

## Theoretical study of small niobium sulphide clusters, $\text{Nb}_n\text{S}_m$ ( $n, m=1, 2$ )

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**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  $\text{Nb}_n\text{S}_m$  ( $n, m=1, 2$ ) 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.

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

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## 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].

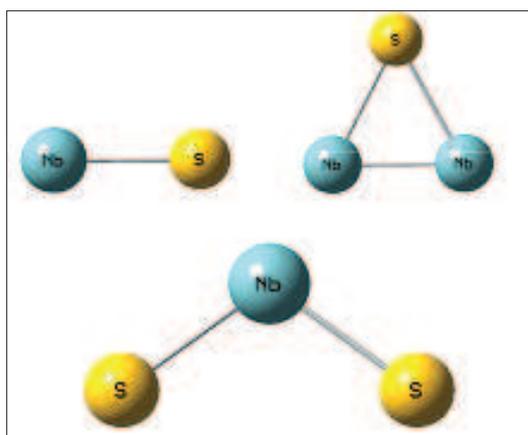
### 2.1 Structural analysis

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<sub>2</sub>S, NbS<sub>2</sub> and Nb<sub>2</sub>S<sub>2</sub> 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<sub>2</sub>S cluster, however, it is reversed for Nb<sub>2</sub>S<sub>2</sub> cluster. Moreover, for Nb<sub>2</sub>S neutral and ionic clusters all with a

Figure 1: Optimized structure of NbS, Nb<sub>2</sub>S and NbS<sub>2</sub>.Table 1: Bond length, Band Gap and Partial charges of neutral and ionic Nb<sub>n</sub>S<sub>m</sub> clusters.

Clusters (Symmetry)	Bond length			Band Gap		Dipole moment	Partial charge	
	Nb-Nb	Nb-S	S-S	$\alpha$	$\beta$		Nb	S
NbS ( <i>C<sub>infv</sub></i> )	-	2.15	-	2.39	2.01	4.42	0.197	-0.197
NbS <sup>-</sup> ( <i>C<sub>infv</sub></i> )	-	2.18	-	2.09	-	1.32	-0.570	-0.429
NbS <sup>+</sup> ( <i>C<sub>infv</sub></i> )	-	2.11	-	2.14	-	4.36	0.839	0.160
Nb <sub>2</sub> S ( <i>C<sub>2v</sub></i> )	2.20	2.38	-	2.25	-	3.38	0.151	-0.302
Nb <sub>2</sub> S <sup>-</sup> ( <i>C<sub>2v</sub></i> )	2.25	2.41	-	0.59	1.57	2.49	-0.262	-0.475
Nb <sub>2</sub> S <sup>+</sup> ( <i>C<sub>2v</sub></i> )	2.22	2.36	-	2.50	2.01	4.18	0.537	-0.075
NbS <sub>2</sub> ( <i>C<sub>s</sub></i> )	-	2.17	-	2.47	3.34	5.44	0.345	-0.172
NbS <sub>2</sub> <sup>-</sup> ( <i>C<sub>s</sub></i> )	-	2.20	-	1.52	-	2.61	-0.178	-0.410
NbS <sub>2</sub> <sup>+</sup> ( <i>C<sub>s</sub></i> )	-	2.14	-	2.39	-	4.27	0.659	0.170
Nb <sub>2</sub> S <sub>2</sub> ( <i>C<sub>1</sub></i> )	2.24	2.39	2.14	1.79	-	5.96	0.178	-0.178
Nb <sub>2</sub> S <sub>2</sub> <sup>-</sup> ( <i>C<sub>1</sub></i> )	2.19	2.48	2.15	1.82	1.95	4.12	-0.149	-0.350
Nb <sub>2</sub> S <sub>2</sub> <sup>+</sup> ( <i>C<sub>1</sub></i> )	2.28	2.36	2.13	2.09	2.23	6.53	0.513	-0.013

symmetry of *C<sub>infv</sub>*, the bond angle Nb-S-Nb in cation is slightly greater than those in neutral and anion while angle S-Nb-Nb is smaller. The angle S-Nb-S in NbS<sub>2</sub> clusters, all with symmetry *C<sub>s</sub>*, is larger 111.5° in anionic form. For Nb<sub>2</sub>S<sub>2</sub> clusters, the bond distance S-S is slightly larger than characteristic value of 2.0 Å [15] and the angle S-Nb-Nb, 89.5° is larger in anions.

