A Lennard-Jones plus Coulomb potential for Al \(^{3+}\) ions in aqueous solutions
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I. INTRODUCTION

The aluminum ion plays a very important role in many chemical and industrial processes, including alumina-based sol-gel synthesis and hydrolysis, and is used in large quantities as flocculants in water treatment plants all over the globe.\(^1,2\) The aluminum ion (\( \text{Al}^{3+} \)) is also known to be toxic for many living organisms\(^3-6\) and has long been implicated in the development of Alzheimer’s disease\(^7-12\) and dyslexia\(^13,14\) in humans. The mechanisms by which \( \text{Al}^{3+} \) may trigger Alzheimer’s disease are not fully understood. One possible mechanism involves the aluminum induced aggregation and fibrillogenesis of \( \beta \)-amyloid proteins which has been observed even at small, micromolar concentrations.\(^15\)

Like other highly charged metal ions, \( \text{Al}^{3+} \) strongly polarizes its surrounding medium, leading to highly structured solvation shells in solution and structural and conformational changes in proteins. The hydration shell of \( \text{Al}^{3+} \) seems to be ordered well beyond the first coordination layer. X-ray and neutron scattering data indicate that the first hydration shell comprises of 6 water molecules octahedrally arranged in \( T_e \) symmetry.\(^16,17\) There is also experimental\(^17\) and theoretical\(^18\) evidence that each water molecule in the first hydration shell hydrogen (\( H \))-bonds to two other molecules in a trigonal structure, thus forming a second hydration shell comprised of 12 water molecules on average. The estimated characteristic exchange time of water molecules between the first and second hydration shells is quite long, of the order of seconds, indicating that the first hydration layer of \( \text{Al}^{3+} \) is very stable.\(^19,20\)

The structural and dynamical properties of \( \text{Al}^{3+} \) aqueous solutions have been investigated by means of quantum chemical calculations,\(^21-25\) \( \text{ab initio} \) Car–Parrinello\(^26,27\) and mixed quantum classical molecular dynamics (MD),\(^28-30\) and purely classical MD simulations.\(^21-23,31\) Overall, first principles quantum chemical calculations performed on [\( \text{Al(H}_2\text{O})_6 \)]\(^{3+} \) clusters and quantum MD simulations of \( \text{Al}^{3+} \) aqueous solutions reproduce very well the available experimental data, including the structure of the hydration shells, solution thermodynamics, and spectroscopic properties.\(^29\) MD simulations using effective classical interaction potentials have also been able to account for several physicochemical properties. However, in this case, ion-solvent potentials considerably more complex than those usually employed in simulations of mono- or divalent cations have been used in order to account for the behavior of highly charged ions such as \( \text{Al}^{3+} \) in aqueous solutions. The most successful empirical interaction potentials for \( \text{Al}^{3+} \)-water solutions proposed so far represent the octahedral complex [\( \text{Al(H}_2\text{O})_6 \)]\(^{3+} \) as a supramolecular entity with an explicit intramolecular potential\(^22,23\) or use a combination of two- and three-body potentials.\(^22,23,31\) Nonadditive polarizable models have also been developed with less success.\(^22\)

One common feature of these potential models is that they all have been derived by fitting the ion-water potential energy landscape from \( \text{ab initio} \) cluster calculations. In spite of the ability of some of these models in describing the behavior of \( \text{Al}^{3+} \) aqueous solutions, their functional forms dif-
fer from those commonly used in computer simulations of biomolecular systems, such as peptides, proteins, and nucleic acids, for instance. Therefore, it is highly desirable to devise simpler potential models that could be readily used in molecular simulations of $\text{Al}^{3+}$ in biologically oriented contexts. Evidently, such a model should, first of all, describe the behavior of $\text{Al}^{3+}$ in aqueous environments.

