Accurate analytic intermolecular potential for the simulation of Na\(^+\) and K\(^+\) ion hydration in liquid water

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**ABSTRACT**

Structural and dynamical properties of the hydration of K\(^+\) and Na\(^+\) ions have been investigated at atomistic level of detail by molecular dynamics simulations of the ion and 253 water molecules with periodic boundary conditions at the temperatures of 300 and 450 K. The intermolecular interactions involved have been modelled by a recently developed approach targeted to accuracy and low computational cost. Radial distribution functions and coordination numbers have been obtained to assess overall reliability of the model. Two different types of water models, rigid and flexible, have been used in simulations, evaluating the effect of adding flexibility to water.

1. Introduction

Small ions such as Na\(^+\) and K\(^+\) in aqueous solution play a ubiquitous role in chemical and biological processes. They are involved in the active transport phenomenon that ensures relatively high concentrations of potassium ions but low concentrations of sodium ions in cells. The mechanism responsible for the control of Na\(^+\) and K\(^+\) concentrations in the cells is the sodium–potassium pump, which moves these two ions in opposite directions across the plasma membrane \([1]\). This was investigated by following the passage of radioactively labelled ions across the plasma membrane of certain cells \([1]\). It was found that the concentrations of sodium and potassium ions on the two sides of the membrane are interdependent, suggesting that the same carrier transports both ions. It is now known that the carrier is an ATPase and that it pumps three sodium ions out of the cell for every two potassium ions pumped in \([2]\).

The understanding of the complex interplay of ion–molecule and molecule–molecule interactions in the sodium–potassium pump requires the study of ion hydration by modelling the microscopic environment of the ions in solution and, on the experimental side, the investigation of gas-phase ion–water clusters, where the size and composition of the system are detectable and to a certain extent controlled \([3]\). In this respect, the main issue is perhaps the modelling of intermolecular interactions, since the delicate balance and the cumulative effect of the wide variety of these competing non-covalent forces control several physical, chemical and biochemical processes that contribute to the mechanism. Relevant aspects are the formation of hydrogen bonds \([4,5]\), the interaction with hydrogen-bonded solvent molecules (see for instance Ref. \([6]\)) and the competitive solvation of ions \([7–9]\). In fact, the extraction and transport of ions require their partial dehydration, which can be achieved when other molecules interact with ions and/or H\(_2\)O perturbing the surrounding hydrogen bond network.

The strongest non-covalent forces are indeed those involving molecules possessing dipole or quadrupole moment, with ions. For instance, in many different ionophores and ion channels, the most relevant interactions involving alkali ions are via dipolar moieties located on the molecule \([10]\). Such interactions are size-specific so that, in the case of alkali ions, interactions with side chains of aromatic nature have been proposed as a mechanism for selectivity in some K\(^+\) and Na\(^+\) channel proteins \([8]\). Their importance is not limited to the selectivity of ionic channels \([11]\), being fundamental the role played in molecular recognition and drug action \([12–14]\), or more in general in the structures of biomolecules \([13]\).

The use of classical molecular dynamics (MD) simulations for the study of the structure and dynamics of ion solvation in water is subjected to the accurate description of the interactions. From a theoretical point of view, the comparison of predictions with experimental results is primarily a test for the accuracy of the potential energy function and a validation of the approach to the modelling of the interactions. The disentanglement of the effects of competing interactions is particularly important, and can be achieved by designing an interaction model based on well-defined contributions and parameterized on physical properties of the involved molecules. The original potential model used here is based on a formulation of the non-electrostatic contribution to the intermolecular interaction that exploits the decomposition of the molecular polarisability \([15]\) into effective components associated with atoms, bonds or groups of atoms of the involved molecules. This
type of contribution to the intermolecular energy was applied before to investigate several neutral [16–24] and ionic [25–27] systems, often involving weak interactions [16,28], difficult to calculate. The adequacy of the potential energy functions to describe several intermolecular systems was proved by comparing energy and geometry predictions at several configurations with ab initio calculations. In particular, the study of the alkali ion systems [29,30] showed that chemical contributions play a small or negligible role in the aggregates. The study by MD simulations of systems characterized by ion–liquid water interactions and solvation effects at an atomistic level (e.g. biomolecules) often requires massive calculations for which a reduction of computing times, with the least possible lost of accuracy in the interaction description, is highly desirable. This can be done exploiting the ease of trajectories for the implementation in distributed computing environments (e.g. Grid computing [31,32]) and accurate analytical intermolecular potentials, as the one we propose here. Because of that, and in view of using our potential model to investigate increasingly complex systems, in the present study we analyse the results obtained using two ensembles (rigid and flexible) of 253 molecules of water, where the molecular polarisability of H$_2$O has not been decomposed. The comparative study has been made at 300 K and 450 K, the two temperatures considered in the work of Liu et al. [33]. The paper is organized as follows: in Section 2, we outline the construction of the potential energy function. The details of the molecular dynamics simulations are given in Section 3. Results are presented in Section 4 and concluding remarks are given in Section 5.

