})	-	1.69	-	3.68	1.69
PdO_2^- (C_{2v})	-	1.76	-	3.01	1.73
PdO_2 (C_{2v})	-	1.71	-	5.33	1.96
PdO_2^+ (C_{2v})	-	1.69	-	4.14	$\alpha = 2.57$ $\beta = 2.76$
PdO_2^- (C_{2v})	-	1.75	-	4.09	$\alpha = 1.88$ $\beta = 2.09$
PdO_2 (C_{2v})	-	1.94	-	2.24	2.04
PdO_2^+ (C_{2v})	-	1.89	-	5.35	$\alpha = 2.27$ $\beta = 2.25$
PdO_2^- (C_{2v})	-	1.98	-	1.81	$\alpha = 2.23$ $\beta = 1.98$
PdO_2 (C_{2v})	-	1.96	-	2.60	0.75
PdO_2^+ (C_{2v})	-	1.88	-	6.57	$\alpha = 1.25$ $\beta = 1.62$
PdO_2^- (C_{2v})	-	1.95	-	2.34	$\alpha = 1.41$ $\beta = 1.33$
PdO_2 (C_{2v})	-	1.99	-	3.84	0.82
PdO_2^+ (C_{2v})	-	1.91	-	6.16	$\alpha = 2.47$ $\beta = 1.54$
PdO_2^- (C_{2v})	-	2.00	-	3.47	$\alpha = 1.30$ $\beta = 0.81$

Table 3: Symmetry, bond lengths (\AA), binding energy and band gap for TM_2O_2 like clusters.

Parameters (Symmetry)	$R(\text{TM-TM})$ (\AA)	$R(\text{TM-X})$ (\AA)	$R(\text{X-X})$ (\AA)	D_e (eV)	Band gap (eV)
PdO_2 (C_{2v})	-	1.98	-	2.97	1.82
PdO_2^+ (C_{2v})	-	1.95	-	5.12	$\alpha = 2.61$ $\beta = 2.39$
PdO_2^- (C_{2v})	-	2.03	-	1.96	$\alpha = 2.01$ $\beta = 1.88$
Rh_2O_2 (C_{2v})	-	1.92	-	3.71	1.91
Rh_2O_2^+ (C_{infv})	-	1.73-1.95	-	6.46	$\alpha = 2.70$ $\beta = 1.81$
Rh_2O_2^- (C_{infv})	-	1.78-1.85	-	2.75	$\alpha = 1.80$ $\beta = 1.78$
Ru_2O_2 (C_{2v})	2.46	1.91	-	4.79	1.82
Ru_2O_2^+ (C_{2v})	-	1.89	-	6.28	$\alpha = 2.15$ $\beta = 0.99$
Ru_2O_2^- (C_1)	2.35	1.84	-	6.28	1.78

2.1.3 Cationic state

For the cationic case (the ionized electron comes out from a bonding orbital), The calculated bond length (R_e) for PdO, RhO and RuO is 1.84, 1.71 and 1.66 \AA , respectively, whereas the corresponding vibrational frequencies (ω) are 549, 935 and 917 cm^{-1} , respectively. Palladium is a 4d group element with all filled electrons in outer shell and as the electron is removed it shows an increase in the bond length (1.84 \AA) and a decrease in the frequency value (549 cm^{-1}) indicating that the bond in cationic state is weaker than the corresponding one in the neutral monomer. For the cationic case, the calculated bond length (R_e) for PdO_2 , RhO_2 and RuO_2 is 1.75, 1.69 and 1.69 \AA , respectively. Decrease in bond length indicates that the bond in cationic state is stronger than the corresponding one in the neutral monomer. The calculated bond length (R_e) for Pd_2O , Rh_2O and Ru_2O is 1.89, 1.88 and 1.91 \AA , respectively. Among all the initial configurations the square type structure is found to be the most stable one for Pd_2O_2 and Ru_2O_2 cluster but linear (4c) for Rh_2O_2 cluster. For Pd_2O_2 , The value of the Pd-O bond length is 1.95 \AA . For Rh_2O_2 , the value of the Rh-O bond length is 1.73-1.95 \AA . For Ru_2O_2 , the value of Ru-O bond length is 1.89 \AA .