Motivated by the need of a simpler pair-additive effective potential for $\text{Al}^{3+}$ that would capture reasonably well the properties of the hydrated ion and, at the same time, have the same functional form of most force fields for biomolecular systems, we have developed a simple Lenard-Jones (LJ) plus Coulomb potential for $\text{Al}^{3+}$ which accounts very well for the behavior of aluminum aqueous solutions. The model, with point charge equal to $+3$, was obtained by adjusting the values of the LJ distance ($\sigma$) and energy ($\epsilon$) parameters targeting the experimental ion-water radial distribution function (RDF). The proposed model yields hydration structures, enthalpy of hydration, single-particle translational, and reorientational dynamics, and, to less extent, vibrational spectral features, which are in very good agreement with available experimental data and MD simulations using more complex many-body classical potentials, as well as mixed quantum classical quantum mechanics/molecular mechanics (QM/MM) simulations and Car–Parrinello MD (CPMD) using B3LYP and Perdew-Burke-Ernzerhof (PBE) density functionals. Very recently, however, it has been shown that CPMD based on either functionals is unable to provide a reliable molecular picture of water at ambient conditions.

It seems that B3LYP/PBE-based CPMD simulations carried out at room temperatures yield an overstructured liquid that actually resembles supercooled water. Therefore, similar effects of the hydration structure of $\text{Al}^{3+}$ obtained from such calculations cannot be ruled out.

**II. POTENTIAL AND SIMULATION DETAILS**

The $\text{Al}^{3+}$ ion is represented here by an effective LJ plus Coulomb potential. Ion-water and water-water interactions are described by a set of radial site-site pair potentials given by

$$V_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r^2},$$

where $r$ is the distance between site $i$ on one particle and site $j$ on another particle (water molecule or ion), $\sigma_{ij}$ and $\sigma_{ij}$ are the energy and distance LJ parameters, and $q_i$ the partial charge associated with site $i$. The aluminum partial charge was fixed at $q_{\text{Al}} = +3e$, whereas the LJ parameters where systematically varied such as to best reproduce simultaneously the positions of the first and second peaks of the experimental ion-water oxygen RDF. The simple point charge/extended (SPC/E) model for water was used in these simulations, with geometric and arithmetic combination rules for energy and distance parameters, respectively, for the cross-interaction between sites of different types. Our best parameters are shown in Table I.

<table>
<thead>
<tr>
<th>$\epsilon$ (kcal/mol)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2166</td>
<td>1.4472</td>
<td>+3</td>
</tr>
</tbody>
</table>

The classical MD simulations carried out for adjusting the aluminum ion potential and subsequent evaluation of the solution’s physicochemical properties with our best set of parameters were performed with DL_POLY (Ref. 38) on a system comprised of a single $\text{Al}^{3+}$ cation and 500 water molecules in a cubic box with periodic boundary conditions at 1 g/cm$^3$ density in the $NVE$ ensemble. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 2 fs. More than 50 independent, fully equilibrated, 150 ps simulations were performed in the $NVE$ ensemble for analysis using our final potential (Table I). A few $NpT$ runs were performed to estimate volume changes upon solvation of the cation. The LJ interactions were cutoff at half the box length, whereas the electrostatic forces were treated by the particle mesh Ewald sum method, assuming a neutralizing background. We have also run additional simulations with our final model using separately 3 $\text{Cl}^-$ and 3 $\text{NO}_3^-$ as counterions, using available potentials, as well as the TIP3P (Ref. 42) and SPC (Ref. 43) water models. With these simulations we have verified that the overall structure of the hydration shells was preserved under similar thermodynamic conditions.

**III. RESULTS AND DISCUSSION**

**A. Hydration structures**

The ion-water RDFs obtained from the simulations are shown in Fig. 1, along with results of classical MD simulations from the supramolecular model of Wasserman et al. and CPMD simulations reported by Bylaska et al. The first and second peaks of our RDF, located at 1.86 and 3.90 Å, respectively, appear at slightly shorter distances than the experimental $\text{Al}–\text{O}$ RDF, which are located in the ranges of 1.87–1.90 and 3.98–4.15 Å. This suggests that our model yields somewhat compressed hydration layers. Nevertheless, the position and shape of the second peak of the $\text{Al}–\text{O}$ RDF of our $\text{Al}^{3+}$ model in SPC/E water are in better agreement with the more sophisticated CPMD (Ref. 18) or
TABLE II. Structural parameters of the Al\textsuperscript{3+} hydration shells. Distances are in angstrom and angles in degrees.

