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## *Ab Initio* study of small Germanium Sulphide Clusters, $Ge_nS_m$ ( $n, m=1, 2$ )

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### ABSTRACT

*In this study, the structures and electronic properties of simple prototype  $Ge_nS_m$  ( $n, m=1, 2$ ) clusters are studied in their neutral, anionic and cationic states. The geometries of these small clusters are optimized by generalized gradient approximation. Their stabilities are discussed by calculating the binding energies per atom and fragmentation energies against dissociation to S atom. Various electronic parameters such as the HOMO–LUMO gap (band gap), electron affinity, ionization potential, chemical potential and chemical hardness are calculated and discussed.*

**Keywords:** Germanium Sulphide, stability, electronic property, DFT.

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### INTRODUCTION

Chalcogenides are an important class of materials which possess significant electrical properties, optical properties and chemical characteristics. The word “chalcogenenide” is generally used to refer to the compounds of sulphur, selenium and tellurium elements. The sulphur compounds have a wide range of properties which attract the scientific community, predominantly in thin film technology and nanoparticle synthesis. The applications of chalcogenide materials include a variety of chalcogenide glasses, infrared sensors, solar energy conversion and window layer [1–6].

The structural and electronic properties of small clusters have become a subject of academic, scientific and technological interest and significance. In spite of many advances in the experimental techniques, theoretical studies often complements and provide better insights into structures, energetics and related properties for a variety of systems. Much attention has been paid to the structure and properties of small clusters from theoretical point of view such as ground state geometry, electronic properties, etc. The present study is devoted to the small clusters of germanium sulphide (GeS).

In the present work, we have made attempt to address a number of questions like how Ge atom interacts with S atom, which structure is stable out of the different possible conformers, how electronic properties vary with different structures while we change the proportion of atom and how these properties as well as topology of a given structure vary if we consider ionic states of these clusters. An attempt to answer all such questions has been made by employing density functional theory (DFT) which has emerged as an effective tool for predicting structures and related properties of clusters as well as a variety of molecules [7-15]. 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  $Ge_nS_m$  clusters which may offer a better understanding about similar systems in the absence of any experimental data.

## MATERIALS AND METHODS

In the present work, the initial structures of various conformers of  $\text{Ge}_n\text{S}_m$  ( $n, m=1, 2$ ) clusters were modelled by using Gauss View 5.0 package [16] and then optimized by using DFT at hybrid functional B3LYP level in which Becke three parameter exchange [17] is combined with Lee-Yang-Parr correlation term. GeS is an ionic cluster, hence we use DGTZVP as a basis set. For all system, a full geometry optimization was performed and various optimized geometries were analysed to determine the lowest energy equilibrium structures for each cluster. Geometry optimization of conformers of  $\text{Ge}_n\text{S}_m$  was followed by frequency calculation at same level of theory in order to ensure that optimized geometries belongs to a minimum in potential energy surface. The optimised conformers were further investigated in their cationic and anionic state. All calculations were performed using Gaussian 09 program [18]. The relevant graphics were created with the help of Gauss View 5.0 package.

## RESULTS AND DISCUSSION

### 3.1. Geometric properties

The structures of various conformers of  $\text{Ge}_n\text{S}_m$  ( $n, m=1, 2$ ) clusters are optimised and followed by frequency calculations. After full optimization, all the frequency found are real which shows that optimized structure belongs to a minimum in potential energy surface. The geometries of monomers (neutral and ionic) are shown in Figure 1. Figure 2(a), 2(b), 2(c) and 2(d) shows the HOMO LUMO Plots of GeS,  $\text{Ge}_2\text{S}$ ,  $\text{GeS}_2$ ,  $\text{Ge}_2\text{S}_2$  in neutral and ionic forms.

For the sake of simplicity of discussion, we have focussed on only the most stable conformers. The calculated bond-lengths, HOMO-LUMO gap, dipole moment and partial charges for neutral as well as for ionic species of  $\text{Ge}_n\text{S}_m$  clusters are listed in Table 1.

