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Dynamical properties of water molecules in the hydration shells of Na^+ and K^+: ab initio QM/MM molecular dynamics simulations

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Abstract

The librational and vibrational motions of water molecules in the first hydration shells of Na^+ and K^+ have been studied by combined ab initio quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulations, in which the ion and its first hydration sphere were treated at the Hartree–Fock level using LANL2DZ basis sets. The frequency shifts, together with the detailed analysis of water exchange processes and the mean residence times of the water molecules surrounding the ions, in comparison to those observed from a QM/MM simulation of pure water, provide a clear evidence for the background of the experimentally observed transition from structure-making to structure-breaking behavior from Na^+ to K^+.