Development of transferable water-halide potentials

Raúl Rodríguez-Segundo[*1], **Daniel J. Arismendi-Arrieta**[*2], **Rita Prosmiti**[*3]

* Institute of Fundamental Physics (IFF-CSIC), Serrano 123, 28006 Madrid, Spain

Synopsis The behavior of ions in aqueous environment is of fundamental interest in physics and chemistry. A topic of research is focused on the modeling of the ion-ion, ion-water, and water-water interactions. So far, the water-water interactions has been widely studied what has lead to a variety of water potential models of increasing complexity. However, how ions change the water network is an open debate in the literature. Thus, the development of a generalized representation for the ion-water interactions coupled to available reliable water models provide a rational route to follow for studying ion-hydrates from finite-size cluster systems to condensed phase.

Despite experimental and theoretical efforts to provide a direct molecular-level understanding of hydration of ions in different environments, from gas to condensed phases, investigations have been constrained by the limited predictive abilities of the empirical models, the high computational cost for correlated *abinitio* methods, and the intrinsic deficiencies of common functionals in describing weak interactions. A fully *ab initio* approach to these appears, at first glance, daunting. However, progress has been made, with the most advanced *ab initio*-based approaches clearly being a step forward combining computational efficiency with fitting accuracy.

Thus, the first step to achieve it to adopt a bottom-up approach starting from the study of small to medium size clusters, where valuable information has been acquired by IR experimental studies and *ab initio* computations. We focus on the representation of the interactions based on first-principle data of solvated monovalent (halide $X = F^-$, Cl^-, Br^-, I^-) ions [1]. The new ion-water potential energy surfaces (PESs) are constructed by an extended version of the Thole type model (TTM) to describe halide ion-water interactions in conjunction with different TTM-based water model potentials. So, $V_{tot} = V_{w_n}^{inter} + V_w^{intra} + V_{i-TTM}^{inter}$, where $V_{w_n}^{inter}$ corresponds to MB-pol, TTM4, TTM3 and TTM2 water models, and V_w^{intra} the PS water monomer PES. The new $V_{i-TTM}^{inter} = V_{TTM,elec} + V_{TTM,ind} + \sum_{i=1}^{n}(V_{rep}(X,i) + V_{disp}(X,i))$ PESs count with four contributions: electrostatic, induction, repulsion and dispersion interaction energy terms, with n being the number of surrounding water molecules. Thus, the potential functions explicitly count with polarization terms, include angular anisotropy in short- and long-range terms by adjusting to *ab initio* energies and polarizabilities from explicitly correlated CCSD(T)-F12/cc-pVQZ-F12/aug-cc-pVQZ-PP and CCSD(T)/t-aug-cc-pV5Z/t-aug-cc-pV5Z-PP calculations, respectively, while dispersion coefficients are obtained from DFT/LC-ωPBE/aug-cc-

pVTZ calculations using the XDM model (see Figure 1). The quality of the generalized V_{tot} PESs and their performance are checked by comparing to computationally expensive *ab initio* CCSD(T)-F12/DF-MP2 calculations on optimized structures and energies of larger ion-water (with n up to 8) systems. In addition, DFT approaches have also employed, and in a systematic way the performance of various functionals with and without dispersion corrections is investigated. [2, 3]
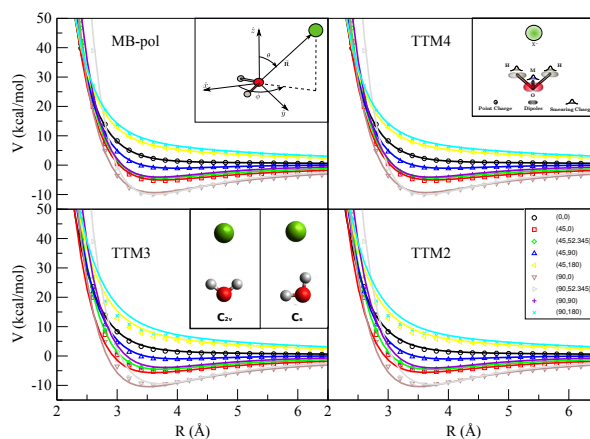

Figure 1. Potential curves (solid lines) and corresponding CCSD(T)-F12 reference data (symbols) calculated for different (θ, ϕ) orientations of the $I^-(H_2O)$ dimers employing the indicated TTM water models. In the insert panels we display the coordinate system used (upper/left), the charge and dipole-moment positions for i-TTM4/MB-pol models (upper/right), and the C_s and C_{2v} minimum and saddle-point geometries of $I^-(H_2O)$ (lower/left).

References

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[3] R. Rodríguez *et al.* 2017 *in preparation*

[1] E-mail: raul@iff.csic.es

[2] E-mail: d.arismendi@iff.csic.es

[3] E-mail: rita@iff.csic.es