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Baddeleyite/aqueous solution interfaces from MD-DFT calculations and experiments

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Bulk zirconia (ZrO_2) is of scientific and technological interest because it has high thermal stability and is stable across oxidizing and reducing environments. The application of zirconia is diverse, including as a catalyst, in support materials for CO and CO_2 adsorption–conversion reactions, in dental biomaterials, and for the disposal of spent nuclear fuel. Consequently, zirconia is a well-studied metal oxide, but much remains unknown about the ZrO_2–water interface. Furthermore, a description of the surface charging behavior of ZrO_2 phases in aqueous media, over a broad temperature range, is incomplete.

In this work, we present molecular and macroscopic studies that focus on the molecular structure of the extended ZrO_2–water interface and surface charging behavior of ZrO_2 in NaCl media, respectively. Results from the two studies were integrated through surface complexation modeling (SCM). Baddeleyite, the monoclinic ZrO_2 phase, was used in both the molecular-scale calculations and experimental studies. The molecular simulations focused on the most stable (-111) baddeleyite surface, which was also the dominant face on the powdered sample used for the experiments. We performed first-principle molecular dynamics (FPMD) simulations, using the Vienna *ab initio* simulation package (VASP). Surface charging behavior was evaluated from potentiometric titrations performed in NaCl media at 0.03 and 0.3 *m* ionic strength, from 10 to 250 °C.

From the FPMD results, the (-111) baddeleyite surface is complex, with eight distinct surface functional groups (-OH, μ-OH, and μ_3-OH). Six surface oxygen atoms hydroxylated readily. Our results revealed distinct interactions between the surface and interfacial water molecules, suggesting a hydrophilic character. There was a well-defined first solvation layer, comprising preferentially ordered water molecules. From the titration results, temperature and ionic strength effects were typical for metal oxide phases. The pH_{znpc} values decreased almost linearly from 10 to 150 °C, then decreased slightly to 250 °C (i.e., from pH 7.6 to 5.6). To interpret the titration data, we used SCM following the CD-MUSIC formulation. We constrained the CD-MUSIC model fits with molecular-scale information from our FPMD calculations.