J. At. Mol. Sci.
doi: 10.4208/jams.040214.062114a

Vol. **5**, No. 3, pp. 231-237
August 2014

# Theoretical study of small niobium sulphide clusters, $Nb_nS_m$ ($n$,$m$=1, 2)

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Received 2 April 2014; Accepted (in revised version) 21 June 2014
Published Online 8 August 2014

**Abstract.** Clusters are well known for their extensive applications in various fields as their properties are quite different from their bulk analog. In the present study, we have investigated various conformers of $Nb_nS_m$ ($n$,$m$=1, 2) clusters in their neutral as well as anionic and cationic states. Their stabilities are discussed by calculating binding energies per atom and fragmentation energies against dissociation to S atom. The electronic properties are also explored for all the species.

**PACS**: 31.15.A, 31.15.es, 31.15.V

**Key words**: atomic clusters, stability, density functional theory (DFT)

## 1 Introduction

Study of structural and electronic properties of small clusters has become a subject of academic, scientific and technological interest and significance. Much attention has been paid to the structure and properties of atomic clusters from both theoretical and experimental point of view such as ground state geometry, electronic properties, optical properties etc. III-V group atomic clusters exhibit tremendous importance for their distinguished electronic properties. For instance, gallium nitride (GaN) is a semiconductor, which is used as LED since 1990. Its well known for a wide band-gap of 3.4 eV and because of this it has been extensively used in optoelectronics [1,2]. Although a number of studies have been carried out on Niobium clusters [3-9] but not many studies have been reported on transition metal sulphides. Particularly the properties of Niobium Sulphides as catalysts have attracted a lot of attention [10].

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In the present work, we have chosen Nb atom combined with a S atom. We have tried to address a number of questions like how a Nb atom binds with a S atom? Which structure is stable out of the different conformers? How electronic properties vary with different structures while we go from monomer to dimer? How these properties as well as topology of a given structure varies if we work on ionic states of these clusters? An attempt to answer all such questions has been made by employing density functional theory (DFT) [11] which has emerged as an effective tool for predicting structures and related properties of clusters. A good compromise is offered between accuracy and computational cost by DFT when used with proper exchange-correlation functional. We have performed a purely theoretical study on some small $Nb_nS_m$ clusters which presumably should give a better understanding about them in the absence of any experimental data.

## 2 Methodology

Structures of twenty possible conformers of $Nb_nS_m$ cluster were modelled using Gauss View 5.0 package and after that these conformers were optimized using DFT at hybrid functional B3LYP level in which Becke three parameter exchange [12] is combined with Lee-Yang-Parr correlation term. The DGTZVP basis set was used which has been reported to be a very useful basis set for study of ionic clusters. Frequency calculations were performed at the same level of theory in order to ensure that optimized geometries belong to a minimum in potential energy surface. Thus optimized and minimum energy conformers were further investigated in their cationic and anionic states. All the computations are performed with Gaussian 09 program [13]. The relevant graphics were created with the help of Gauss View 5.0 package [14].

### 2.1 Structural analysis

The optimization of structures of $Nb_nS_m$ clusters was followed by a frequency calculation. After full optimization, all the frequencies found were real. It ensures that optimized structures belong to, at least, global minima in potential energy surface. All conformers of monomers are given in Fig. 1.

To make the findings more focussed and relevant we have discussed only the most stable conformers. The calculated bond-lengths, band gap and partial atomic charges for neutral as well as ionic species are listed in Table 1.

Figs. 2(a), 2(b), 2(c) and 2(d) show the HOMO-LUMO Plot for NbS, $Nb_2S$, $NbS_2$ and $Nb_2S_2$ in neutral and ionic forms.

The bond length Nb-S in anionic forms is larger than the neutral while in the cationic form, it is smaller as expected, due to the redistribution of charges on Nb and S as given in Table 1. In anionic NbS last electron goes to the LUMO of Nb atom hence bond length of NbS increases, however in the case of cationic form last electron comes from LUMO. A similar trend can be seen for Nb-Nb bond length in case of $Nb_2S$ cluster, however, it is reversed for $Nb_2S_2$ cluster. Moreover, for $Nb_2S$ neutral and ionic clusters all with a