Ab initio quantum chemical investigation of arsenic sulfide molecular diversity

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The structural diversity of arsenic sulfide molecules in compositions between As\textsubscript{4}S\textsubscript{6} and As\textsubscript{4}S was investigated using ab initio quantum chemical calculations. The As\textsubscript{4}S\textsubscript{6} molecule consists of four trigonal pyramid coordinations of As atoms bonding to three S atoms. In the As\textsubscript{4}S\textsubscript{5} composition, only one type of molecular configuration corresponds to an uzonite-type molecule. In the As\textsubscript{4}S\textsubscript{4} composition, two molecular configurations exist with realgar-type and pararealgar-type molecules. Three molecular configurations are in the As\textsubscript{4}S\textsubscript{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 As\textsubscript{4}S\textsubscript{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 atom, bonding to one S atom and two As atoms, and bonding to three As atoms. The As\textsubscript{4}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 As\textsubscript{4}S composition permits only one molecular configuration, which suggests that the mineral duranusite comprises the As\textsubscript{4}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