<table>
<thead>
<tr>
<th>Source</th>
<th>$R_{\text{Al-OI}}$</th>
<th>$R_{\text{Al-OII}}$</th>
<th>$R_{\text{Al-H}}$</th>
<th>$N_I$</th>
<th>$N_{II}$</th>
<th>$\theta_{\text{O(OI)}}$</th>
<th>$\theta_{\text{O(OII)}}$</th>
<th>$\theta_{\text{Al-OI}}$</th>
<th>$\theta_{\text{Al-OII}}$</th>
<th>$\theta_{\text{Al-H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>1.86</td>
<td>3.90</td>
<td>2.56</td>
<td>4.53</td>
<td>2.63</td>
<td>6</td>
<td>12.3</td>
<td>12.8</td>
<td>24.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Wasserman et al.</td>
<td>1.88</td>
<td>3.83</td>
<td>2.47</td>
<td>4.50</td>
<td>6</td>
<td>28.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Martinez et al.</td>
<td>1.91</td>
<td>4.00</td>
<td>2.60</td>
<td>4.62</td>
<td>2.57</td>
<td>6</td>
<td>14</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bylaska et al.</td>
<td>64 H\textsubscript{2}O, 400 K</td>
<td>1.94</td>
<td>4.09</td>
<td>2.68</td>
<td>6</td>
<td>11–12</td>
<td>27.8</td>
<td>24.0</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>64 H\textsubscript{2}O, 300 K</td>
<td>1.94</td>
<td>4.12</td>
<td>2.68</td>
<td>6</td>
<td>11–12</td>
<td>25.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>128 H\textsubscript{2}O, 300 K</td>
<td>1.93</td>
<td>4.08</td>
<td>2.66</td>
<td>6</td>
<td>12</td>
<td>29.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spangberg et al.</td>
<td>P2</td>
<td>2.07, 2.95</td>
<td>3.70</td>
<td>2.51</td>
<td>2.69</td>
<td>8–10</td>
<td>64.9</td>
<td>67.6</td>
<td>63.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E2(6)</td>
<td>1.86</td>
<td>3.55</td>
<td>2.53</td>
<td>2.64</td>
<td>6</td>
<td>14.6–18.0</td>
<td>25.4</td>
<td>23.2</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>E3</td>
<td>1.90</td>
<td>3.79</td>
<td>2.59</td>
<td>2.66</td>
<td>6</td>
<td>13.6–18.1</td>
<td>17.2</td>
<td>20.7</td>
<td>14.9</td>
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<td></td>
<td>EPOL</td>
<td>1.89</td>
<td>3.92</td>
<td>2.59</td>
<td>2.54</td>
<td>6</td>
<td>18.7–23.9</td>
<td>12.1</td>
<td>15.7</td>
<td>10.2</td>
</tr>
<tr>
<td>Lauenstein et al.</td>
<td>2-body potential</td>
<td>1.89</td>
<td>3.91, 4.45</td>
<td>2.70</td>
<td>4.53, 5.02</td>
<td>2.74</td>
<td>9</td>
<td>18°</td>
<td>0°</td>
<td></td>
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<tr>
<td></td>
<td>(2+3)-body potential</td>
<td>1.97</td>
<td>4.25, 4.48</td>
<td>2.80</td>
<td>4.93, 5.04</td>
<td>2.76</td>
<td>6</td>
<td>20°</td>
<td>0°</td>
<td></td>
</tr>
<tr>
<td>Hofer et al.</td>
<td>Classical MD</td>
<td>1.9</td>
<td>4.2, 4.5</td>
<td>2.75</td>
<td>4.2, 4.95</td>
<td>6</td>
<td>16.8</td>
<td>10°</td>
<td>0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 shell QM/MM</td>
<td>1.9</td>
<td>4.2</td>
<td>2.6</td>
<td>4.05, 4.8</td>
<td>6</td>
<td>13.8</td>
<td>11°</td>
<td>0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 shell QM/MM</td>
<td>1.8</td>
<td>4.1</td>
<td>2.55</td>
<td>4.7</td>
<td>6</td>
<td>12.2</td>
<td>19°</td>
<td>9°</td>
<td></td>
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<tr>
<td>Exp.\textsuperscript{1}</td>
<td></td>
<td>1.87–1.90</td>
<td>3.98–4.15</td>
<td>2.61</td>
<td>2.68–2.73</td>
<td>6</td>
<td>12–14</td>
<td></td>
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</tr>
</tbody>
</table>

