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Water Ionization at Extreme Conditions: Insights from Car–Parrinello Molecular Dynamics and DFT Calculations

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The auto-ionization of water ($2H_2O = OH^- + H_3O^+$) is arguably one of the most fundamental features which characterizes aqueous fluids. The ionization behaviour of water at extreme conditions is of profound importance to processes in hydrothermal geochemistry including inorganic hydrolysis, complexation and clustering equilibria [Lemke & Seward, 2018]. For example, one particularly interesting aspect of liquid water is the large (~10^3-fold) increase in electrical conductivity over the temperature range 300 ^oC -1000 ^oC (1.5 g/cc), which is rooted in the enhanced water auto-ionization and proton mobility at these conditions.

Water ionization processes at extreme conditions however remain ambiguous and are still poorly understood. Prompted by some of these knowledge gaps, we have initiated a systematic study of the auto-ionization of water using Car-Parrinello molecular dynamics (CPMD) and density functional theory calculations at temperatures ranging from 25 ^oC - 1000 ^oC and fluid densities ranging from 0.01 g/cc - 2.5 g/cc. CPMD calculations have been set up with 100 water molecules contained in a periodic cubic cell with volumes ranging from (13.4 Å)^3 to (21.4 Å)^3 using the BLYP functional and Vanderbilt (VDB) pseudo-potential together with a cutoff at 25 Ry, and a Nosé thermostat to maintain the target temperature. The initial molecular configuration of each simulation cell was obtained from trial MD simulations in preparation for CPMD production runs. A review of preliminary results from CPMD simulations of the 100 water system shows that with increasing temperature, the first peak in the water O-O RDF shifts from ~2.815 Å (25 ^oC, 1.00 g/cc) to 2.696 Å (1000 ^oC, 1.56 g/cc) as the fluid becomes dominated by multiple ionic water species. For example, at 1000 ^oC and 1.56 g/cc, we observed the presence of transient (5-10 fs) Zundel-type clusters $H_5O_2^+$. These observations, in particular, the emergence of transient molecular ions, such as $H_5O_2^+$, and larger protonated water clusters at extreme temperatures and densities, are consistent with simulations [Rosza, 2018] and experiments [Holzapfel, 1969; Goncharov, 2005] at similar conditions.

[Lemke, Seward, *Rev.Min.Geochem*, 2018, **84**, 57], [Rosza, *PNAS*, 2018, **115**, 6952], [Holzapfel, Frank, *Ber.Bunsenges.Phys.Chem*. 1966, **70**, 1105], [Goncharov, *Phys.Rev.Lett.* 2005, **94**, 125508]