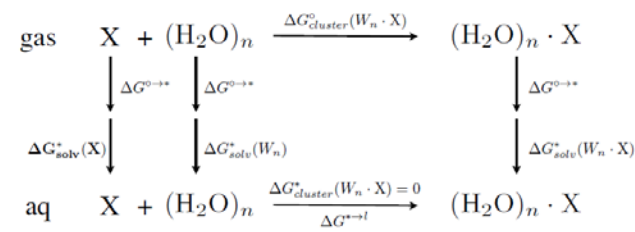


Cluster-Continuum Calculations of Hydration Free Energies of Anions and Group 12 Divalent Cations

Contact: **Jeremy C. Smith** (smithjc@ornl.gov, 865-574-9635)
DOE/Office of Science/Biological & Environmental Research

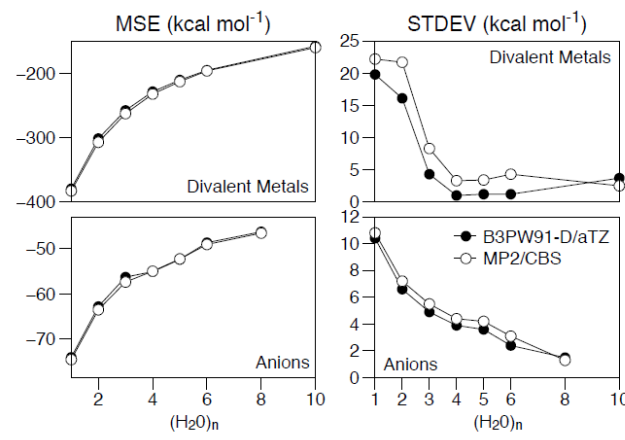
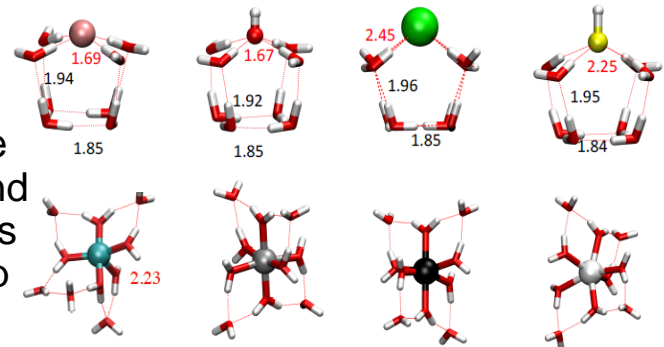
Objective

- Understand the hydration of Hg^{2+} , several of its aquatic ligands, and other divalent metal ions, with which Hg^{2+} competes for biologically relevant binding sites.



New Science

- Systematic analysis of local and long-range contributions to the hydration free energy carried out in terms of absolute (MSE) and relative (STDEV) error for a set of ions with experimental values ranging from -72.4 to -505.9 kcal mol⁻¹. Thermocycle shown top right.
- Relative errors due to the level of theory and structural variation identified and understood. Structures shown middle right.
- Local contributions are sufficient to capture trends within sets of ions. Long-range contributions needed to combine sets. Comparison between gas phase cluster free energies and experimental hydration free energies shown bottom right.



Significance

- Establishes methods that will be used to understand the molecular details of metal speciation and transformation.

Cluster-Continuum Calculations of Hydration Free Energies of Anions and Group 12 Divalent Cations

Contact: Jeremy C. Smith (smithjc@ornl.gov, 865-574-9635)

DOE/Office of Science/Biological & Environmental Research

Understanding aqueous phase processes involving group 12 metal cations is relevant to both environmental and biological sciences. Here, quantum chemical methods and polarizable continuum models are used to compute the hydration free energies of a series of divalent group 12 metal cations (Zn^{2+} , Cd^{2+} , and Hg^{2+}) together with Cu^{2+} and the anions OH^- , SH^- , Cl^- , and F^- . A cluster-continuum method is employed, in which gas phase clusters of the ion and explicit solvent molecules are immersed in a dielectric continuum. Two approaches to define the size of the solute-water cluster are compared, in which the number of explicit waters used is either held constant or determined variationally as that of the most favorable hydration free energy. Results obtained with various polarizable continuum models are also presented. Each leg of the relevant thermodynamic cycle is analyzed to determine how different contributions yield the observed mean signed error (MSE) and the standard deviation of the error (STDEV) between theory and experiment. The use of a constant number of water molecules for each set of ions led to predicted relative trends that benefit from error cancellation. Overall, the best results are obtained with MP2 and the Solvent Model D polarizable continuum model (SMD), with eight explicit water molecules for anions and ten for the metal cations, yielding a STDEV of $2.3 \text{ kcal mol}^{-1}$ and MSE of $0.9 \text{ kcal mol}^{-1}$ between theoretical and experimental hydration free energies, which range from $-72.4 \text{ kcal mol}^{-1}$ for SH^- to $-505.9 \text{ kcal mol}^{-1}$ for Cu^{2+} . B3PW91 with DFT-D3 dispersion corrections (B3PW91-D) and SMD yields a STDEV of $3.3 \text{ kcal mol}^{-1}$ and MSE of $1.6 \text{ kcal mol}^{-1}$, to which adding MP2 corrections from smaller divalent metal ion water molecule clusters yields very good agreement with the full MP2 results. Using B3PW91-D and SMD, with two explicit water molecules for anions and six for divalent metal cations also yields reasonable agreement with experiment, due in part to error cancellation associated with the metal cations. Overall, the results indicate that the careful application of quantum chemical cluster-continuum methods provides valuable insights into aqueous ionic processes that depend on both local and long-range electrostatic interactions with the solvent.

Riccardi, D., H.-B. Guo, J.M. Parks, B. Gu, L. Liang, and J.C. Smith. 2013. Cluster-continuum calculations of hydration free energies of anions and group 12 divalent cations. *J. Chem. Theor. Comp.* 9:555-569 (doi: 10.1021/ct300296k).