2.1.4 Anionic state

The calculated bond length (R_e) for PdO, RhO and RuO is 1.85, 1.81 and 1.77 \AA , respectively, whereas the corresponding vibrational frequencies (ω) are 672, 756 and 851 cm^{-1} . Increase in bond length and decrease of the frequency value indicates that the bond in anionic state is weaker than the corresponding one in the neutral monomer. The calculated

bond length (R_e) for PdO_2 , RhO_2 and RuO_2 is 1.81, 1.76 and 1.75 Å, respectively. Increase in bond length indicates that the bond in anionic state is weaker than the corresponding one in the neutral monomer. The calculated bond length (R_e) for all Pd_2O , Rh_2O and Ru_2O is 1.98, 1.95 and 2.00 Å, respectively. Among all the initial configurations the square type structure is found to be the most stable one for Pd_2O_2 , linear (4c) for Rh_2O_2 cluster and 4f distorted linear structure after optimization for Ru_2O_2 cluster. For Pd_2O_2 , The value of the Pd-O bond length is 2.03 Å. For Rh_2O_2 , the value of the Rh-O bond length is 1.78-1.85 Å. For Ru_2O_2 , the value of Ru-O and Ru-Ru bond length is 1.84 and 2.35 Å.

3 Stabilities

In this subsection, the relative stabilities of TM_nO_m clusters are analysed based on the average binding energies.

Binding energy per atom of the TM_nO_m clusters is defined as follows:

$$EBE = (n * E[\text{TM}] + m * E[\text{O}] - E[\text{TM}_n\text{O}_m]) / (n + m) \quad (\text{For neutral clusters})$$

$$EBE = (n * E[\text{TM}_+] + m * E[\text{O}] - E[\text{TM}_n\text{O}_{m+}]) / (n + m) \quad (\text{For cationic clusters})$$

$$EBE = (n * E[\text{TM}] + m * E[\text{O}_-] - E[\text{TM}_n\text{O}_{m-}]) / (n + m) \quad (\text{For anionic clusters})$$

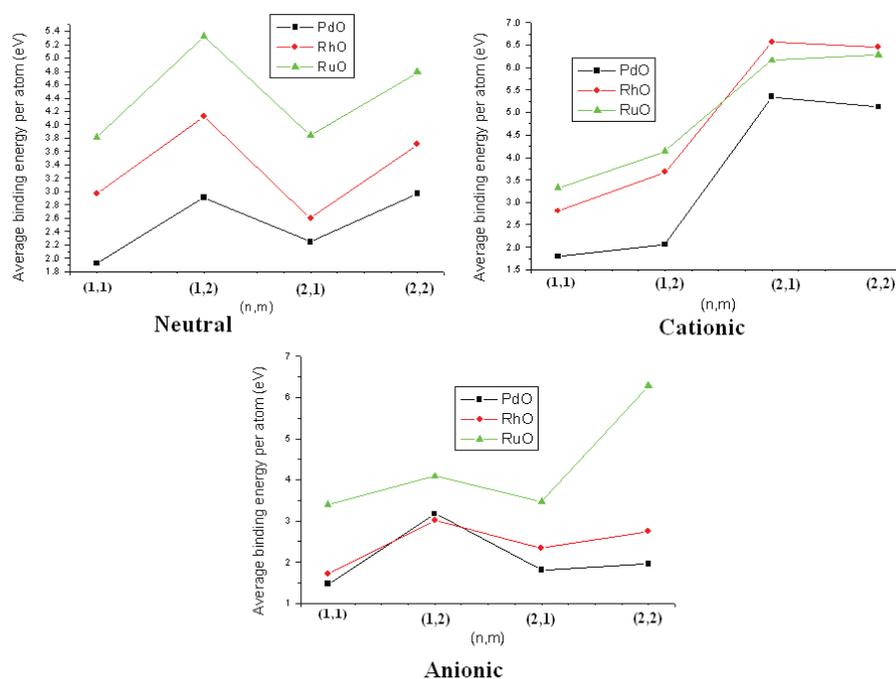


Figure 2: variation of binding energy per atom with different combinations

The values of binding energy per atom of all clusters (TMO, TMO₂, TM₂O and TM₂O₂) are given in Tables 1, 2 and 3 respectively. The variation of binding energy per atom of all clusters shows same trend for neutral and ionic states given in Fig. 2. It can be said that the average binding energy of all the clusters have a gradually increasing and decreasing trend depending upon the cluster size. The prominent and sudden peak occurs in case of Rh₂O (BE=6.57 eV) as well as in case of Pd₂O (BE=5.35 eV) and also in case of Ru₂O (BE=6.16 eV), all in cationic states.

3.1 Electron affinity, ionization potential, chemical potential and chemical hardness for monomers and dimers

The calculated electron affinity, the ionization potential, chemical potential and chemical hardness for the monomers, dimers and trimers are listed in Table 4. We define the electron affinity to be $EA = E(\text{neutral}) - E(\text{anion})$ and the ionization potential to be $IP = E(\text{cation}) - E(\text{neutral})$. We define the chemical potential to be $\mu = -(IP + EA)/2$ and chemical hardness to be $\eta = (IP - EA)/2$. In view of the importance of the hardness as an alternative measure of the stability of the system it would be good idea to relate it to some of the molecular descriptors also.

