Ab Initio Molecular Dynamics and Multiscale Simulation of Formate Ion Hydration—a Comparative Study

by ***Kevin Leung and Susan B. Rempe***

Motivation—The interaction of water with molecular/ionic species and material surfaces is crucial to understanding biology, corrosion, water transport in nanochannels, adhesion, and wetting of microelectromechanical systems (MEMS) components. A major theoretical goal is to accurately model hydration structure using multiscale, quantum mechanics/molecular mechanics (QM/MM) methods. In this scheme, the solute or surface atoms, and sometimes the first hydration shell water molecules, are treated quantum mechanically, while cost-effective empirical force fields suffice for the rest of the water. The accuracy of existing QM/MM results has never been systematically tested. For the biologically important glycine tautomerization reaction in water, QM/MM in fact strongly overestimates free energy differences between tautomers. This is a prototype proton transfer reaction, and its modeling aspects are pertinent to acid/base related problems like corrosion and geochemistry. Our goal is to improve the accuracy of existing multiscale methods by (a) implementing existing QM/MM methods; and (b) performing costly but accurate, purely *ab initio* molecular dynamics simulations as benchmarks. Glycine molecule fragments will be used as test cases.

Accomplishment—We implemented a QM/MM capability into the Vienna atomistic simulation package (VASP) and applied it to analyze glycine hydration. There are two functional groups in glycine, namely the ammonium and carboxylate groups. We treat these fragments—the ammonium (NH_4^+) and formate ($HCOO^-$) ions—quantum mechanically, and model water molecules using force fields. *Ab initio* molecular dynamics predictions for NH_4^+ hydration exist in the literature but not for $HCOO^-$. Thus we also simulate formate ions solvated in water, with all species treated quantum mechanically. VASP as well as CPMD (the Car-Parrinello Molecular Dynamics code) are used.

Figure 1 compares the formate ion-water pair correlation functions at ambient conditions as predicted by *ab initio* molecular dynamics and QM/MM methods. The results are significantly different. The former predicts roughly two and a half hydrogen bonds between water and each HCOO- formate oxygen, in agreement with recent experiments. Figure 2 depicts snapshots of the hydration structure. In *ab initio* molecular dynamics, one formate oxygen typically forms two hydrogen bonds while the other forms three. In contrast, QM/MM incorrectly predicts a total of seven hydrogen bonds, similar to molecular dynamics simulations where all species are treated empirically. On the other hand, the hydration structure of NH_4^+ is well predicted by QM/MM methods.

Significance—This work shows that the accuracy of multiscale QM/MM methods needs to be improved and benchmarked against *ab initio* molecular dynamics simulations and experiments. Much of the body of existing, widely accepted theoretical results, including those pertaining to water interacting with biomimetic, COOH group-functionalized surfaces, needs to be re-evaluated. Sandia's theoretical and computational expertise is leading to improved multiscale methods.

