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Quantum chemical calculations and experimental measurements of solvation processes in high temperature low density fluids

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Explanations for the high ion content in steam goes back to H.R. Carlon´s proposstion of "high temperature ion- and neutral water clustering" over half a century ago. Subsequent experimental and theoretical efforts in this field have refined this thinking by invoking strongly bound ion-solvent aggregates, for instance, Eigen- or Zundel type proton clusters, for instance $H_3O^+(H_2O)_n$, and weakly bonded van der Waals molecules, such as $CO_2(H_2O)_n$ and $(H_2O)_n$ clusters. The study of cluster thermochemistry has been actively pursued for decades and has yielded important information on cluster structures as well as the energetics of solvation of the single molecule to bulk liquid continuum. Here we present results from mass spectrometric experiments and quantum chemical calculations indicating that hydration energies of protonated water clusters evolve toward bulk solvation values following attachment of around 4-6 solvent H_2O molecules. As part of this work we also adress questions regarding molecular properties of both neat (H_2O) and mixed solvent (H_2O, H_2S) clusters and the prospect of quantum chemical calculations in elucidating energetic trends in solvation at elevated temperatures.