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Equilibrium Constants of Sulfur Dioxide Clustering in Volcanic Vapors

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Molecular hydration and SO_2 clustering are pivotal processes in volcanic gases ultimately leading to the formation of sulfurous acid and the sulfite ion forms. These reaction are also critical in understanding metal-sulfite complexation and solvation equilibria, and therefore play a central role in metal reactivity and vapor phase transport in volcanic gas systems. Another interesting feature of the SO_2-SO_2 and SO_2-H_2O cluster systems, is their remarkably high stability, both at ambient and elevated temperatures, with important implications for their distribution in volcanic vapor up to the critical region. Vapor-phase SO_2 clustering and solvation reactions, particularly those leading to the dimer and larger water-sulfur dioxide clusters, however, remain still poorly understood, with notable knowledge gaps about their clustering energies, and how isotopic substitutions influence vibrational frequencies and their thermodynamic stability. To bridge these gaps, we have embarked on a detailed study of the self-reaction of sulfur dioxide (with and without water) towards the dimer, trimer, and larger mixed clusters, using both static and dynamic CPMD type *ab initio* theory calculations. The initial focus of this work is on estimating clustering equilibria for parent clusters and their isotopologue species upon incorporating substitutions with ^{32}S, ^{34}S, ^{18}O, and ^{16}O using DFT and higher level CCSD(T)/aug-cc-pV(Q+d)Z theory. We report the geometries of four dimer species, and larger SO_2 clusters, with varying number of water molecules, at the CCSD(T) level of theory, with VPT2 anharmonic corrections in order to estimate the effect of isotopic substitution on the stability of these clusters. For the global minimum $(SO_2)_2$ dimer we estimate a CCSD(T) binding energy of around -2.05 kcal/mol, which does not fall too short of the measured value of -2.52 kcal/mol, yet is noticeably weaker bound than the water dimer (-3.16 kcal/mol). Isotopic substitution in the sulphur dioxide dimer, i.e $(^{32}S^{16}O_2)_2$ vs $(^{34}S^{18}O_2)_2$, results in a binding energy adjustment of roughly 2%, shifting to -2.10 kcal/mol. These results, especially the observed stabilization of heavy isotopologues species will be further examined alongside solvation effects on $(^{32/34}S^{16/18}O_2)_n$ in water clusters and nanodroplets.