2. Potential energy surface

To obtain a potential energy surface suitable for running MD simulations, the $M^+−(H_2O)_m$ ($M^+ = K^+,Na^+$) intermolecular interaction energy, $V$, is decomposed in terms of ion–molecule and molecule–molecule pair contributions, as follows:

$$V = \sum_{k=1}^N V_{M^+−(H_2O)_k} + \sum_{k=1}^{N-1} \sum_{j=k}^N V_{(H_2O)_k−(H_2O)_j}$$

(1)

where $N$ is the total number of water molecules and any intermolecular term in Eq. (1) includes both electrostatic and non-electrostatic contributions.

The non-electrostatic contributions to the sum of Eq. (1) are evaluated assigning a value of polarisability (denoted hereinafter as $\varepsilon$) to the two interacting centres of each term, so to account for both the strength of the induced dipoles (the attraction) and the average atomic and molecular sizes (exchange–repulsion). See i.e. Refs. [17,34] and reference therein for a detailed account of the use of polarisabilities. As it has been mentioned above, in this case the H$_2$O molecule has a low value of polarisability and the quantities $\varepsilon_{M^+}$ ($M^+ = K^+,Na^+$) and $\varepsilon_{H_2O}$ have neither been decomposed as a sum of contributions nor displaced with respect to the ion and molecule positions, meaning that, besides K$^+$ and Na$^+$, also H$_2$O is considered in our model as single interaction centre placed coincident with the O atom and to which the total value of $\varepsilon_{H_2O}$ is assigned. It can be seen, in fact, that a model considering the presence of more interaction centres (i.e. bond and effective atom polarisabilities) predicts very similar structural and energetic properties of the ion–water interaction [35,36].

However the model could be improved taking into account, if needed, the anisotropy in water–water interaction by explicitly considering the water molecule bonds as interacting centres. This can be done by defining a set of angular degrees of freedom, explicitly appearing in the potential energy function after being expanded in terms of spherical and hyperspherical harmonic functions, following a well established approach to the intermolecular interactions (see e.g. [37–45]) where angular variables are used to build up collective coordinates.

The pairwise interaction contributions between centres placed on different molecules, are described by means of the improved Lennard Jones (ILJ) function $V_{ij}$ [46,47],

$$V_{ij} = \varepsilon \left[ \left( \frac{r_0}{r} \right)^{n_i} - \left( \frac{r_0}{r} \right)^{m_i} \right]$$

(2)

with

$$n_i = \beta + 4.0 \left( \frac{r}{r_0} \right)^2$$

(3)

The reliability of the ILJ function given above has been validated by reproduction of accurate scattering data experiments under high angular and energy resolution conditions [47]. Further reliability tests were performed by comparing calculated vibrational spacings with experimental values and calculated interaction energies at short-range with those obtained from the inversion of gaseous transport properties. The analysis, extended also to systems involving ions, suggests that the ILJ potential model can be used to estimate the behaviour of a variety of systems and can help to assess the different roles of the leading interaction components [48].

In Eq. (2), $r$ is the distance between the interaction centres and $\varepsilon$ and $r_0$ represent the interaction well depth and equilibrium distance, respectively. When effective atoms are considered, $\varepsilon$ and $r_0$ are directly obtained from basic physical properties of the interaction centres. In our case we have the K$^+-$H$_2$O, Na$^+-$H$_2$O and H$_2$O–H$_2$O pairs. The interaction centres are placed on the cation and on the oxygen atom of the water molecule and $\varepsilon$ and $r_0$ are calculated from the polarisability and charge of the potassium and sodium ions and the average polarisability of water [49].

