

***Ab initio* molecular dynamics study of aqueous H₂SO₃ at ambient and hydrothermal conditions**

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Sulphurous acid H₂SO₃ evolves as a consequence of the hydration of sulphur dioxide, and has been shown to undergo rapid ionization to its bisulphite [HSO₃]⁻ and sulfite [SO₃]²⁻ ion forms [1-2]. In this study, we explore the solvation dynamics and temperature-dependent stability of the H₂SO₃ molecule in aqueous solution by performing Car-Parrinello molecular dynamic (CPMD) simulations at room temperature, and at temperatures characteristic of hydrothermal conditions (up to 300°C). The aim of this study is to better understand the stability of the H₂SO₃ molecule in aqueous solution, and its propensity to dissociate to [HSO₃]⁻, [SO₃]²⁻, and the solvated proton species H₃O⁺(H₂O)_{*n*}, both at ambient conditions and at elevated temperatures. Our preliminary CPMD simulation results show that, at 25°C, H₂SO₃ undergoes rapid (~1 ps) deprotonation to HSO₃⁻ and H₃O⁺. These CPMD simulations and those conducted up to 200°C, for the same system, appear to suggest that the HSO₃⁻ ion remains as the dominant solution species, however, starting at around 250°C, H₂SO₃ decomposes rapidly to its constituent SO₂ and H₂O building blocks, prior to ionization. Building on these CPMD results, we have also attempted to quantify acidity constants values pK_{a1} and pK_{a2} for H₂SO₃ by performing constrained CPMD simulations in combination with thermodynamic integration. Our results predict values of pK_{a1} and pK_{a2} at 0.62 and 7.10, which are, in general, in good agreement with the experimentally measured values of 1.76 and 7.21 [3], respectively. This approach is currently being expanded to higher temperatures, with the aim of probing changes in the acidity constants values pK_a and tendencies for H₂SO₃ to deprotonate with increasing temperatures, which would have important implications for the speciation of sulphur dioxide in hydrothermal fluids.

[1] Terraglio & Manganelli (1967), *J. Air Pollut. Control Assoc.* 17, 403.

[2] Boniface, *et al.* (2000), *J. Phys. Chem. A* 104, 7502.

[3] Tartar & Garretson (1941), *J. Am. Chem. Soc.* 63, 808.

Figure. Snapshots taken from CPMD simulations at 25°C (top) and 250°C (bottom).

