

# MODELING AND AB INITIO CALCULATIONS OF MOLECULAR- AND 2D NETWORK-LIKE ISOMERS OF LIGHT SENSITIVE CHALCOGENIDES

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Research into physical properties of non-crystalline chalcogenides revealed their remarkable structural, electronic, optical properties and large functionality, and has attracted significant attention both from fundamental and applied points of view, representing an important scientific and technological challenge. In addition to their intrinsic infrared properties, they offer a wide possibilities in domains such as information technologies (optical data storage, ultrafast optical transmitting and information processing), photolithography, renewable energy technologies (high efficiency solar cells, solid electrolytes), medicine, thermal imaging, sensing and biosensing *etc.* thanks to the advantageous combination of infrared properties, optical activity, structural photosensitivity and high third-order optical non-linearity. Recent progress in photonics shows that amorphous chalcogenides are among the best candidates as an active optical media for ultrafast *all-optical* processing systems.

The structure and its coupling to the fundamental physico-chemical and optical properties of amorphous chalcogenides has been the subject of intensive studies for decades. In particular, special interest is dedicated to the light-matter interactions and photo-structural phenomena in various chalcogenide systems. Furthermore, the local structural changes and possibility of selective modifications of the material properties can be the great advancements of modern nanophotonics and nanofabrication technology. During the last few years vast effort was focused on investigation of ultrathin chalcogenide films and surface nanolayers in context of surface states, surface morphology, atomic structure, photo transformations, induced mass transport, temporal degradation, surface contamination *etc.*

The present work is aimed to perform molecular modeling and *ab initio* calculations of molecular- and network-former As-S chalcogenide clusters in order to elucidate the induced structural transformations at the atomic scale. The molecular or cage-like As-S clusters are building blocks of corresponding crystals known in As-S system such as realgar ( $\text{As}_4\text{S}_4$ ) and dimorphite ( $\text{As}_4\text{S}_3$ ). Different (low temperature,  $\alpha$  and high temperature,  $\beta$ ) phases of these crystals can be obtained depending on packing of these molecules into the crystal lattice. However, each of cage-like molecule can have *so called* constitutional (structural) isomer(s) in which the structure is different while the atomic composition is the same as in basic molecule (Figure 1A). The one of the most important example of this kind isomers is photosensitive realgar molecule (r- $\text{As}_4\text{S}_4$ ) and their light-induced alteration product - pararealgar (p- $\text{As}_4\text{S}_4$ ). The mechanism of this transformation is related with As-As bond breaking and subsequent bond rearrangement. It is know that the arsenic

trisulphide ( $\text{As}_2\text{S}_3$ ) in crystalline state form a layered 2D structure. Each layer represent the network-like 12-membered ring structure build by corner-sharing  $\text{AsS}_3$  pyramids. Two types of  $\text{As}_2\text{S}_3$  2D crystal (orpiment and anorpiment) configurations based on 12-membered rings are possible to realize. The basic building block of these ring can be the bipyramidal  $\text{As}_2\text{S}_{1+4/2}$  cluster (Figure 1B).

*Ab initio* calculations show that this cluster have two energetically favorable states obtained by rotation of terminal  $\text{AsS}_2$  blocks (Figure 2). The existence of these conformational states of  $\text{As}_2\text{S}_{1+4/2}$  cluster allow to form two types of 12-membered As-S rings through different combinations of  $\text{As}_2\text{S}_{1+4/2}$  conformers. The conformational isomerism found in As-S network can be responsible for special type of light induced transformations taking place without bond breaking.

