

## QUANTUM COMPUTATIONAL STUDIES OF 3D TRANSITION SERIES METAL OXIDE MONOBORIDES

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### ABSTRACT

The density functional technique was used in the current work to analyze 3D transition metal monoborides using the basic set B3LYP/LanL2Dz level. Calculations are made for the dimers, lowest spin state, bond length, and vibrational frequencies. The cation and anion of these dimers are also studied. These dimers were found to have ionization potentials that are much greater than their electron affinities. Three-dimensional transition metal monocarbides have the widest range of electron affinities, whereas three-dimensional transition metal mononitrides have the smallest range. According to previous study, the ionization potential ranges are shortest for 3d transition metal monocarbides and highest for 3d transition metal monoborides. The spin multiplicity, vibrational frequencies, and bond length of monoborides are examined in this article.

**Key words:** Mullikan, Gaussian software, Oxides, and Monoborides.

### 1. INTRODUCTION

Molecules which form the small clusters or nanoparticles exhibit properties that are often quite different from those in the bulk phase. For example, small metal clusters exhibit novel electronic, magnetic, optical, and chemical properties.<sup>1-17</sup> The geometric and electrical structures of transition metal containing clusters are critical for understanding their growth behavior as well as the associated catalytic, magnetic, thermal, and optical capabilities. Transition metal nanoparticles are gaining popularity in technological applications. A lot of theoretical and experimental.<sup>18-72</sup> Works on transition metal containing clusters have been carried out in the past several years for their importance in many fields, such as heterogeneous catalysis, nanotechnology, microelectronics, materials sciences, optoelectronics, etc. Clusters containing B, atoms have received considerable attention from various aspects. One area of interest is their potential importance in interstellar space. Until now, several Borides containing molecules have been detected in interstellar medium. Small clusters have been the subject of intense investigation in recent years.

Clusters containing transition metals are also of significant interest, because of their potential applications in developing new nanodevices.<sup>73-77</sup> Theoretical studies on molecules containing a single transition metal atom are extremely challenging because of the vast array of electronic states that result from the partially occupied d shell. The situation is further complicated when studying molecules containing several metal atoms such as metal clusters or mixed metal boride clusters. A relatively simple method of calculation known as density functional theory (DFT) has been shown to provide accurate predictions of geometric and electronic structures of these clusters.

In this article, we report DFT calculations of 4d transition metal monoboride, monocarbide, mono-nitride, monoxide, and monofluoride. The cation and anion of these dimers are also studied. For these dimers, the optimized geometries, the lowest

spin state, bond length, vibrational frequency, dipole moment, binding energy, electron affinity, ionization potential, and atomic charges are obtained. We also compare the properties of these dimers. The article is structured as follows. The next section gives the computational details. Results are presented, discussed, and compared in the section "Results and Discussion." Conclusions are inferred in the last section.

## 2. Experimental Computational Detailed Analysis

The DFT method has been used to predict and compare the properties of 4d transition metal Monoborides, (hereafter called Monoborides). The geometry optimizations were performed at B3LYP/LanL2Dz level.<sup>78-82</sup> The *B3LYP density functional* is a combination of Becke's three parameter hybrid exchange functional and the Lee Yang Parr correlation functional. Vibrational frequencies are also calculated at the same level of theory for all the optimized dimers. We have also performed geometry optimization for the cations and anions of these dimers. All our calculations were performed using Gaussian 98 suit of program.<sup>83,84</sup>

