Stability of sulfur molecules and insights into sulfur allotropy

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Elemental sulfur occurs in more allotropic forms than any other element in the periodic table except, perhaps, carbon [1]. In nature, elemental sulfur occurs in over 30 allotropes, including both native forms and inclusions in minerals and biological systems. Due to the importance of sulfur in natural processes, we applied the evolutionary algorithm USPEX [2, 3, 4] and ab initio calculations to determine the structures (Fig. 1) of sulfur molecules (Sₙ, where n = 2-21). We examined the stability of the molecules using several criteria, including the second derivative of energy with respect to composition (Δ²E), fragmentation energy (Efrag), and HOMO-LUMO energy levels. Based on these data, we identified the most stable (“magic”) clusters, which are expected to be the most prevalent. In our work we have shown that “magic” molecules play a special role in the structural chemistry and geochemistry of sulfur. All low-pressure crystalline sulfur allotropes have molecular crystal structures. As it is easier to grow the crystal from the most abundant molecules, nearly all known sulfur allotropes are made of “magic” molecules (such as S₈, S₁₂, S₆ and others) [5]. This rule can also be applied to other molecular crystals, because individual molecules in them are weakly bound to each other.

Taking into account vibrational and entropic effects, we have calculated the proposed stability measures at different temperatures. The obtained values (Gₘ, Δ²G and Gfrag) can be used for predicting which molecules will be the most abundant at different temperatures. Typically, ΔE (or ΔG at finite temperatures) is a quantitative measure of stability, which allows us to predict the ease of formation of molecules and corresponding molecular crystals. For example, the S₈ molecule has the highest value of ΔE and forms the most common allotrope of sulfur (orthorhombic α-S), which eventually transforms into this form at room temperature. Another well-known molecule, S₇, has a negative ΔG at temperatures around 300 K, but thermal effects make the S₇ molecule magic above 900 K, explaining its relatively high abundance. The temperature dependence of these stability indicators explains the wide range of facts about sulfur crystal allotropes, gas-phase molecules, and so on.

Figure 1. Lowest-energy structures of sulfur molecules Sₙ (n = 2 – 21).