**Table 1. Bond length, Band Gap and Partial charges of neutral and ionic  $\text{Ge}_n\text{S}_m$  clusters**

| Clusters<br>(Symmetry)              | Bond length |      |      | HOMO-LUMO Gap |         | Dipole<br>moment | Partial charge |        |
|-------------------------------------|-------------|------|------|---------------|---------|------------------|----------------|--------|
|                                     | Ge-Ge       | Ge-S | S-S  | $\alpha$      | $\beta$ |                  | Ge             | S      |
| GeS ( $C_{\infty v}$ )              | -           | 2.04 | -    | 0.18          | -       | 2.35             | 0.148          | -0.148 |
| $\text{GeS}^-$ ( $C_{\infty v}$ )   | -           | 2.15 | -    | 0.04          | 0.14    | 2.32             | -0.454         | -0.545 |
| $\text{GeS}^+$ ( $C_{\infty v}$ )   | -           | 2.20 | -    | 0.17          | 0.07    | 1.31             | 0.716          | 0.293  |
| $\text{Ge}_2\text{S}$ ( $C_s$ )     | 2.57        | 2.27 | -    | 0.08          | -       | 1.56             | 0.037          | -0.075 |
| $\text{Ge}_2\text{S}^-$ ( $C_s$ )   | 2.49        | 2.37 | -    | 0.08          | 0.08    | 1.94             | -0.314         | -0.369 |
| $\text{Ge}_2\text{S}^+$ ( $C_s$ )   | 2.84        | 2.25 | -    | 0.11          | 0.14    | 1.40             | 0.436          | 0.126  |
| $\text{GeS}_2$ ( $C_s$ )            | -           | 2.25 | -    | 0.11          | -       | 2.68             | 0.165          | -0.082 |
| $\text{GeS}_2^-$ ( $C_s$ )          | -           | 2.39 | -    | 0.09          | 0.12    | 2.01             | -0.317         | -0.341 |
| $\text{GeS}_2^+$ ( $C_s$ )          | -           | 2.34 | -    | 0.14          | 0.12    | 1.35             | 0.503          | 0.248  |
| $\text{Ge}_2\text{S}_2$ ( $C_s$ )   | 3.14        | 2.31 | 3.39 | 0.10          | -       | 0.10             | 0.199          | -0.199 |
| $\text{Ge}_2\text{S}_2^-$ ( $C_s$ ) | 3.27        | 2.33 | 3.33 | 0.07          | 0.12    | 0.09             | -0.148         | -0.352 |
| $\text{Ge}_2\text{S}_2^+$ ( $C_s$ ) | 3.68        | 2.36 | 2.92 | 0.01          | 0.07    | 0.02             | 0.479          | 0.020  |

In case of  $\text{Ge}_2\text{S}$ , bond length Ge-S in anionic form is larger than neutral while in cationic form it is smaller as expected due to the redistribution of charge of Ge and S as shown in Table 1. Similar trend can be seen for the Ge-S bond length for  $\text{GeS}_2$  cluster in which anionic form have larger bond length as compared to neutral and cationic form. However, it is interesting to note that in  $\text{Ge}_2\text{S}_2$  cluster, the bond length Ge-S in cationic form is larger than neutral and anionic form. Among all these conformers of GeS dimer, the square shaped structure has been found to be stable as all the frequencies after geometry optimization were real it ensure that optimised structure belongs to global minima in potential energy surface. In case of cationic form, loss of electron comes from antibonding molecular orbitals which decrease the bond length of S-S with increase in Ge-Ge to induce stability as shown in Table 1.