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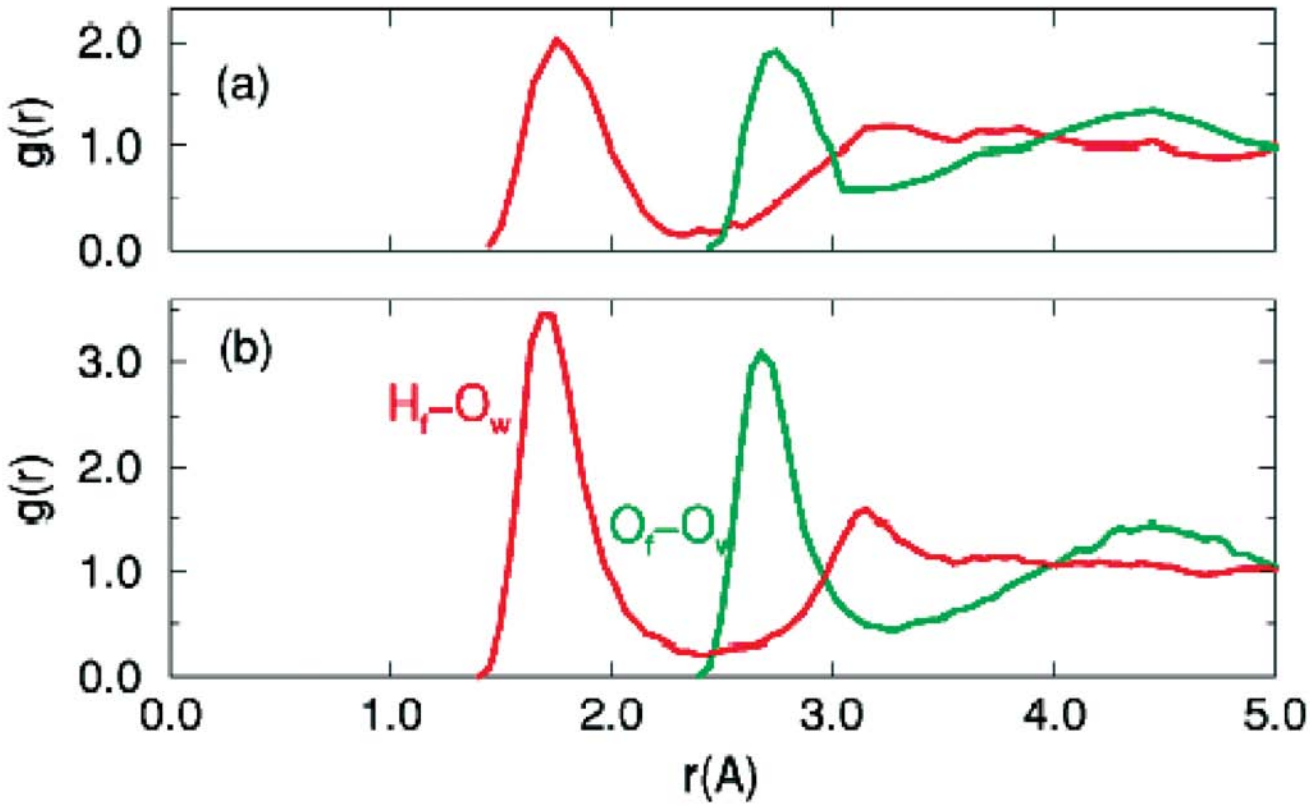

Figure 1. Pair correlation functions between the oxygen and hydrogen sites of the formate ion and the oxygen atom in water molecules. (a) *ab initio* molecular dynamics; (b) QM/MM.

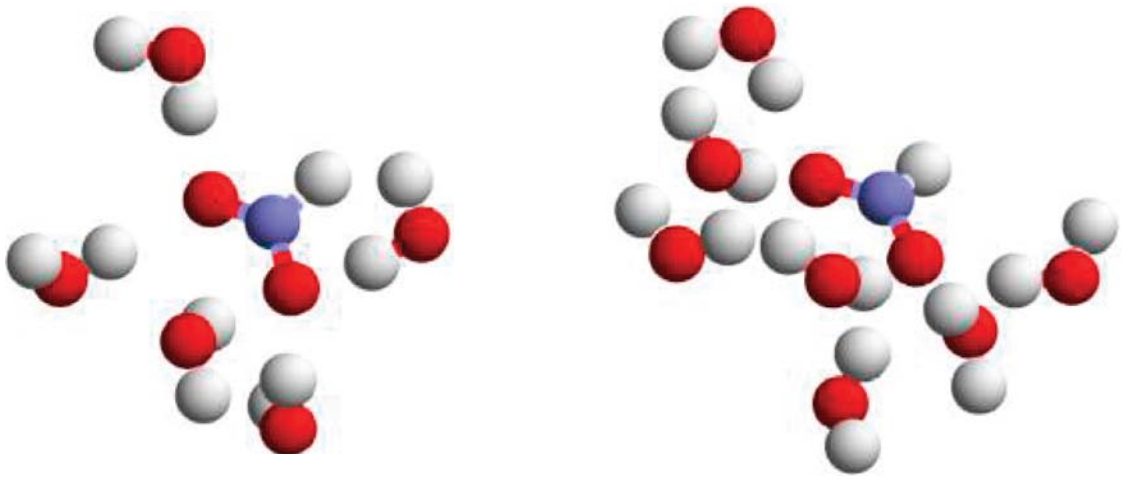

Figure 2. Snapshots of formate ion in water. Oxygen, hydrogen, and carbon atoms are depicted as red, white, and blue spheres, respectively. Left panel: *ab initio* molecular dynamics; right panel: QM/MM. They predict 5 and 7 water molecules in the first hydration shell, respectively.