## 3. Results and Discussions

We first discuss the properties of individual dimer and then compare the properties of monoborides. For the ScOB the lowest spin state is the quintet for the ScOB dimer the bond distance of neutral, cation, and anion of this dimer is 2.324, 2.325, and 2.245 Å, respectively. The vibrational frequency at lowest spin quintet is 581.2 cm<sup>-1</sup>. TiOB The ground state for the TiOB dimer is the sextet. The calculated bond distance and vibrational frequency are 2.1977 Å and 608.1 cm<sup>-1</sup>, respectively. For VOB dimer, the calculated ground state is at spin multiplicity 3 (triplet) and the VOB bond distance is 1.9842 Å, which is shortened by 0.039 Å in anion, whereas it is longer by 0.014 Å in cation. The calculated vibrational frequency at lowest spin triplet is 661.7 cm<sup>-1</sup> respectively. For the boride of CrOB the calculated ground state for the CrOB dimer is doublet and the second lowest spin state is the quartet, the CrOB bond distance is 1.8166 Å and vibrational frequency is 821.1 cm<sup>-1</sup> for the lowest spin state doublet. The CrOB bond distance is shortened by 0.0017 Å in anion whereas it is longer by 0.061 Å in cation than the neutral dimer. For MnOB the Doublet is the lowest spin state for the MnOB dimer with bond distance of 1.7511 Å and its vibrational frequency is 911.2 cm<sup>-1</sup> respectively. The boride of FeOB The lowest spin state of FeOB dimer is singlet and the vibrational frequency is 935.1 cm<sup>-1</sup>. The calculated bond distance for neutral FeOB dimer is 1.7461 Å, for cation 1.851 Å, and for anion 1.764 Å respectively. The monoboride dimer of CoOB the ground state found for the CoOB dimer is the doublet the calculated bond distances for neutral, cation and anion CoOB dimer are 1.856, 1.829, and 1.866 Å, respectively. The monoboride dimer of NiOB having calculated ground state for the NiOB dimer is singlet and the second lowest spin state is the triplet, which is higher in energy by 14.34 kcal/mol than the singlet state. The CuOB bond distance is 2.1879 Å and vibrational frequency is 415.6 cm<sup>-1</sup> for the lowest spin state singlet. The NiOB bond distance is longer by 0.035 Å in cation and by 0.044 Å in anion than the neutral dimer respectively. Similarly at the end of the calculation the monoboride of 3d series at the last ZnOB has lowest spin state of ZnOB dimer is the doublet and is 37.53 kcal/mol lower in energy than the second lowest spin state quartet.

The calculated bond distances are 2.6784, 2.696, and 2.459 Å for neutral, cation, and anion ZnOB dimer, respectively.

### Study of Mulliken and Natural Orbital Charges

The atomic charges are derived from Mulliken and natural orbital population analyses. Except for the FeOB, CoOB, NiOB, and ZnOB dimers, the charge on the metal atom is positive and the charge on the boron atom is negative in all neutral dimers. Mulliken and natural orbital population analysis charges demonstrate that when an electron is taken from the neutral dimer to form cation, the majority of the total positive charge is concentrated on transition metal atoms. The natural orbital population analysis charges demonstrate that when one electron is added to a neutral dimer to produce an anion, the majority of the negative charge is focused on the boron atom. According to the natural orbital electronic configuration for neutral dimers, the electrons originally localized on the 4s atomic orbital of an isolated transition metal atom have been transferred to the 3d orbital of the corresponding transition metal atoms in the dimer and to the 2p orbital of the boron atoms in the dimer upon bonding for ScOB, TiOB, VOB, MnOB, and FeOB dimers. Upon bonding, the electron previously localized on the 2s and 2p orbitals of the boron atoms was transported to the 5s and 3d orbitals of the Rh atom. The electrons formerly located in the 3d orbital of transition metal atoms have been transferred to the 4s orbital of the corresponding transition metal atoms for NiOB and ZnOB dimers. The electron previously located on the 4s orbital of these transition metal atoms has been shifted to the 2p orbital of boron atoms for CdOB dimer.

**Table 1 : - The ground state obtained at spin multiplicity, Vibrational frequency, and bond length for Monoborides using the basis set B3LYP/Lan12dz level.**

Monoborides of 3d Series	Spin multiplicity (S)	Vibrational frequency (Cm <sup>-1</sup> )	Bond Distance
Sc-X	5	581.2	2.2451
Ti-X	6	608.1	2.1977
V-X	3	661.5	1.9842
Cr-X	2	821.1	1.8166
Fe-X	2	911.2	1.7511
Co-X	1	935.1	1.7461
Ni-X	2	724.1	1.8977
Cu-X	1	421.6	2.1879
Zn-X	2	157.3	2.6784

### 4. Conclusions

At the B3LYP/Lan12dz level, first-row transition metal monoborides are studied using the DFT calculation technique. The geometries of these dimers are tweaked at different spin multiplicities to generate the ground state. The optimal geometries at ground state

are provided. We also looked at the cation and anion of the dimers. Additionally examined is the change from neutral to cation and anion. The neutral, cation, and anion optimized structures of the dimers are used to compute the ionization potential and electron affinity. The binding energies of these dimers are also found.

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