

This study investigates the role of air-water and air-ice interfaces in accelerating the formation of hydroxymethanesulfonate and its structural isomer hydroxymethyl sulfite from the reaction of formaldehyde with bisulfite. The work aims to provide a molecular-level mechanistic basis for the long-standing discrepancy between modeled and observed sulfate concentrations, commonly referred to as the “sulfur budget gap” in atmospheric chemistry. By employing Born-Oppenheimer molecular dynamics simulations, the authors reveal a distinctive stepwise water-mediated proton transfer mechanism at the air-water interface that dramatically lowers the free energy barrier for HMS formation relative to the bulk aqueous phase. The research perspective is novel, and the extensions to strongly acidic aerosol environments and cold-region ice surfaces are of considerable atmospheric relevance. As a well-designed theoretical study with clear implications for atmospheric sulfur cycling, I recommend this work for publication after the following comments have been adequately addressed.

1. The authors identify four distinct mechanistic regimes for HMS and HMSi formation: the bulk aqueous phase, the air-water interface, the strongly acidic aerosol interface, and the air-ice interface. Each regime exhibits different reaction selectivity and kinetics, with free energy barriers ranging from near-zero at the air-water interface to approximately $7.7 \text{ kcal mol}^{-1}$ in the bulk phase. These interfacial mechanisms could have significant implications for atmospheric sulfur budgets, but their impact can only be fully assessed by incorporating them into atmospheric chemical transport models. What challenges do the authors foresee in translating these molecular-level findings into parameterizations suitable for regional or global models?
2. The authors describe HMS formation at the air-water interface by noting that the distance between the carbon atom of HCHO and the sulfur atom of HOSO_2^- decreases to approximately 1.95 \AA during the reaction, which is interpreted as covalent bond formation (Section 3.2, Figure 2d). However, the assignment of covalent bond formation currently relies primarily on the shortening of interatomic distance, which is suggestive but not definitive. The conclusion would be more convincing if the authors could supplement this geometric evidence with a quantitative bond order analysis along the reaction coordinate.
3. The manuscript reports that under strongly acidic conditions, product selectivity reverses from preferential HMS formation to HMSi dominance, with an HMS: HMSi ratio of approximately 1:3 based on analyses of 25 independent BOMD trajectories (Section 3.3). This is a mechanistically significant finding, particularly given that strongly acidic aerosols span approximately 20% of the global surface atmosphere. Given that HMS and HMSi differ in their bonding arrangements, with HMS characterized by a direct C-S bond and HMSi by a C-O-S linkage, it would be helpful if the authors could comment on whether existing analytical techniques, for example, ion chromatography or high-resolution mass spectrometry, are sufficient to distinguish these two isomers. Addressing this point would help the observational community assess the testability of the paper’s predictions.
4. The air-ice section is both interesting and potentially important. However, the atmospheric relevance of this chemistry could be articulated more clearly. Could the authors explain why reactions on ice surfaces should be considered important in the atmosphere, rather than simply being treated as a special case under low-temperature conditions?
5. While the simplified model used here is reasonable for mechanistic exploration, the authors may wish to note more clearly that real atmospheric aerosol and cloud-droplet interfaces are chemically much more complex. In addition to HCHO and HOSO_2^- , these interfaces may

contain dissolved oxidants, organic species, transition metal ions, and other S(IV) components, all of which could influence interfacial reactivity by competing for reactive sites or modifying the local environment. The authors should acknowledge this chemical complexity as a limitation of the current simulations.