\textsuperscript{1}Reference 23.
\textsuperscript{2}Reference 21.
\textsuperscript{3}Reference 18.
\textsuperscript{4}Average values estimated from digitized reported data.
\textsuperscript{5}Reference 22.
\textsuperscript{6}Reference 31.
\textsuperscript{7}Reference 28.
\textsuperscript{8}References 16, 17, and 44.

QM/MM simulations\textsuperscript{28} than the available effective classical potentials. In the scanning of the cation’s $\sigma$ and $\epsilon$ parameters, we noticed that the first peak position could be somewhat improved by adopting larger $\sigma$ values. However, other properties, such as the vibrational spectrum of the hydrated complex, resulted quite unsatisfactory.

The computed coordination numbers reveal that the aluminum ion is coordinated by 6 water molecules in the first hydration shell and by an average of 12 water molecules in the second hydration layer alone. The zero intensity gaps between the first and second peaks of the ion-water RDFs indicate absence of water molecules exchange between the first coordination shell and the bulk, suggesting the formation of a stable [Al(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3+} complex during the course of the simulations. Several structural parameters obtained from our simulations are shown in Table II. Results from other works are also shown for comparison.

A representative simulation snapshot of the hydrated Al\textsuperscript{3+} complex in solution is depicted in Fig. 2 showing an octahedral coordination of the first hydration layer around the ion [Fig. 2(a)] and a second shell composed of 12 water molecules trigonally coordinated to the inner layer through hydrogen bonding [Fig. 2(b)]. The results shown in Fig. 2 and Table II are strikingly consistent with the experimental x-ray diffraction\textsuperscript{16,17,44} and CPMD (Ref. 18) or QM/MM (Ref. 28) structures. Only a few other classical effective potential for Al\textsuperscript{3+} available in the literature capture such structural features. Previous MD simulations using different potentials usually fail to predict a trigonal second hydration shell. Three exceptions are the supramolecular models of Martinez et al.\textsuperscript{21} and Wasserman et al.\textsuperscript{23} and the effective three-body ion-water E3 potential of Spångberg and Hermansson,\textsuperscript{22} which yield slightly compressed trigonally coordinated second shells in comparison to experiments and may contain a few extra water molecules. The present potential performs somewhat better in this respect, with the additional advantage of being functionally much simpler.