The main advantage of using the ILJ function (Eq. (2)) is due to the presence of an additional parameter $\beta$, that corrects most of the inadequacies of the well known Buckingham (exp 6) and Lennard Jones (ILJ) models [46,50], for which alternative forms have yet been proposed [51]. These models, although satisfactorily reproducing the mid-range features of the potential well, fail in describing accurately both the short-range repulsion and the long-range attraction. Moreover, the introduction of the parameter $\beta$, allowing the portable use of the same values of $\varepsilon$ and $r_0$ for the same interaction centres in different environments, adds the necessary flexibility to the $V_{ij}$ function in comparison with the $V_{ij}$ one [52]. A wise use of $\beta$ (the only adjustable parameter in Eq. (2)), permits to incorporate some additional effects, for instance charge transfer, in an effective way [53]. The parameter $\varepsilon$ is set equal to 4 or 6 to describe ion–neutral and neutral–neutral interactions, respectively. The parameters $\varepsilon$, $r_0$, and $\beta$ adopted for K$^+-$H$_2$O, Na$^+$–H$_2$O and H$_2$O–H$_2$O interaction pairs are reported in Table 1.

The electrostatic interaction contributions contained in each term of Eq. (1) are calculated placing on any single water molecule a set of point charges, whose distribution reproduces the H$_2$O dipole and quadrapole moments, and applying to them the Coulomb law.

It is important to mention here that the dipole moment of the H$_2$O monomer has been again considered only as an effective model parameter, related to the true dipole moment of H$_2$O in the ionic aggregate but not necessarily coincident with it. The parameterization of the H$_2$O–H$_2$O non-electrostatic interaction contribution was performed from scaling

| $K^+$–(H$_2$O) | 102.10 | 3.161 | 7.0 |
| $Na^+$–(H$_2$O) | 151.89 | 2.732 | 6.0 |
| (H$_2$O)–(H$_2$O) rigid | 9.060 | 3.730 | 6.6 |
| (H$_2$O)–(H$_2$O) flexible | 9.060 | 3.730 | 7.5 |
laws [54] exploiting the overall molecular polarisability. The electrostatic charge distribution for the dimer was derived from its dipole moment, equal to 2.1 D [55]. The potential energy function allows obtaining second virial coefficients in excellent agreement with experimental results [56]. By using the same parameters of the potential and only increasing slightly the dipole moment of the monomer, radial distribution functions were calculated for both rigid and flexible ensembles. The energy, self diffusion coefficients, radial distribution functions and structural parameters calculated in the interval ranging from 278 K to 378 K were compared successfully with experimental results [36]. As a matter of fact, in our simulations the values 2.1 and 2.07 D (for Na\(^+\) and K\(^+\), respectively) have been used in order to best reproduce the information available from the literature [57–60]. To reproduce the dipole moment of the water molecules we placed charges of \(-0.74726\) a.u. and \(-0.7366\) a.u. on the O atom and of 0.37363 and 0.3683 a.u. on the H atoms for Na\(^+\) and K\(^+\) in solution, respectively. We have considered [61] the OH bond distances as equal to 1.00 Å and the HOH angle as equal to 105.47°.

The solvent water molecules in simulations have been considered both as rigid (i.e. frozen at their equilibrium geometry, see above) or flexible, freeing the OH stretching and the HOH bending modes, in order to assess the effects of the internal degrees of freedom. In the latter case, a harmonic potential function describes the dependence of the internal molecular potential energy on the atom displacements from the equilibrium positions, for each mode of vibration. In this case, the intramolecular potential functions for the flexible water are given for the bond and angle interactions by a harmonic potential.

