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Synopsis Ions play an important role in many heterogeneous processes, and understanding specific ion effects is a key point in studying solvation mechanisms in liquids as well as reactivity of aerosol particles. In this regard, a crucial issue to be resolved is the extent to which ions influence the structural and dynamical properties of the surrounding hydrogen bond network and, at the same time, to provide a direct molecular-level interpretation of the experimental measurements.

So far, water-halide ion systems have attracted the interest of both experimentalists and theorists [1]. On the experimental side diffraction techniques and x-ray absorption spectroscopy have been used to understand the hydration of ions, while for their interpretation rather simplified models have been employed in the post-processing of raw data [2]. On the theoretical side, computational simulations have been limited by the accuracy of the models in describing weak interactions and hydrogen bonds, as well as due to the computational cost for an effective sampling of the molecular configurations.

Thus, we developed first-principles water-halide ion potentials [3], namely i-TTM (ion-Thole-type), by combining a newly constructed intermolecular ion-water one with the water-water MB-pol model [4]. The potentials include anisotropy in both short- and long-range interactions, and their parameters were determined by a two-step fitting procedure to electronic structure calculations for the X^-H_2O (X=F, Cl, Br, I) complex. In particular, the dispersion coefficients were evaluated first from DFT computations employing the XDM model, imposing the correct asymptotic behaviour, while for the electrostatic part the reparameterized TTM4-F variant of the Thole-type model was used, with the anion polarizabilites and the interaction energies calculated at the CCSD(T) and CCSD(T)-F12 level of theories, respectively.

The quality of the i-TTM model is validated through comparisons with high level *ab initio* calculations at optimized configurations of low-lying stationary points of each X^-H_2O system, as well as for small $X^-(H_2O)_n$ clusters (see Fig. 1). The obtained data suggest that the polarizable two-body i-TTM potentials can indeed be used to describe the halide ion-water gas phase interactions, while in conjuction with the MB-pol water-

water model can be also used in molecular simulations of condensed-phase systems.
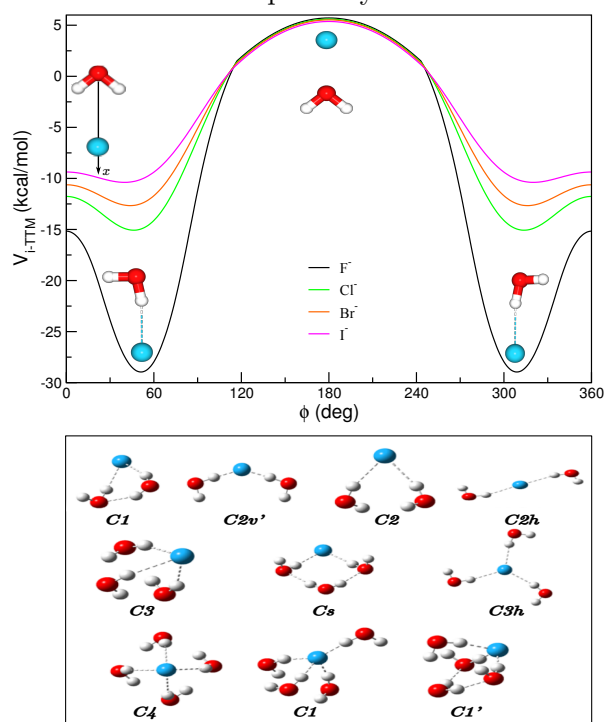

Figure 1. Upper panel: Minimun energy paths as a function of the azimuthal angle for the indicated X^-H_2O system, together with the configurations of the corresponding stationary points. Lower panel: Optimal structures for the indicated $X^-(H_2O)n$ clusters from the i-TTM model.

References

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