Poster #191

Biomolecular Insights into the Transport and Transformations of Mercury

Jerry M. Parks, [1, 2], Jing Zhou[1],Ryne C. Johnston[1], Alexander Johs[1], Todd A. Olsen[1], Micholas D. Smith[1], Xiaolin Cheng[1], Scott C. Brooks[1] and Jeremy C. Smith[1,2]

[1] Oak Ridge National Laboratory, Oak Ridge, TN
[2] University of Tennessee–Knoxville, Knoxville, TN

Contact: Jerry Parks [parksjm@ornl.gov]

The natural biogeochemical cycling of highly mobile, bioavailable and extremely neurotoxic methylmercury significantly elevates the ecological and public health risk of environmental mercury (Hg). The mechanisms by which microorganisms take up inorganic Hg^{II} substrates and export CH_3Hg-containing molecular species remain unclear. As a first step in understanding microbial Hg uptake/export, we assess the plausibility of passive diffusion of neutral Hg^{II} *bis* thiolate and CH3Hg-thiolate complexes across a model microbial cytoplasmic membrane in the absence of membrane proteins. Through extensive molecular dynamics simulations, we quantify the energetics of passive diffusion and show that it is energetically feasible for neutral Hg-containing species.

In other work, we have used density functional theory (DFT) to investigate mechanisms of the formation of dimethylmercury from monomethylmercury mediated by reduced sulfur-containing compounds. The calculations reveal chemical trends in Hg–C bond strengths under different thiolate coordination environments and show how the stabilization of Hg permits methyl ligand exchange to a more electrophilic partner. Furthermore, we show that two adjacent $[CH_3Hg]^+$–thiolate complexes form an unusual dinuclear Hg^{II} complex that serves to accomplish maximal Hg stabilization during the transmethylation reaction. These findings are rationalized within the context of our previous work on the mechanisms of demethylation of methylmercury by MerB and the methylation of inorganic Hg^{II} by HgcA. Together, these studies demonstrate the unique ability of computation to reveal important physicochemical insights while circumventing the handling of hazardous materials.