3. Molecular dynamics details

The molecular dynamics simulations were performed by means of the DL_POLY [62] classical dynamics program. The simulated systems contain ions K\(^+\) or Na\(^+\) and a liquid water part made up by 253 water molecules in a pre-equilibrated elementary cubic box of 19.98 Å of side. The density of the system corresponds to that of the pure solvent at 300 K (997.11 kg/m\(^3\)). The cubic periodic boundary conditions were enforced, with spherical cutoff at 9.20 Å for short-range interactions. Ewald lattice sums were used to evaluate Coulomb interactions. The velocity Verlet integrator was employed in order to integrate the equations of motion. The system was equilibrated for 10 ps. After achieving equilibration, trajectories were further integrated for 3 ns using a time step of 0.001 ps short enough to ensure the conservation of the total energy within a relative fluctuation of 10^{-5}. All the simulations were done on a NVE ensemble, setting the conditions for average temperatures of 300 and 450 K for each simulation, by a kinetic energy scaling during the equilibration time. The total energy, \(E_{\text{tot}}\), is expressed as a sum of potential and kinetic energies. The first one, as it has been indicated before, is decomposed in non-electrostatic and electrostatic contributions and its mean value at the end of the trajectory is represented by the average configuration energy \(E_{\text{cfg}} = E_{\text{tot}} + E_{\text{el}}\), where \(E_{\text{tot}}\) and \(E_{\text{el}}\) represent the non-electrostatic and electrostatic contributions to the potential energy, respectively. At each \(i\)-th time step, the kinetic energy \(E_{\text{kin}}\), and the related instantaneous temperature, \(T_i\), can be calculated, while the corresponding simulation mean values (\(E_{\text{kin}}\) and \(T\), respectively) can be calculated at the end of each run.

Each batch of molecular dynamics simulations of ions in water was run twice, with flexible and rigid water molecules. This required different values of the parameter \(\beta\) (see previous section and Table 1) for the water–water interaction in the two cases. The values have been obtained by test simulations and theoretical calculations considered in previous works (see e.g. Ref. [63]). The choice of a second higher temperature value of 450 K is motivated by the opportunity of assessing the behaviour of our model with respect to temperature, also by comparison with previous calculations available in the literature (see e.g. [33]). Moreover overstructured water shells are obtained from ab initio molecular dynamics [33] and simulations nominally at room temperature may result in supercooled liquids. As a matter of fact, the current state-of-the-art of simulations gives to temperature a weaker physical meaning, so that, to some extent, \(T\) is to be considered nothing but an input parameter, which might not be consistent with real conditions.

4. Results

The present study, as it has been outlined above, focuses on structure and energetic of the solvated K\(^+\) and Na\(^+\) ions. To this aim we calculated the radial distribution function (RDF) and the corresponding running coordination number for the solvation of the two K\(^+\) and Na\(^+\) alkali ions in liquid water. Two kinds of simulations for each system and temperature were performed, one with water molecules frozen at their equilibrium configuration and the other with flexible water molecules with vibration modes modelled as harmonic oscillators. Results have been compared with data available in the literature.

4.1. The coordination number

Radial distribution function (RDF) is the collective name for pair, triplet or higher order radial functions. In this work we limit to the pair distribution function, denoted as \(g(r)\) meaning for RDF simply the probability of finding a pair of particles separated by a distance \(r\), relative to the probability expected in an ideal gas distribution of the same overall density. The RDF therefore contains information about the local structure of a fluid by describing how many particles (in this case water molecules) surround a particle \(M^+\) (see Eq. (4) below and a schematic representation given in Fig. 1). The RDF can be conveniently expressed as follows, in terms of the shell volume \(V\), the number of particles (coordination number) \(n_i(r)\) and the density \(\rho\):

\[
g(r) = \frac{n_i(r)}{\rhoV(r)}.
\]

Note that \(n_i(r)\) is the number of particles (water molecules) in the thin spherical shell between the distances \(r\) and \(r + dr\) from an \(M^+\) particle, while \(\rho\) is the number density of particles (total number of particles over total volume) and \(\rhoV(r)\) is the volume of the thin spherical shell.

![Fig. 1. Schematic representation of the ion \(M^+\) (dark purple) surrounded by six solvent water molecules (pink) in the inner sphere and four water molecules (blue) on the spherical shell.](image-url)
By integrating the radial distribution function, an estimate of the number of water molecules surrounding the M⁺ particle can be obtained (see Eq. (5) below). The coordination number is most often defined as the number of water molecules surrounding the M⁺ particle between 0 and the distance \( r_{min} \) where \( g(r) \) has its first minimum [64].

\[
\eta_c(r_{min}) = \int_0^{r_{min}} g(r) 4\pi r^2 dr
\]

(5)

### 4.1.1. Hydration structure

The RDFs are the primary theoretical tool for examining at a molecular level the structure of a liquid. The RDF describes the structure of the hydration shells around the ions in solution, since it contains information on the particle distribution on spherical shells. The maxima of the RDF represent the values of \( r \) with a high population of distances from the central ion and can be interpreted as major components of the average bond length for a given shell. Hydration shells can be identified by the positions of the minima of the RDF, that correspond to changes of the concavity of the \( \eta_c(r) \) function.