In case of PdO₂, the noticeable feature is the electron affinity which comes out to be equal to 3.96 and of course the stability with chemical hardness equal to 3.57 eV and this is further supported by the work of Fu *et al.*[19] in which it has been stated that the PdO₂ formed under UV254+185nm irradiation can trap the photogenerated electrons, thus increasing the photocatalytic activity of Pd-TiO₂.

Table 4: Electron affinity and ionization potential, chemical potential and chemical hardness for monomers and dimers.

Structures	Electron affinity (eV)	Ionization potential (eV)	Chemical potential (eV)	Chemical hardness (eV)
PdO	2.28	8.82	5.55	3.27
RhO	0.66	9.55	5.11	4.45
RuO	2.36	7.78	5.07	2.71
PdO ₂	3.96	11.10	7.53	3.57
RhO ₂	2.97	10.56	6.76	3.79
RuO ₂	2.86	10.40	6.63	3.77
Pd ₂ O	1.88	7.80	4.84	2.96
Rh ₂ O	2.37	6.55	4.46	2.09
Ru ₂ O	2.06	6.67	4.36	2.31
Pd ₂ O ₂	2.29	8.57	5.43	3.14
Rh ₂ O ₂	2.49	7.43	4.96	2.47
Ru ₂ O ₂	0.11	7.67	3.89	3.78

Table 5: Charge on atoms of the configurations of (TM_nO_m) nanoclusters.

Nano clusters	Atomic charges			
	q1	q2	q3	q4
PdO	0.464753	-0.464753	-	-
PdO ⁺	1.030679	-0.030679	-	-
PdO ⁻	-0.368010	-0.631990	-	-
RhO	0.403940	-0.403940	-	-
RhO ⁺	1.080860	-0.080860	-	-
RhO ⁻	-0.374622	-0.625378	-	-
RuO	0.403739	-0.403739	-	-
RuO ⁺	1.080698	-0.080698	-	-
RuO ⁻	-0.479737	-0.520263	-	-
PdO ₂	0.691167	-0.345584	-0.345584	-
PdO ₂ ⁺	1.166664	-0.083332	-0.083332	-
PdO ₂ ⁻	0.152546	-0.576273	-0.576273	-
RhO ₂	0.733271	-0.366636	-0.366636	-
RhO ₂ ⁺	1.227167	-0.113583	-0.113583	-
RhO ₂ ⁻	0.120556	-0.560278	-0.560278	-
RuO ₂	0.788508	-0.394254	-0.394254	-
RuO ₂ ⁺	1.281823	-0.140911	-0.140911	-
RuO ₂ ⁻	0.162980	-0.581490	-0.581490	-
Pd ₂ O	0.238238	0.238238	-0.476476	-
Pd ₂ O ⁺	0.714185	0.714185	-0.428369	-
Pd ₂ O ⁻	-0.227399	-0.227399	-0.545201	-
Rh ₂ O	0.242712	0.242712	-0.485423	-
Rh ₂ O ⁺	0.675743	0.675743	-0.351486	-
Rh ₂ O ⁻	-0.226253	-0.226253	-0.547495	-
Ru ₂ O	0.262937	0.262937	-0.525875	-
Ru ₂ O ⁺	0.696745	0.696745	-0.393490	-
Ru ₂ O ⁻	-0.204437	-0.204437	-0.591125	-
Pd ₂ O ₂	0.486221	0.486221	-0.486221	-0.486221
Pd ₂ O ₂ ⁺	0.834128	0.834128	-0.334128	-0.334128
Pd ₂ O ₂ ⁻	0.078256	0.078256	-0.578256	-0.578256
Rh ₂ O ₂	0.498069	0.498069	-0.498069	-0.498069
Rh ₂ O ₂ ⁺	0.879610	0.909653	-0.611973	-0.177291
Rh ₂ O ₂ ⁻	0.088104	0.051169	-0.596465	-0.542808
Ru ₂ O ₂	0.514936	0.514936	-0.514936	-0.514936
Ru ₂ O ₂ ⁺	0.907336	0.907336	-0.407336	-0.407336
Ru ₂ O ₂ ⁻	0.293840	0.520086	-0.342297	-0.471628

Table 6: Vibrational frequencies and dipole moment of different (TM_nO_m) most stable structures [cm^{-1}].