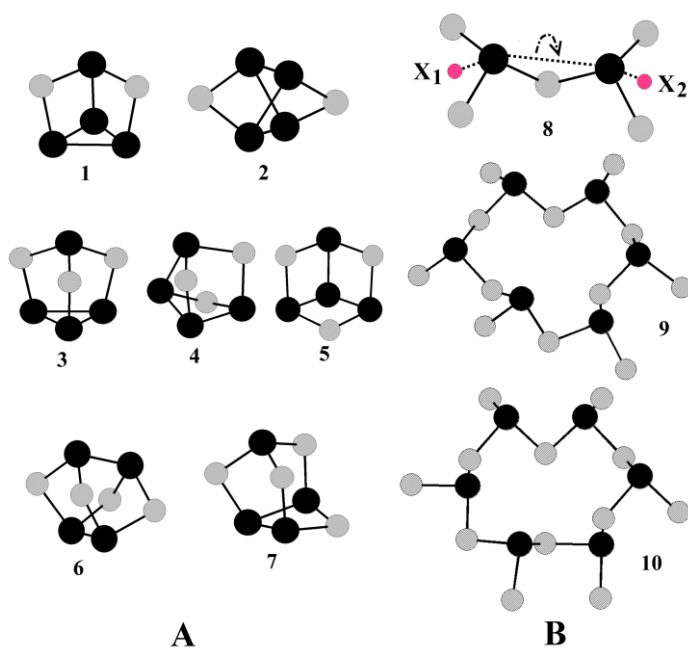


Figure 1. (A) Cage-like  $\text{As}_4\text{S}_x$  structural isomers:  $\text{As}_4\text{S}_2$  (1,2),  $\text{As}_4\text{S}_3$  (3,4,5) and  $\text{As}_4\text{S}_4$  (6,7). (B) Network-former  $\text{As}_2\text{S}_{1+4/2}$  cluster (8) together with 12-membered orpiment- (9) and anorpiment-like (10) rings. (Black and white circles denotes As and S atoms, respectively;  $\text{X}_1$  and  $\text{X}_2$  are dummy atoms located at S-As-S angle bisectors)

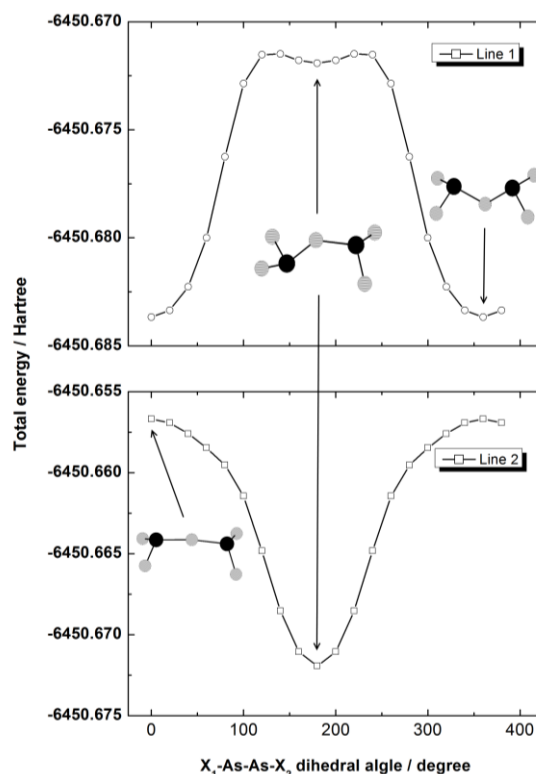


Figure 2. The results of relaxed potential energy scan for  $\text{As}_2\text{S}_{1+4/2}$  conformers around  $\text{X}_1\text{-As-As-X}_2$  dihedral angle (HF/6-31G level of theory)

The total energies, electronic structure, vibrational IR and Raman spectra of all constitutional and conformational As-S isomers were calculated at B3LYP/6-311G\* level of theory using Gaussian-09 software. The comparative analysis and characterizations of geometry evolution, stability, electronic and vibrational properties of As-S isomers were performed as well as their role in light induced phenomena discovered in amorphous chalcogenides were discussed in detail.

1. Ihnatolia P., Holomb R., Mitsa A., Mitsa V., Feher A. Modeling and ab initio DFT studies of  $As_4S_m$  ( $m=0-6$ ) cage-like nanoclusters and 12-membered As-S ring conformers // International research and practice conference «Nanotechnology and nanomaterials», 24-27 August 2016, Lviv, Ukraine, p. 534.