## 2.2 Dimers

In Fig. 3 the various conformers of NbS dimer are shown. Among all these conformers, the square shaped structure was found to be stable as all the frequencies after geometry optimization were real. All conformers of the neutral state are singlet (<sup>3</sup>Σ) however, in ionized state it becomes a doublet (<sup>2</sup>Σ). In case of cationic form loss of electron comes

Table 2: Binding energies (BE) and Fragmentation energies (FE) of  $Nb_nS_m$  clusters.

Species	Binding energy per atom (eV)			Fragmentation energy (eV)		
	Neutral	Cationic	Anionic	Neutral	Cationic	Anionic
NbS	4.11	0.43	4.55	-	-	-
Nb <sub>2</sub> S	4.93	2.73	5.02	-	-	-
NbS <sub>2</sub>	5.02	2.32	5.55	6.82	6.11	7.55
Nb <sub>2</sub> S <sub>2</sub>	5.00	2.99	5.05	3.76	3.79	5.12

from the antibonding molecular orbitals which decreases bond lengths Nb-S and S-S with the increase in Nb-Nb to induce stability. In the case of anionic dimer, square shaped structure turns into a pi shaped geometry in which two S are not bound but with an imaginary frequency. This frequency corresponds to antisymmetric stretching mode of S atoms. So to find a stable conformer, we moved S atom along this mode and reoptimized the structure. The trend of bond length should be reversed in this case because a stress is generated due to the moment of Nb atom out of plane. This fact is in congruence with the analysis of the LUMO of a neutral dimer.

### 3 Stabilities

#### 3.1 Binding energies per atom

The stabilities of  $Nb_nS_m$  clusters can be analyzed on the basis of the average BEs. The BEs per atom of all neutral and ionic species are calculated as follows ( $n, m=1, 2$ ):

For neutral clusters,  $BE = n * E[Nb] + m * E[S] - E[Nb_nS_m] / (n + m)$

For cationic clusters,  $BE = n * E[Nb] + m * E[S] - E[Nb_nS_m^+] / (n + m)$

For anionic clusters,  $BE = n * E[Nb] + m * E[S] - E[Nb_nS_m^-] / (n + m)$

The calculated BE values are given in Table 2. In all the cases, the BEs of anionic species are higher than their neutral and cationic counterparts. This may suggest that  $Nb_nS_m$  clusters are more stable in anionic states. Out of all these species, anionic NbS<sub>2</sub> is the most stable with BE of 5.55 eV. The BE of anionic Nb<sub>2</sub>S is found to be comparable to that of neutral NbS<sub>2</sub>. Furthermore, the BE values of neutral and anionic species are almost equal in case of Nb<sub>2</sub>S<sub>2</sub> cluster.

Table 3: Electron affinity ( $A$ ), Ionization potential ( $I$ ), Absolute negativity ( $\chi$ ), Global hardness ( $\eta$ ) and Electrophilicity ( $\omega$ ) for monomer and dimers.

Clusters	$A$ (eV)	$I$ (eV)	$\chi$ (eV)	$\eta$ (eV)	$\omega$ (eV)
NbS	0.87	7.37	4.12	3.25	2.61
Nb <sub>2</sub> S	0.28	6.59	3.43	3.15	1.86
NbS <sub>2</sub>	1.60	8.08	4.84	3.24	3.61
Nb <sub>2</sub> S <sub>2</sub>	1.64	6.56	4.10	2.46	3.41

