Abstract Submitted
for the MAR11 Meeting of
The American Physical Society

Quantum-mechanical and QM/MM simulations of proton dissociation free energies in solution NOAM BERNSTEIN, Naval Research Laboratory, CSILLA VARNAI, University of Cambridge, MONIKA FUXREITER, Hungarian Academy of Sciences, GÁBOR CSÁNYI, University of Cambridge — Chemical reactions often occur in the presence of a solvent, in particular water for biological systems. To describe such processes a quantum mechanical (QM) description of the reaction site is needed, combined with a large number of solvent molecules that affect the reaction via their electrostatic fields and free energy effects of their long-range structure. We have simulated the dissociation of a proton from the side chain of a tyrosine molecule, as a realistic model system. We compute a free energy difference, using umbrella integration, from the average restraint force as a function of O^{-}-H^{+} distance as the proton is transferred from the side-chain to nearby water molecules to form H_3O^+. We use a combination of periodic QM calculations using DFT and force-mixing QM/MM simulations implemented in QUIP and CP2K. The pure QM calculations are used for reference values and for determining appropriate restraint conditions for the free energy calculations. The force-mixing QM/MM method, which gives accurate forces throughout the system, is used to evaluate free energies for comparison with experiment. We extrapolate the free energy for the initial transfer of the proton to the bulk solvated proton regime by analytically computing electrostatic and entropy contributions.

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Date submitted: 17 Nov 2010 Electronic form version 1.4