The M⁺−O and M⁺−H (M = K, Na) radial distribution functions (hereinafter denoted simply as M−O and M−H) and their corresponding coordination numbers as obtained from classical molecular dynamics are shown in Figs. 2 and 4 for the K⁺ ion and in Figs. 3 and 5 for the Na⁺ ion at 300 K (solid lines) and 450 K (dashed lines). The same results, as obtained from simulations with flexible water molecules, are also reported in these figures. The resulting maximum and minimum positions and the values of the coordination number obtained from \( \eta_c(r) \), along with some theoretical and experimental values available from the literature are summarized in Table 2 for simulations at \( T = 300 \) K.

First of all, we remark that the main qualitative difference, at first glance, between results obtained from rigid and flexible water is in the RDF first peak height, which is higher for rigid water at both temperatures and in the more structured RDF shape at distances larger than the first shell radius (more pronounced for K−O and Na−O RDFs in Figs. 2 and 3). The physical meaning of that is of a less structured first shell when water molecules are free to vibrate favouring relaxation (less molecules at equal distance), but an increase in the long range order when water molecules are free to vibrate favouring relaxation (less free degrees of freedom of water in causing more compact solvation shells). No appreciable difference is found in the second peak positions of the two K⁺ RDFs obtained using rigid and flexible water (see Table 2).

A number of experimental works are available that have determined the K⁺−O mean distance (estimated in simulations as the RDF first peak position). EXAFS [66] and LAXS [67] measure yield values of 2.71 and 2.81 Å respectively, in agreement with our value of 2.83 Å (see Table 2).

In general, only small differences are observed when comparing rigid and flexible water results for potassium. However, it can be seen that the flexible water model yields first peak positions for the K⁺−O and K⁺−H RDFs at slightly lower distances with differences of 0.04 and 0.06 Å respectively. This effect of the flexibility of water is indeed much more pronounced for the second peak position of the K⁺−O RDF, that we estimate from simulations, and that comes out to be at a distance 0.52 Å closer when flexibility is added, in good agreement with data from Ref. [65]. These discrepancies suggest a role of the internal degrees of freedom of water in causing more compact solvation shells. No appreciable difference is found in the second peak positions of the two K⁺ RDFs obtained using rigid and flexible water (see Table 2).

### Table 2

Maximum and minimum positions in Å and coordination number \( \eta_c(r_{min}) \) for the first and second hydration shell as obtained from classical molecular dynamics simulations of Na⁺ and K⁺ in aqueous solution at 300 K, compared to theoretical and experimental (“exp”) values from literature. “*” indicates flexible water. MD here stands for classical molecular dynamics, and MD-Carp stands for Car-Parrinello ab initio molecular dynamics.

<table>
<thead>
<tr>
<th>Ion−H₂O</th>
<th>( r_{max1} )</th>
<th>( r_{min1} )</th>
<th>( r_{max2} )</th>
<th>( r_{min2} )</th>
<th>( \eta_c(r_{min1}) )</th>
<th>Ref.</th>
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<td>5.35</td>
<td>6.86</td>
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<td>4.83</td>
<td>6.51</td>
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<tr>
<td>K−OH</td>
<td>2.70</td>
<td>3.45</td>
<td>7.1</td>
<td>6.0</td>
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<td>K−OH*</td>
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<td>3.65</td>
<td>4.99</td>
<td>5.88</td>
<td>7.9</td>
<td>MD [65]</td>
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Neutron diffraction techniques [68] give values of the neighbour K$^+$$-$$O$ and K$^+$$-$$H$ distances of 2.65 and 3.25 Å respectively, while our calculations yield in comparison the larger values of 2.83 and 3.37 Å respectively.