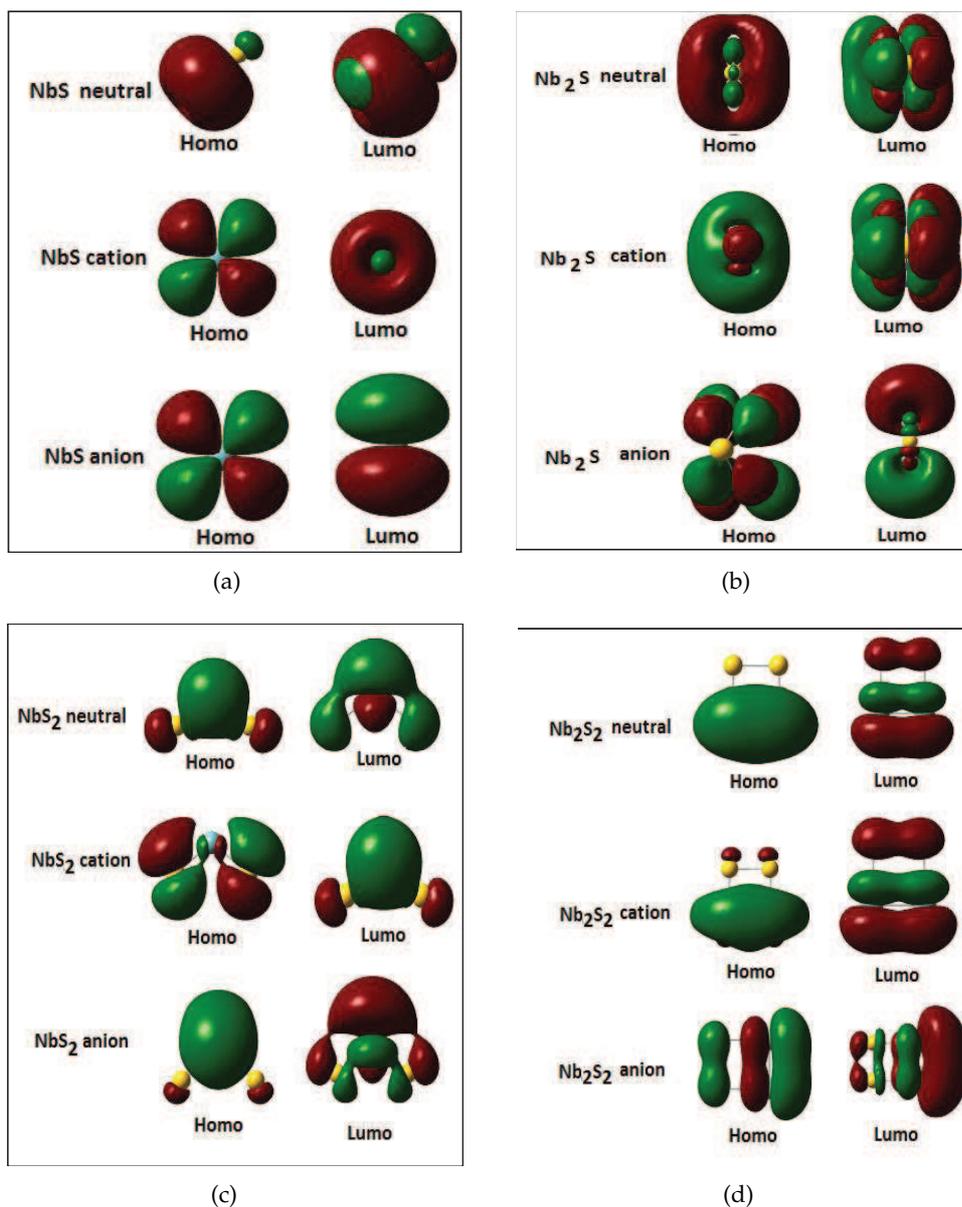
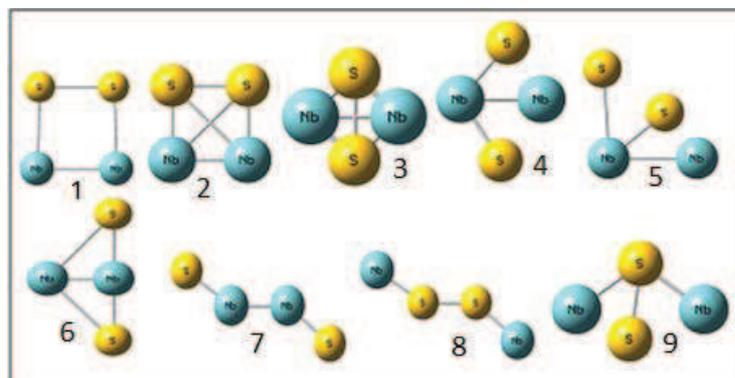


Figure 2: (a)HOMO-LUMO surfaces of NbS; (b)HOMO-LUMO surfaces of Nb<sub>2</sub>S; (c)HOMO-LUMO surfaces of NbS<sub>2</sub>; (d)HOMO-LUMO surfaces of Nb<sub>2</sub>S<sub>2</sub>.