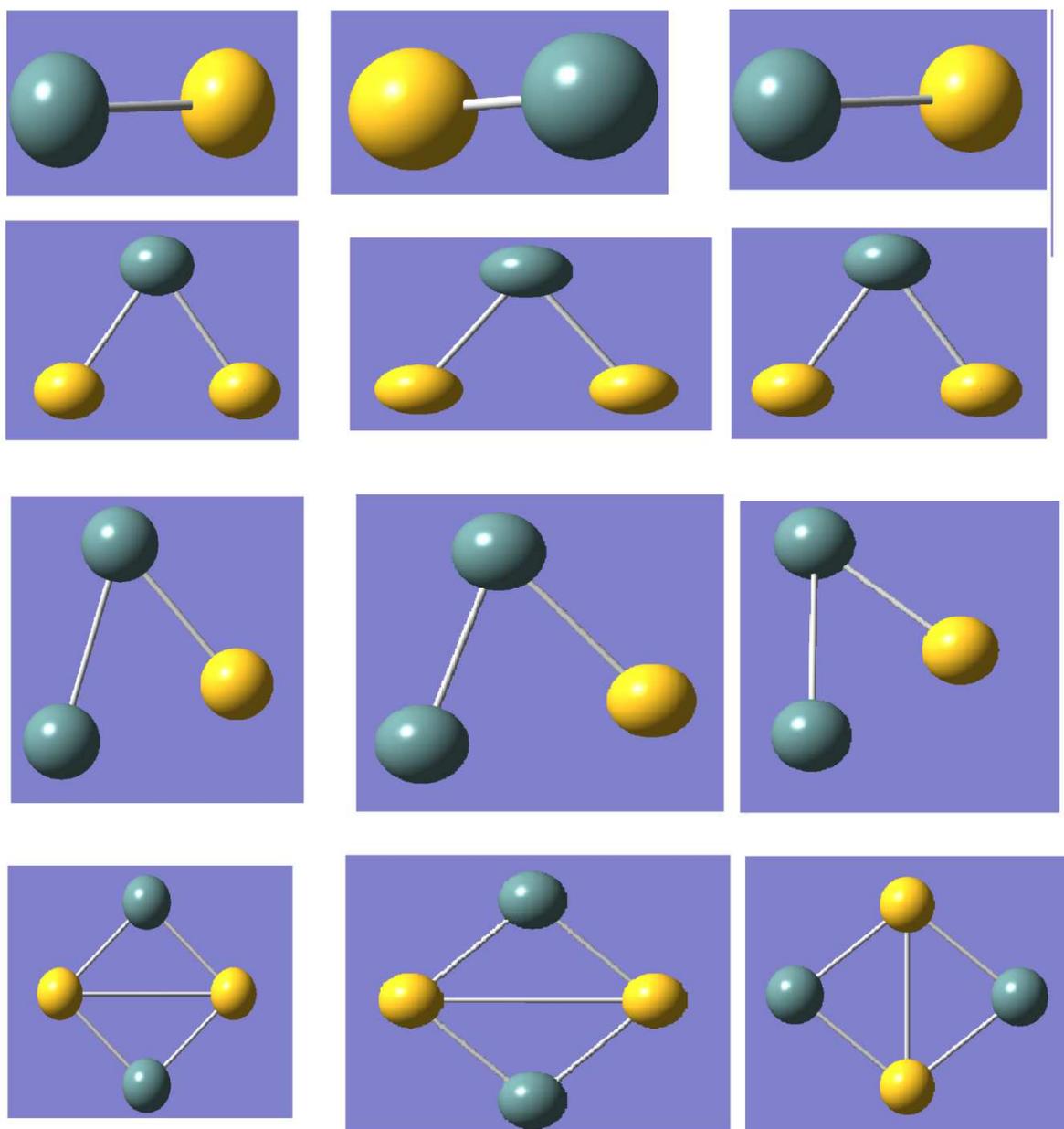


Figure 1. The lowest energy structures of neutral (right), anionic (middle) and cationic (left)  $\text{Ge}_n\text{S}_m$  ( $n, m=1, 2$ ) clusters

