Ab initio QM/MM dynamics of anion–water hydrogen bonds in aqueous solution

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Abstract

Dynamical properties of F⁻–water and Cl⁻–water hydrogen bonds in aqueous solution have been studied by ab initio QM/MM molecular dynamics simulations, in which the whole first hydration sphere of the anion was treated at Hartree–Fock level using D95V+, 6-31+G and D95V++ basis sets for F⁻, Cl⁻ and water, respectively. According to a detailed analysis of the bond distortions and shifts in the corresponding bending and stretching frequencies as well as the mean residence times of water molecules surrounding the ions, F⁻ clearly acts as a 'structure-maker', while Cl⁻ solvation leads to a more flexible structure with frequent re-arrangements of the hydrogen bonds.

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1. Introduction

The dynamics of hydrogen bonds in aqueous electrolyte solutions of charged particles, in particular anions, has been an important subject of both experimental and computational studies [1–4]. In general, the interactions of anion with water are relatively weak and dominated by ionic hydrogen bonding. These interactions are, in several cases, even energetically comparable with the water–water interactions in pure water, implying that the dynamical properties of such weakly hydrated anions can be very sensitive to the relative strength of anion–water and water–water interactions. Recently, the dynamics of water molecules in the solvation shell of halide ions were experimentally studied by a nonlinear spectroscopic technique [1]. Following these experiments, water molecules in the solvation shells of Cl⁻, Br⁻ and I⁻ were proposed to display mean lifetimes ranging from 12 to 25 ps, which is about 20–50 times longer than in pure liquid water.

On the other hand, time-dependent simulation methods, in particular molecular dynamics (MD) technique, have been employed to provide dynamics information not accessible by experimental approaches, especially for very fast reactions as they permit to characterize specific reactions and mechanisms of the involved interactions in the femto- and picosecond scale [3,4]. Recent classical MD simulations [4], using extended simple point charge (SPC/E) model [5] for water and Lennard–Jones interactions for anions [6,7], have shown that the dynamics of anion–water hydrogen bonds for Cl⁻ and Br⁻ at room temperature should be about two times slower than that of water–water hydrogen bonds. However, the main drawback of this work, as well as the earlier MD results of Impey et. al. [3], is the neglect of charge transfer and thus changing polarization of the molecules, an important factor determining many-body interactions. These effects of polarization have been shown to be very crucial for the hydrogen