### 3.2 Fragmentation energies

The stabilities of NbS<sub>2</sub> and Nb<sub>2</sub>S<sub>2</sub> clusters are further analysed by considering their fragmentation. Fragmentation energy (FE), the energy needed to dissociate Nb<sub>n</sub>S<sub>m</sub> clusters to Nb<sub>n</sub>S<sub>m-1</sub> and S atom, are calculated as below ( $n=1, 2$  and  $m=2$ ),

Figure 3: Various Conformer of Nb<sub>2</sub>S<sub>2</sub>.

For neutral clusters,  $FE = E[S] + E[Nb_n S_{m-1}] - E[Nb_n S_m]$

For cationic clusters,  $FE = E[S] + E[Nb_n S_{m-1}^+] - E[Nb_n S_m^+]$

For anionic clusters,  $FE = E[S] + E[Nb_n S_{m-1}^-] - E[Nb_n S_m^-]$

Table 2 lists the fragmentation energies for neutral, cationic as well as anionic forms of NbS<sub>2</sub> and Nb<sub>2</sub>S<sub>2</sub> clusters. The calculated values further assert that NbS<sub>2</sub> is the most stable anion because of its higher dissociation energy, 7.55 eV. The fragmentation energy may be an useful parameter to discuss relative stabilities of various species having equal BE. As we can see the FE of anionic Nb<sub>2</sub>S<sub>2</sub>, 5.12 eV is higher than that of neutral Nb<sub>2</sub>S<sub>2</sub>, 3.76 eV, however, both share equal BE. This may allow us to infer that anionic Nb<sub>2</sub>S<sub>2</sub> is relatively more stable.

## 4 Electronic properties

The band gap is defined as the energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The band gap shows the ability of electrons to move from HOMO to LUMO. Lesser the band gap, greater will be ability to move and so it indicates the change of chemical interaction to a certain extent. The ionization potential (*I*) and electron affinities (*A*) are numerically defined as below,

$$I = E(\text{cation}) - E(\text{neutral})$$

$$A = E(\text{neutral}) - E(\text{anion})$$

Where *E* denotes electronic energy of respective species. Other electronic parameters are calculated using finite difference approximation [16-20] as follows,

$$\text{Absolute electro-negativity, } \chi \approx (I + A) / 2$$

$$\text{Global hardness, } \eta \approx (I - A) / 2$$

$$\text{Electrophilicity, } \omega = \chi^2 / 2 / 2\eta$$

The electronic parameters calculated for Nb-*n*S<sub>*m*</sub> clusters are presented in Table 3. The comparatively higher band gap, 2.47 eV of NbS<sub>2</sub> indicates its chemical stability while

lower band gap, 1.79 eV of Nb<sub>2</sub>S<sub>2</sub> may explain its chemical reactivity. Dipole moment measures the overall polarity of a system. The calculated values suggest that Nb<sub>2</sub>S<sub>2</sub> cluster is relatively more polar than other species. The higher ionization potential of Nb<sub>2</sub>S<sub>2</sub> may establish more electro-negative behaviour of the same. This feature is further supported by absolute electro-negativity value which is higher, 4.84 eV, in case of NbS<sub>2</sub> cluster. In fact, absolute electro-negativity tells the strength to attract electrons in a chemical bond. The global hardness gives a quantitative measurement of stability of a molecule. In the case of partial charge transfer in a system, electrophilicity decides the energy lowering due to maximum electron flow from donor to acceptor. The calculated values of hardness and electrophilicity are also listed in Table 3.

## 5 Conclusions

We have performed a DFT study on neutral, anionic as well as cationic Nb<sub>n</sub>S<sub>m</sub> (*n, m*=1, 2) clusters. Structural parameters viz. bond length and angles are calculated. Stabilities of species are discussed by binding energy and fragmentation energy calculations which revealed that Nb<sub>n</sub>S<sub>m</sub> clusters have more tendencies to form anionic species. Various electronic parameters describing chemical reactivity are calculated and discussed.

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