Nuclear Quantum Effects in Ion-Mediated Hydrogen-Bond Rearrangements

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A microscopic picture of hydrogen-bond structure and dynamics in ion hydration shells remains elusive. In this context small aqueous ionic clusters represent ideal systems to investigate the interplay and competition between ion–water and water–water interactions as well as the role played by nuclear quantum effects in hydrogen-bond rearrangements. Here, we perform quantum dynamics calculations on data-driven many-body potential energy surfaces to unravel specific ion effects in hydrogen-bond rearrangements in small $X^-(H_2O)_n$ complexes (X = F, Cl, Br, and I). Our results provide evidence for tunneling in hydrogen-bond rearrangements in both halide–dihydrate and halide–dihydrate complexes. Furthermore, a systematic analysis of hydrogen-bond rearrangements in the $X^-(H_2O)_2$ complexes at low temperature the provides fundamental insights into the competition between halide–water and water–water interactions depending on the properties of the halide ion. While the halide–water hydrogen-bond strength decreases as the size of the halide ion increases, the opposite trend is observed in the strength of the water–water hydrogen-bond, suggesting that nontrivial many-body effects may also be at play in the hydration shells of halide ions in solution, especially in frustrated systems (e.g., interfaces) where the water molecules can have dangling OH bonds.

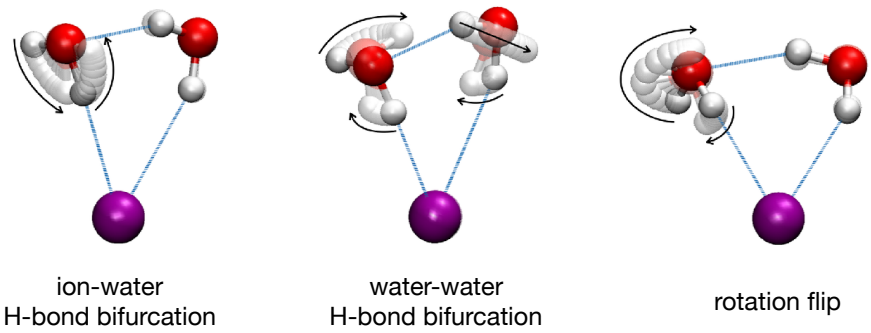

Figure 1: Tunneling pathways in the $X^-(H_2O)_2$ complexes.

References

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