In order to characterize more quantitatively the hydration structure, we have computed several properties as follows. Figure 3(a) depicts the ensemble distribution of the O–Al–O angles computed from the simulations. The distribution is sharply peaked at $-1^\circ$ and $0^\circ$ and vanishingly small between the peaks, indicating that there are only two relative dispositions for each pair of oxygen atoms in the immediate vicinity of the cation: diametrically opposed ($180^\circ$) and perpendicular ($90^\circ$) arrangements. Integrating the peaks yields that these configurations appear at a $1:4$ ratio, characteristic of an octahedral structure. The distribution of O–AI–O angles obtained from our pair potential is sharper than that obtained from mixed quantum classical QM/MM.
simulations, suggesting, not surprisingly, that incorporation of quantum forces tend to yield softer hydration structures. Figure 3(b) depicts the distribution of the relative orientation between the planes of a pair of water molecules in the first hydration shell of the cation, computed separately for pairs with O–Al–O angles around 180° (solid line) and 90° (dashed line). Both distributions are broad and span the entire range with appreciable intensities, indicating that water molecules within the first hydration shell can rotate about the Al–O axes. Diametrically opposed water molecules tend to align their molecular planes somewhat more parallel (half of them has relative orientation between molecular planes of at most 40°), whereas water molecules perpendicularly arranged (O–Al–O ~ 90°), prefer larger relative orientation (nearly half of them are at angles larger than 69°). Figures 3(c) and 3(d) show the RDFs between first shell oxygen pairs (O1–O1) and hydrogen pairs (H1–H1). The \( g_{\text{O1-O1}} \) function is sharply peaked at 2.62 and 3.72 Å with zero intensity outside the vicinity of the peaks, indicating the stability of the octahedral configuration. The coordination numbers associated with each \( g_{\text{O1-O1}} \) peak have a 1:4 ratio, as expected for octahedrons. The \( g_{\text{H1-H1}} \) function, in contrast, exhibits three well-defined, but broader, peaks centered at 2.9, 4.1, and 5.0 Å.

The broadening stems from the allowed rotational motions of the water molecules around the Al–O axes. The first two peaks correspond to water pairs at \( \angle \text{O-Al-O} \sim 90° \), whereas the 5.0 Å peak correspond to water molecules diametrically opposed. Consistently, the average coordination numbers associated with these peaks turn out approximately 4.0, 4.0, and 2.0, respectively.

In addition, we have computed the tilt of the water molecules in the first hydration shell with respect to the Al–O axis using four different definitions for the tilt angles \( \theta \). Namely, \( \theta_{\text{dip}} \) defined according to a geometrical criterion and the average structure of the first solvation shell:

\[
\theta_{\text{dip}} = \arccos \left( \frac{R_{\text{Al-H}}^2 - R_{\text{Al-O}}^2}{2R_{\text{Al-O}}R_{\text{O-H}}} \right),
\]

with \( R_{\text{Al-H}} \) and \( R_{\text{Al-O}} \) the average Al–H and Al–O distances in the first hydration shell, respectively (see Table II), and \( R_{\text{O-H}} \) and \( \varphi \) the bond length and angle of a water molecule; \( \theta_{\text{dip}} \) defined as the average angle between the Al–O axis and the water dipole moment; \( \theta_{\text{sheet}} \) defined as the average angle between the Al–O axis and the water molecular plane, and the Spångberg and Hermansson’s \( \theta_{\text{sheet}} \).

\[ O' = \text{O} - \left( \frac{\text{H1} + \text{HII}}{2} \right), \]

\[ H1' = \text{H1} - \left( \frac{\text{H1} + \text{HII}}{2} \right), \]

\[ H2' = \text{H2} - \left( \frac{\text{H1} + \text{HII}}{2} \right). \]

The computed tilt angles are listed in Table II, along with the results from other works, which vary from one simulation to the other. Our results for the tilt angle agree best with the MD simulations using the E3 potential. Good agreement is found with the results from CPMD (Ref. 18) for \( \theta_{\text{dip}} \) but less so for the other tilt definitions. Remarkably, our average values for \( \theta_{\text{dip}} = 24.3° \) and \( \theta_{\text{sheet}} = 10.4° \) are in very good agreement with results from QM/MM MD simulations by Hofer et al., who report average values of approximately 19° and 9° for these angles from two-shell calculations.

