

Ab initio and classical molecular dynamics simulations of
electrode reactions

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The role of the solvent is central to many charge transfer reactions taking place at the metal-liquid interface, and is what distinguishes electrocatalytic reactions from surface-catalyzed reactions in the gas phase or the vacuum. In this paper, we describe some of our recent results in applying large-scale computer simulations to the modeling of reactions at metal-liquid interfaces.

Classical molecular dynamics simulations have been applied to study the role of solvent reorganization in electron and ion transfer processes at metal electrodes. The results of these simulations are compared to the assumptions of the classical Marcus electron transfer theory. We find that the solvent reorganization energy depends quite strongly on the charge of the reacting species, in contrast with the continuum theory of Marcus. The charge dependence of the solvent reorganization is governed by non-continuum effects, such as electrostriction and dielectric saturation. Deviations from Marcus theory are especially significant for redox reactions involving a neutral and a monovalent negatively charged ion. A possible relevant example could be the first step in oxygen reduction. We also find that for charged species the solvent reorganization depends on the distance of the species from the electrode surface, whereas for neutral species this is much less the case. This is because for charged species long-range forces are involved in the solvation.

Ab initio molecular dynamics is used to study a water-vacuum interface and water layers on metal surfaces. These calculations are computationally very expensive, and therefore we must restrict ourselves to very small system sizes of only several tens of atoms or molecules. Particular attention is paid to the energetics, orientation, dynamics, and vibrational properties of water at these interfaces. Finally, we treat the co-adsorption of OH and water on a Rh(111) surface, demonstrating the high mobility of surface-bonded OH due a Grotthus-like transport mechanism of the proton with neighboring water molecules.