The K–O and K–H first shell coordination numbers, as obtained from the $n_i(r)$ function by statistical averaging over trajectories and listed in Table 2, are 6.51 and 21.33 respectively. The 6.51 value is in fairly good agreement with the experimental value of 6.0 ± 1.2 in Ref. [68] obtained from neutron diffraction, while the 21.33 value seems to be an overestimation of the corresponding experimental value of Ref. [68], 16.5 ± 2. Such a remarkable difference in the structure at larger distances from the central ion can be due to the different ion concentrations (three times larger in Ref. [68]) and to the absence of anions in our simulated system. Our ion concentration was kept low, to avoid possible complex effects due to near ions. X-ray measurements [67] suggest 7 as coordination number of sodium in liquid water.

On the other hand, the available theoretical results give values for the K–O and K–H first shell features (maximum and minimum positions) in agreement with our results (see Table 2). The substantial agreement extends also (with some exception) to the K–O and K–H RDF second peak positions. Less agreement is found by comparison with other theoretical values of the K–O coordination numbers, which are often much larger than our value of 6.5. The theoretical values for the K–H coordination number are in agreement with our overestimated value (compared to the neutron scattering data in Ref. [68]), with the remarkable exception of Ref. [69].

The Na–O and Na–H radial distribution functions corresponding to the two temperatures of 300 and 450 K are shown in Figs. 3 and 5 respectively, as obtained from simulations with rigid and flexible water molecules. The Na–O and Na–H RDF first peak positions obtained (2.42 and 3.07 Å respectively, see Table 2) are in substantially good agreement with the available experimental and theoretical data, also listed for comparison of Table 2. The effect of adding flexibility has no or little impact on the resulting Na–O and Na–H peak positions.

The Na–O and Na–H first shell coordination numbers (see Table 2), as obtained from the corresponding $n_i(r)$ functions by statistical averaging over trajectories are 5.72 and 16.07 respectively. The effect of adding flexibility to the water molecules is here more pronounced for the Na–O coordination number since the simulations with rigid water give the higher value of 6.39. Comparison with theoretical [70,65,69] and experimental [68,71,72] values indicates substantial agreement for the Na–O coordination number, while our value of 16.07 for the Na–H coordination number is still higher than any of those from the referenced works, somewhat confirming, also for sodium, a tendency of our model to give higher hydrogen atom numbers at larger distances from the central ion. Coordination numbers are likely to be sensitive, to a not negligible extent, to more subtle features of the ion–water and water–water interaction, whose effects, in turn, can also vary depending on the ion concentration. This remains for us an open question, also due to the fact that some experimental techniques might be less sensitive at larger distances. The value positions of the first minimum and second maximum of the Na–O and Na–H RDFs are instead in agreement with the corresponding values found in the literature (see Table 2).

The effect on the RDF of raising the temperature of our simulations to 450 K has been evaluated in order to assess the reliability of our interaction model towards a reasonable temperature behaviour. It can be seen from Figs. 2–5 that for both K$^+$ and Na$^+$ the RDF shows at the higher temperature a lower first peak (for both flexible and rigid water), reminding the rigid/flexible effect abovementioned, but a less structured profile of the long distance tail ($r > r_{cut}$) correctly accounting for less structured liquid and shells at 450 K. For comparison to previous calculations at 450 K, we observe here that the first peak of the K–O RDF is centred at 2.82 and 2.87 Å for flexible and rigid water respectively, in good agreement with the value of 2.86 Å obtained by Liu et al. [33]. The K–O coordination number is 6.20 Å consistent with the value of 6.53 Å of Ref. [33].

5. Conclusions

We have investigated the properties of the solvation shells of Na$^+$ and K$^+$ ions by classical MD simulations at two different temperatures by using a semiempirical intermolecular potential energy surface based on the LJ pair interaction function. The underlying interaction model is targeted to an accurate description of the weak interactions, whose reliability has been validated here by comparison of our results with those available in the literature from theory and experiments. In doing that, we have assessed the effect of the water internal degrees of freedom in contributing to the overall relaxation and in favouring a more effective action of the ions in the long range. This can be understood in terms of an increase in the dipole moment of water, a fact that might suggest a larger value of the water dipole moment for simulations. In comparison with the majority of the results available in the literature our model depicts a situation in which the alkali ions have a major effect in altering the water structure beyond the first shell. A further valuable aspect of our approach is the relatively low computational cost to be contrasted with a higher accuracy with respect to the commonly used standard force-fields. Perspectives regard the application to extensive studies of ions and molecules in water.

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