The RDFs between the water molecules directly coordinated to the Al\(^{3+} \) cation and those external to the first hydration layer (Fig. 4) yield structural parameters of the second solvation shell. The first peaks in the \( g_{\text{O1-O}} \) and \( g_{\text{H1-H}} \) functions, respectively, located at 2.63 and 1.68 Å, are character...
B. Enthalpy of hydration

A rough estimate for the hydration enthalpy of Al$^{3+}$ was obtained from the difference between the total energy of the solution and the pure solvent from a series of NVT simulations combined with the gas phase enthalpy of the ion (the neutralizing background assumed in the Ewald sums contributes approximately $-2.6$ kcal/mol):\(^{47}\)

$$\Delta_{\text{hyd}}H = U_{\text{Al}^{3+}(\text{aq})} - U_{\text{water}} - 5/2RT - 2.6$$

$$= -1009 \text{ kcal/mol}.$$  

The simulated $\Delta_{\text{hyd}}H$ misses by some 10% the experimental solvation enthalpy of the cation, estimated between $-1115$ and $-1140$ kcal/mol.\(^{48,49}\) The average molar volume of neat SPC/E water at 298 K and 1 atm reduces from 78.01 to 17.90 cm$^3$/mol for the simulated solution (1 Al$^{3+}$ in 500 water molecules) under the same temperature and pressure conditions.

C. Single particle dynamics

Single particle translational and reorientational dynamics of the [Al(H$_2$O)$_{6}$]$^{3+}$ complex in solution were analyzed by computing its self-diffusion coefficient using the Stokes–Einstein relation

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle$$

and the time correlation functions for the reorientation of the complex Al–O1 unit vector $\hat{u}$:

$$C_\ell(t) = \langle P_\ell(\hat{u}(0) \cdot \hat{u}(0)) \rangle,$$

with $P_\ell[x]$ the Legendre polynomial of rank $\ell$. The mean squared displacements of the ion and waters of the first hydration shell were computed from for times up to 150 ps and averaged over 50 of such runs. The cation and first coordinated water self-diffusion coefficients turned out identical averaged over 50 of such runs. The cation and first coordination shell of the cation, defined by the molecular dipole moment $\mu$,\(^{50,52}\) is roughly one order of magnitude larger than that of a water molecule in the neat liquid (4.5–5.5 ps and 0.53–0.72),\(^{50,52}\) respectively. The later is in excellent agreement with NMR experiments,\(^{51}\) which give $\tau_2 \sim 44–53$ ps. The ratio between the $\ell = 1$ and $\ell = 2$ reorientational times, $\tau_1/\tau_2 \sim 3$, indicates an overall isotropic rotational-diffusion motion of the hydrated complex. We have also computed $C_1(t)$ and $C_2(t)$ functions for three unit vectors fixed on the center of masses of the water molecules in first coordination shell of the cation, defined by the molecular dipole moment ($y$ direction), normal to the molecular plane ($z$), and along the H–H direction ($x$). The reorientational times (Table III) are roughly one order of magnitude larger than those of a water molecule in the neat liquid ($\tau_1 = 2.6–3.7$ ps and $\tau_2 = 1.6–2.0$ ps for SPC/E water),\(^{46}\) indicating restricted rotational motions of the solvent in the vicinity of Al$^{3+}$. Moreover, $\tau_1^2$ and $\tau_2^2$ are several times larger than $\tau_1^2$ and $\tau_2^2$, which indicate that the rotational motions of the individual first shell water molecules are highly anisotropic, with rotations about the molecular bisector being significantly more facile, as expected for this hydration shell structure.
At short times, the $C_1(t)$ and $C_2(t)$ functions show fast oscillations that arise from the structural fluctuations (internal deformations) of the [Al(H$_2$O)$_6$]$^{3+}$ complex and its hindered reorientational motions (librations) due to the H-bonding restoring forces between the complex and the outer aqueous environment. The characteristics of these motions are better seen from the cosine Fourier transform of $C_1(t)$, depicted in Fig. 6, which would be grossly related to the far-infrared absorption spectrum. The spectrum exhibits an intense peak at $\sim 460$ cm$^{-1}$ accompanied three secondary bands located at $\sim 100$, 360, and 700 cm$^{-1}$. The lowest frequency band is attributed to the librational motions of the entire complex, whereas the bands at 360, 460, and 700 cm$^{-1}$ are associated with the internal modes of [Al(H$_2$O)$_6$]$^{3+}$. Since the complex is not a rigid molecular species, say, with a fairly fixed unit vector $\hat{u}$ in the body-fixed frame, it is more convenient to describe its internal motions in terms of vibrational spectra.