### 3.2. Stabilities

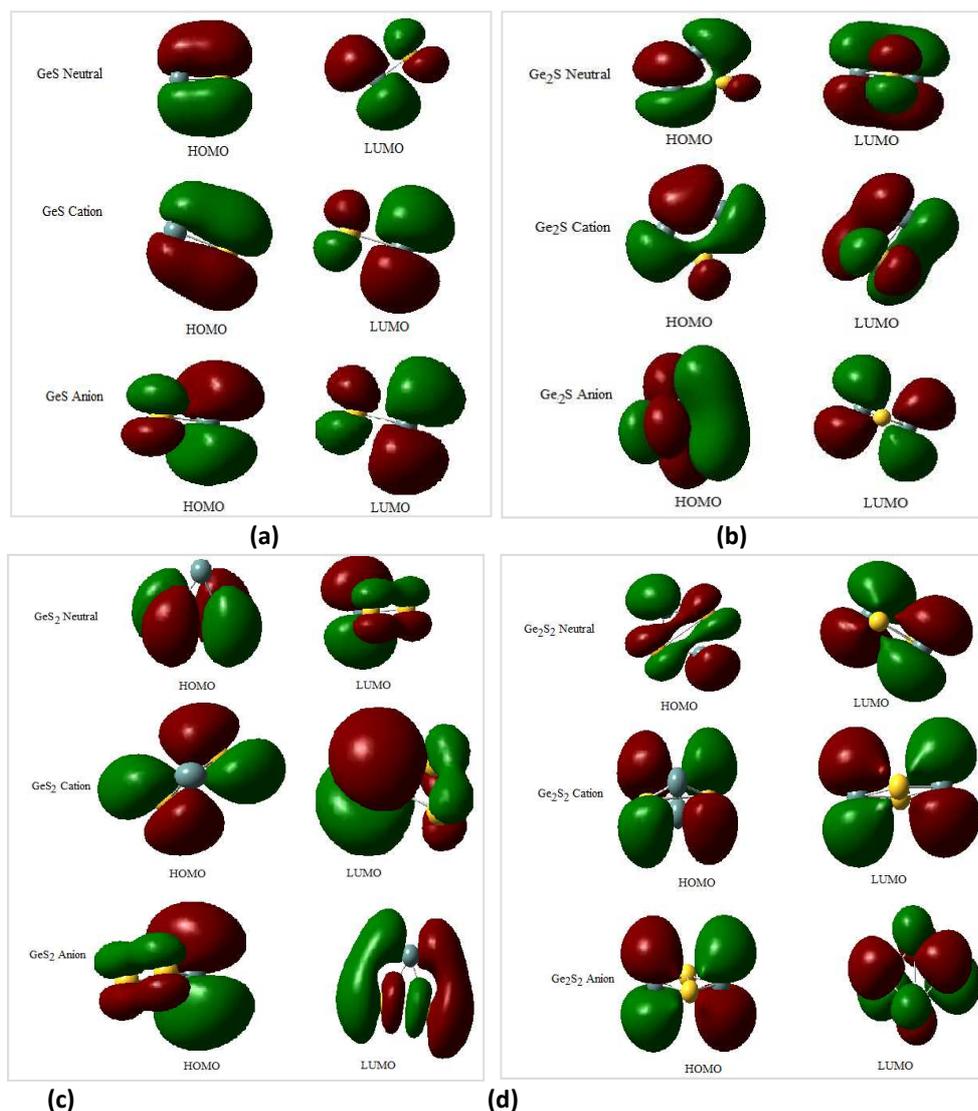
The stabilities of  $\text{Ge}_n\text{S}_m$  clusters can be investigated on the basis of binding energy per atom. The binding energy per atom of all neutral and ionic species are calculated as follows ( $n, m = 1, 2$ ),

For neutral clusters,  $\text{BE} = n \cdot E[\text{Ge}] + m \cdot E[\text{S}] - E[\text{Ge}_n\text{S}_m] / (n + m)$

For cationic clusters,  $\text{BE} = n \cdot E[\text{Ge}] + m \cdot E[\text{S}] - E[\text{Ge}_n\text{S}_m^+] / (n + m)$

For anionic clusters,  $\text{BE} = n \cdot E[\text{Ge}] + m \cdot E[\text{S}] - E[\text{Ge}_n\text{S}_m^-] / (n + m)$

The binding energies per atom (BE) of  $\text{Ge}_n\text{S}_m$  clusters are listed in Table 2. In all cases, the BE of all anionic species are higher than their neutral and cationic species. This may suggest that  $\text{Ge}_n\text{S}_m$  clusters have greater tendencies to form anionic clusters. On the contrary, their cationic forms are less stable due to smaller BEs. Out of all these species, anionic  $\text{Ge}_2\text{S}_2$  cluster is most stable having binding energy of 4.62 eV.