Structures	Frequency values (Mode)[cm^{-1}]	Dipole moment (Debye)
PdO_2	145 (A1), 779 (A1), 895(B2)	1.30
PdO_2^+	135(A1), 781(A1), 845(B2)	1.81
PdO_2^-	117(A1), 727(A1), 808(B2)	1.17
RhO_2	172(A1), 888(A1), 970(B2)	1.31
RhO_2^+	210(A1), 933(A1), 994(B2)	1.61
RhO_2^-	120(A1), 832(A1), 928(B2)	0.29
RuO_2	191(A1), 955(A1), 978(B2)	1.88
RuO_2^+	253(A1), 862(B2), 971(A1)	3.04
RuO_2^-	123(A1), 886(A1), 913(B2)	0.59
Pd_2O	147(A1), 482(B2), 596(A1)	2.81
Pd_2O^+	129(A1), 237(A1), 770(B2)	0.42
Pd_2O^-	142(A1), 411(B2), 543(A1)	2.72
Rh_2O	265(A1), 410(B2), 655(A1)	3.07
Rh_2O^+	144(A1), 586(A1), 597(B2)	2.57
Rh_2O^-	211(A1), 271(B2), 610(A1)	1.72
Ru_2O	330(B2), 363(A1), 675(A1)	2.98
Ru_2O^+	234(A1), 389(B2), 674(A1)	2.97
Ru_2O^-	299(A1), 343(B2), 625(A1)	1.33
Pd_2O_2	43(A1), 198(A1), 410(A2), 414(B2), 572(A1), 609(B1)	0.00
Pd_2O_2^+	136(A1), 200(A1), 379(A2), 385(B2), 561(B1), 578(A1)	0.00
Pd_2O_2^-	66(A1), 192(B1), 199(A1), 355(A2), 458(B2), 578(A1)	0.00
Rh_2O_2	209(A1), 236(A1), 432(B2), 453(A2), 541(B1), 645(A1)	0.00
Rh_2O_2^+	79, 80, 162, 163, 210, 822, 863 (Linear structure)	5.08
Rh_2O_2^-	34, 63, 142, 198, 226, 782, 897 (Linear structure)	7.67
Ru_2O_2	210(A1), 293(A1), 380(B1), 385(A2), 601(B2), 751(A1)	0.27
Ru_2O_2^+	160(A1), 325(A1), 415(A2), 459(B1), 653(B2), 797(A1)	0.00
Ru_2O_2^-	135, 171, 281, 314, 741, 984 (Linear structure)	4.36

3.2 Electronic properties

The electronic properties of TM_nO_m clusters ($n, m = 1-2$) are explored in terms of the energy gaps between the highest occupied molecular orbital(HOMO) and the lowest unoccupied molecular orbital(LUMO). The HOMO-LUMO gap shows the ability of electrons to move from occupied molecular orbital to unoccupied molecular orbital and also indicates the chances of chemical interaction to a certain extent.

For TMO like clusters, HOMO-LUMO gap of anionic RhO cluster is the lowest i.e. 0.84 eV. For TMO_2 like clusters, HOMO-LUMO gap of cationic RhO_2 cluster is lowest i.e. 1.69 eV and for TM_2O like clusters, HOMO-LUMO gap of neutral Rh_2O and Ru_2O clusters are 0.75 eV and 0.82 eV, respectively. For TM_2O_2 like clusters, HOMO-LUMO gap of anionic Ru_2O_2 cluster is 1.78 eV. So neutral Rh_2O cluster is the most reactive among them all having lowest band gap. More the value of band gap, more shall be the stability of the corresponding cluster. It needs to be mentioned here that the structures of Pd_2O_2 , Rh_2O_2 and to a certain extent Ru_2O_2 are found to be stable with a larger value of band gap and hence these clusters can be considered as the building units for the design of a new material.

On the basis of natural population analysis it can be said that there is a dependence of charge variation with the size of cluster, for a monomer it varies from -0.47e to +1.281e (Table 5) and can possibly indicate towards some sort of movement of charge.

3.3 Vibrational analysis and atomic charges of different (TM_nO_m)

Analysis of the normal vibrational modes of monomers and dimers is carried out in this subsection. The study of the normal modes was used to judge the stability of the lowest lying isomers for the transition metal oxides. We have considered four different structures (linear and bend) for TMO_2 and TM_2O configurations and six different structures (Linear, square and rhombus) for TM_2O_2 configuration here for calculations. In Table 1 the vibrational frequencies and their dipole moments of the monomers are collected. For Dimer, the frequencies with their modes and their dipole moments values for the most stable structure are given in Table 6.

4 Conclusions

The geometrical structures, stability and the electronic properties etc of the (TM_nO_m) [(TM- Pd, Rh, Ru) and ($n, m = 1,2$)] clusters have been studied by Density functional theory with the B3LYP exchange-correlation functional using LANL2DZ as the basis set. The important and interesting results obtained are the high electron affinity of PdO_2 along with remarkable stabilities of the neutral and cationic forms of the monomers and dimers. The descriptors like chemical potential, chemical hardness and binding energy of the clusters provide a plethora of information for the experimentalists to tailor new materials of industrial importance.

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