![FIG. 5. Single-molecule $C_1(t)$ and $C_2(t)$ time correlation functions for the Al–Oi unit vectors. Mid- and lower panels show the characteristic librational oscillations in the short-time regime.](image1)

![FIG. 6. $\omega^2$ times the cosine Fourier transform of the first order Al–Oi vector time-correlation function.](image2)

**D. Vibrational spectra**

The internal vibrations of the [Al(H$_2$O)$_6$]$^{3+}$ complex can be analyzed by means of the Fourier transforms of several different time correlation functions. We first analyze the Al$^{3+}$ normalized velocity autocorrelation function (VACF) and the vibrational density of states (DOS), shown in Fig. 7. The VACF exhibits intense fast oscillations up to $\sim 0.5$ ps, suggesting rapid vibrational motions of the cation inside its solvent cage. The characteristic frequencies of these motions appear as well-defined intensities in the DOS at 50, 460, 700, and 1120 cm$^{-1}$. The broad frequency span at which well-defined spectral features appear suggests the complexity of motions of the aluminum cation in the highly organized solvent surroundings. High frequency components (1120 cm$^{-1}$), in particular, are clear manifestations of the effects of the solvent H-bond librations upon the motions of Al$^{3+}$. Interestingly, this band peaks at considerably larger frequencies than the typical librational band of SPC/E water (600–800 cm$^{-1}$). The reason lies in the much shorter (i.e., stiffer) H-bonding between the first and second hydration shell waters in comparison to the neat liquid, as already discussed. The lowest frequency band at 50 cm$^{-1}$, on the other hand, is likely associated with the librational motions of the entire [Al(H$_2$O)$_6$]$^{3+}$ complex. The bands at 460 and 700 cm$^{-1}$ are due to O–Al–O angle bending and totally symmetric (A$_{1g}$) Al–O stretching mode, respectively, as we show next. Using a model devised to treat the [Al(H$_2$O)$_6$]$^{3+}$ complex as a supramolecular species, Martínez et al. report these two bands near 400 and 550 cm$^{-1}$, in good agreement with experimental bending ($E_g$) and symmetric stretching (A$_{1g}$) modes at 438 and 525 cm$^{-1}$, respectively. Our model overestimates the bending mode frequency by $\sim 5\%$ and significantly overestimates the stretching. In this respect, the model of Martinez et al. captures the experimental symmetric stretching (525 cm$^{-1}$) much better than our simple potential and even multibody potentials derived on the basis of ab initio quantum potential energy surface calculations. The supramolecular model, however, fails to capture the low intensity, high frequency mode due to water librations.

In order to characterize the molecular motions underlying the cation VACF spectrum, we have computed the spectra of time correlation functions of dynamical variables that take into account Al–O stretching and O–Al–O angle bending motions, given by:
shows a main band centered at essentially to O–Al–O bending motions. The main bending that vibrational DOS in this frequency region corresponds 

\[ TCF_R(t) = \langle (R(t) - \bar{R})(R(0) - \bar{R}) \rangle \]

and

\[ TCF_\theta(t) = \langle (\cos \theta(t) - \cos \theta)(\cos \theta(0) - \cos \theta) \rangle \]

with \( R(t) \) and \( \bar{R} \) the instantaneous and average scalar distance between the ion and the oxygen atom of a first coordination shell water molecule, respectively, and \( \theta \) the O–Al–O angle. The Fourier transform of the normalized \( TCF_\theta \) (Fig. 8) shows a main band centered at \(~460\) \( \text{cm}^{-1} \), demonstrating that vibrational DOS in this frequency region corresponds essentially to O–Al–O bending motions. The main bending frequency is in good agreement with the experimental \( E_g \) mode at 435 \( \text{cm}^{-1} \). The \( TCF_\theta \) spectrum exhibits secondary shoulders around 330 and 700 \( \text{cm}^{-1} \) and a small hump in the 1120 \( \text{cm}^{-1} \) librational region. The \( TCF_R \) spectrum, in turn, exhibits well-resolved peaks around 490 and 700 \( \text{cm}^{-1} \). The former is attributed to the relative motions between the cation and coordination waters involved in bending of the O–Al–O distance and, therefore, appears in \( TCF_R \) as well. The 700 \( \text{cm}^{-1} \) is due to the symmetric Al–O stretching, as shown next.