**Figure 2.** HOMO and LUMO surfaces of GeS (a), Ge<sub>2</sub>S (b), GeS<sub>2</sub> (c) and Ge<sub>2</sub>S<sub>2</sub> (d)

**Table 2.** Binding energies (BE) and Fragmentation energies (FE) of Ge<sub>n</sub>S<sub>m</sub> clusters

| Species                        | Binding energy per atom (eV) |          |         | Fragmentation energy (eV) |          |         |
|--------------------------------|------------------------------|----------|---------|---------------------------|----------|---------|
|                                | Neutral                      | Cationic | Anionic | Neutral                   | Cationic | Anionic |
| GeS                            | 4.08                         | 0.81     | 4.35    | -                         | -        | -       |
| Ge <sub>2</sub> S              | 3.83                         | 1.33     | 4.08    | -                         | -        | -       |
| GeS <sub>2</sub>               | 3.80                         | 1.08     | 4.35    | 3.84                      | 5.52     | 4.48    |
| Ge <sub>2</sub> S <sub>2</sub> | 4.32                         | 1.90     | 4.62    | 5.75                      | 4.32     | 5.96    |

The stabilities of system may be also investigated on the basis of fragmentation energy (FE). The stabilities of GeS<sub>2</sub> and Ge<sub>2</sub>S<sub>2</sub> cluster are further analysed by considering their fragmentation to S atom. Fragmentation energy, the energy needed to dissociate Ge<sub>n</sub>S<sub>m</sub> clusters to Ge<sub>n</sub>S<sub>m-1</sub> and S atom, are calculated as below (n=1, 2 and m=2).

For neutral clusters,  $FE = E[S] + E[Ge_nS_{m-1}] - E[Ge_nS_m]$

For cationic clusters,  $FE = E[S] + E[Ge_nS_{m-1}^+] - E[Ge_nS_m^+]$

For anionic clusters,  $FE = E[S] + E[Ge_nS_{m-1}^-] - E[Ge_nS_m^-]$

The fragmentation energies for neutral, cationic as well as anionic forms of GeS<sub>2</sub> and Ge<sub>2</sub>S<sub>2</sub> clusters are also given in Table 2. One can see that GeS<sub>2</sub> and Ge<sub>2</sub>S<sub>2</sub> clusters are stable against dissociation to S irrespective of their charges. The larger FE values of Ge<sub>2</sub>S<sub>2</sub> further suggest that it is more stable as compared to GeS<sub>2</sub>.

### 3.3. Electronic properties

The electronic parameters calculated for  $\text{Ge}_n\text{S}_m$  clusters are listed in Table 3. 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 clusters including zero point correction. Other electronic parameters are calculated using finite difference approximations [19-23] as follows,

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

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

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

Ionization potential measures the electro-positive behaviour of system i.e. tendency to give up an electron thus forming a cation. The higher values of ionization potential are consistent with decreased BEs, and hence stability of  $\text{Ge}_n\text{S}_m$  clusters. Electron affinity describes the strength to attract electrons in a chemical bond. The higher electron affinity of  $\text{Ge}_2\text{S}_2$  as compared to other clusters is in accordance with the increased binding energy of its anion. The global hardness gives an alternative measure of the stabilities of system. The calculated values suggest that  $\text{Ge}_2\text{S}_2$  is chemically harder i.e. more stable among all  $\text{Ge}_n\text{S}_m$  clusters.

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

| Clusters                | A (eV) | I (eV) | $\chi$ (eV) | $\eta$ (eV) | $\omega$ (eV) |
|-------------------------|--------|--------|-------------|-------------|---------------|
| GeS                     | 0.53   | 9.92   | 5.25        | 4.69        | 2.93          |
| $\text{Ge}_2\text{S}$   | 1.41   | 7.53   | 4.47        | 3.06        | 3.26          |
| $\text{GeS}_2$          | 1.18   | 8.24   | 4.71        | 3.53        | 3.14          |
| $\text{Ge}_2\text{S}_2$ | 1.62   | 8.95   | 5.28        | 3.66        | 3.80          |

### CONCLUSION

The geometrical structures, stabilities and electronic properties of  $\text{Ge}_n\text{S}_m$  clusters ( $n, m = 1, 2$ ) in neutral, anionic and cationic states have been studied by density functional theory. The thermodynamic stabilities of species are discussed by using binding energy and fragmentation energy calculation which may suggest that  $\text{Ge}_n\text{S}_m$  clusters have more tendencies to form anionic clusters. The chemical reactivity of  $\text{Ge}_n\text{S}_m$  clusters has been discussed on basis of different electronic parameters.

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