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Quantum chemical studies on HSO5 - related nucleation

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Recent laboratory experiments on SO_2 and H_2SO_4 - based nucleation give reason to believe that other sulfur - containing molecules than H_2SO_4 are likely to be involved in atmospheric new-particle formation from SO_2 oxidation in the presence of water. Specifically, reactions involving HSO_5 intermediate radicals have been proposed to give rise to products that either nucleate more efficiently than H_2SO_4 + H_2O, or enhance H_2SO_4 + H_2O nucleation.

We have used quantum chemical methods to study possible first steps of alternative nucleation pathways in the SO_2 oxidation process. Computed formation thermodynamics indicate that a mixture of sulfuric acid with molecules containing more than one sulfur atom, such as peroxydisulfuric acid, $H_2S_2O_8$, is likely to nucleate more effective than sulfuric acid on its own.

The central uncertainty in nucleation mechanisms involving HSO_5 is the lifetime of this metastable intermediate radical. Previous modeling studies have predicted the dissociation of HSO_5 into SO_3 and HO_2 to be very rapid, leading to a short lifetime of HSO_5, and a low net yield for the pathways forming alternative reaction products such as $H_2S_2O_8$. However, these studies have not accounted for the effect of hydration on the stability of HSO_5. High-level quantum chemical calculations demonstrate that HSO_5 is much more strongly hydrated than SO_3 and HO_2, leading to a significant increase in its lifetime with respect to dissociation. At least partial proton transfer from HSO_5 to H_2O is predicted to occur in the $HSO_5(H_2O)_2$ cluster, which may have important implications for the reactivity of hydrated HSO_5.