The assignment of the 700 and 1120 \( \text{cm}^{-1} \) vibrational bands of the cation can be made by examining the spectrum of the VACF for the oxygen atoms in the first coordination shell, shown in Fig. 9, and by a series of VACF auxiliary spectra which were obtained by changing the masses of cation and of the first shell water molecules and hydrogen atoms (Fig. 10). Figure 9 shows that overall structure of the cation vibrational DOS is retained by the velocity spectrum of the first shell waters. Most noticeably, the existence of a low \(<100 \text{ cm}^{-1}\) frequency band, followed by peaks at \(~460\) and 700 \( \text{cm}^{-1} \). The high frequency band in the 1120 \( \text{cm}^{-1} \) region can also be clearly seen in the vicinal water spectrum. Less prominent intensities appear around 330 and 930 \( \text{cm}^{-1} \), which are hardly apparent in the vibrational spectrum of the cation, suggesting the existence of water motions that are only very mildly impacting on aluminum’s vibrational modes. The auxiliary spectra depicted in Fig. 10 were computed from simulations in which the mass of the cation was doubled (red solid line), the masses of the vicinal waters were doubled (dashed blue line), and the masses of only the hydrogen atoms of these molecules were doubled (green). The \(~460\) \( \text{cm}^{-1} \) band is redshifted in all auxiliary spectra, indicating that it depends on the motions of the cation and vicinal water as well, consistent with the O–Al–O bending assignment. The \(~700 \text{ cm}^{-1} \) band, in contrast, remained essentially unshifted when the cation mass is altered, but is strongly redshifted upon doubling the water masses, suggesting a vibrational mode in which the Al\(^{3+}\) is essentially static, that is, the totally symmetric A\(_{1g}\) stretching mode. The highest frequency vibrational band is also strongly redshifted to the 800–900 \( \text{cm}^{-1} \) region upon doubling the masses of the first coordination water molecules or hydrogen atoms, which traces back its origin to the librational motions of these water molecules.

**IV. CONCLUDING REMARKS**

We propose a simple LJ plus Coulomb empirical potential suitable for molecular simulations of the trivalent Al\(^{3+}\) cation in aqueous solutions. With a fixed charge of +3\(e\), the LJ distance and energy parameters were systematically varied, targeting the first and second peak positions of the experimental aluminum-water oxygen RDF, using recursively MD simulations. The model is capable of reproducing the octahedral and trigonal structures of the first and second hydration shells, containing 6 and 12 water molecules, respectively, which has only been captured by quantum mechanical MD techniques such as CPMD and QM/MM simulations and a few much more elaborated two- and three-body classical effective potentials. Although parameterized for SPC/E water in the absence of counterions, the proposed potential works...
well with TIP3P and SPC models, and in the presence of chlorine or nitrate anions. The model yields hydration enthalpy which is only 10% below the experimental value. The self-diffusion coefficient and the second rank single-particle reorientational time of the hydrated complex are in excellent agreement with experimental estimates. The vibrational spectrum of the cation in solution is very rich and shows how the aluminum motions are strongly determined by the highly structured and electrostricted solvent shells around it. The simulations capture the essential spectral features, although the frequency of the Al–O symmetric stretching mode is significantly overestimated. Given the simplicity of its functional form, we think the proposed model will be very useful for simulating Al\(^{3+}\) ions in aqueous environments and in biomolecular systems such as proteins and nucleic acids.

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47. P. H. Hünenberger and J. A. McCammon, *J. Chem. Phys.* 110, 1856 (1999); See also Ref. 22.