Ab initio quantum chemical investigation of arsenic sulfide molecular diversity

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The structural diversity of arsenic sulfide molecules in compositions between $\text{As}_4\text{S}_6$ and $\text{As}_4\text{S}$ was investigated using ab initio quantum chemical calculations. The $\text{As}_4\text{S}_6$ molecule consists of four trigonal pyramid coordinations of As atoms bonding to three S atoms. In the $\text{As}_4\text{S}_5$ composition, only one type of molecular configuration corresponds to an uzonite-type molecule. In the $\text{As}_4\text{S}_4$ composition, two molecular configurations exist with realgar-type and pararealgar-type molecules. Three molecular configurations are in the $\text{As}_4\text{S}_3$ composition. The first configuration comprises trigonal pyramidal As atom coordinations of two types: bonding to two S atoms and one As atom, and bonding to one S atom and two As atoms. The second is the molecular configuration of dimorphite. The third comprises trigonal pyramidal As atom coordinations of two types: bonding to three As atoms, and bonding to one As atom and two S atoms. The $\text{As}_4\text{S}_2$ composition allows molecular configurations of two types. One is comprised of trigonal pyramidal As atom configurations of one type bonding to two As atoms and one S atom. The other comprises trigonal pyramidal As atom coordinations of three types: bonding to two S atoms and one As atoms, bonding to one S atom and two As atoms, and bonding to three As atoms. The $\text{As}_4\text{S}$ molecule has trigonal pyramidal As atom coordinations of two types: bonding one S atom and two As atoms, and bonding to three As atoms. The $\text{As}_4\text{S}$ composition permits only one molecular configuration, which suggests that the mineral duranusite comprises the $\text{As}_4\text{S}$ molecular geometry. In all, ten molecular configurations are predicted in the molecular hierarchy of the arsenic sulfide binary system. The simulated Raman spectral profiles are helpful in searching for undiscovered arsenic sulfide minerals.

Keywords: arsenic sulfide minerals, molecular configuration, diversity, hierarchy, ab initio quantum chemical calculation