Ab initio molecular dynamics simulations of Aluminum solvation

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Abstract

The solvation of Al\textsuperscript{3+} and its hydrolyzed species in water clusters has been studied by means of \textit{ab initio} molecular dynamics simulations. The hexa-hydrate Al(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+} ion formed a stable complex in the finite temperature cluster simulation of one aluminum ion and 16 waters. The average dipole moment of strongly polarized hydrated water molecules in the first solvation shell of Al(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+} was found to be 5.02 Debye. The deprotonated Al(H\textsubscript{2}O)\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{−} complex evolves into a tetra-coordinated Al(OH)\textsubscript{4}\textsuperscript{−} aluminate ion with two water molecules in the second solvation shell forming hydrogen bonds to the hydroxyl groups in agreement with the observed coordination. At high temperature and for low water coordination protons in the first solvation shell are very mobile leading to the formation of hydrolysis species consistent with the acidity of Al\textsuperscript{3+} in water.

1 Motivation

The aqueous chemistry of aluminum, the most abundant metal in the earth’s crust, remains a subject of fundamental research after many years of intensive research\cite{1}. Due to the increased acidity of many natural waters and the corresponding increase in solubility of aluminum containing minerals, environmental and health issues have further focus attention on the solution behavior of this toxic material \cite{2,3}. In addition aluminum hydrolysis products have many practical applications, ranging from the pharmaceutical design to purification of water\cite{1}.

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The aluminum ion, Al$^{3+}$, exists as an octahedral (6-fold coordinated) hexahydrate ion, Al(H$_2$O)$_6^{3+}$ in acidic solutions [4]. Over a narrow pH range, 5.5 ≤ pH ≤ 6.2, the hexahydrate undergoes hydrolysis by four successive deprotonations, producing species with uniformly decreasing coordination numbers [5]. The final product of the hydrolysis process, the aluminate ion, Al(OH)$_4^-$, is tetrahedrally (4-fold) coordinated [5]. The coordination behavior of ions in solution is a sensitive function of the properties of the ions and the solvating molecules and varies widely from species to species. For example, the hydrolyzed aqueous ferric ion, Fe$^{3+}$, remains six-coordinated after four deprotonations [5]. The change in coordination of Al(H$_2$O)$_2$(OH)$_4^-$ from octahedral to tetrahedral form occurs to accommodate changes in ligands charges and polarizations [5]. Because of the small relative size of the Al$^{3+}$ ion, this change in coordination both strongly polarizes the OH bond of water ligands and stabilizes the formation of OH$^-$ . Both these effects should increase acidity constant of Al$^{3+}$ in water solutions, which is about $10^{-5}$ at room temperature [6]. However, the microscopic description of these processes, especially the mechanisms of hydrolysis, remains incomplete.

We will show in this Letter using *ab initio* molecular dynamics (AIMD) [7] that this strong coordination interaction results in highly inhomogeneous electron charge distribution in the first solvation shell of solvating water molecules. D. Marx *et al.* have successfully applied a similar method to the studies of the structural and dynamical properties of bivalent aqueous Be$^{2+}$ ion [8]. However, there have been a number of efforts to simulate highly charged ions in solution using traditional molecular dynamics methods. Given the complexity of many-body interactions in such systems with highly charged ions and hydrogen bonded water molecules, the development of phenomenological potentials describing the interaction of trivalent ions (Al$^{3+}$, Cr$^{3+}$) with water and further classical molecular dynamics simulations often neglect hydrolysis [9,10]. If the goal is to model the solvation of Al$^{3+}$ in the practically important range of pH = 4 − 7, hydrolysis has to be taken into account to correctly describe the stability of the surrounding aluminum water network [11,12].

### 2 Technical details

In this Letter we illustrate the essential features of Al$^{3+}$ hydrolysis in terms of the hydration numbers and structural parameters of the species in aqueous solutions, namely, Al(H$_2$O)$_6^{3+}$ and Al(OH)$_4^-$. We will show that the efficient local density approximation (LDA), which has been used throughout the paper, provides accurate structural information for both species (see Section 3). Vosko *et al*.'s parameterized form for the exchange-correlation energy has been used to implement LDA [13]. Since the potential energy surfaces of small clusters usually have many local minima, we have used the method of dynamical
simulated annealing to find the optimal structures on the ground state potential surface. Such a search for a global minima would be difficult to do using only conventional total energy methods such as steepest descent minimization. To get accurate energetics, the Perdew-Burke-Ernzerhof 1996 (PBE96) generalized gradient approximation [14] has been employed in a postprocessing mode.

The valence electronic wave functions were expanded in plane waves, and their interactions with nuclei and the core electrons were described through generalized norm-conserving Hammann pseudopotentials [15]. The nonlocal part of the pseudopotentials was modified to a completely separable form as suggested by Kleinman and Bylander [16]. Since the original Hammann pseudopotential requires too high cut-off energy for oxygen, a softer potential was constructed by increasing the core radii. Using this potential, the equilibrium bond distances and the binding energies of single water molecule and the water dimer were tested against known LDA results [17] at the cutoff energy $E_{\text{cut}} = 100$ Ryd (see Table 1). Good agreements in these tests indicated that our soft pseudopotential for the oxygen is accurate. This choice of the cut-off energy required about 130,000 plane waves for each molecular orbital in the 20 a.u cubic cell. We performed our calculations without imposing periodic boundary conditions. Because we are dealing with charged isolated clusters with the strong dipoles and long-range Coulomb interactions, an aperiodic convolution method for solving Poisson’s equations for free-space boundary conditions has been used [18]. We have also replaced hydrogen atoms by deuterium in our simulations in order to be able to use sufficiently large values for the time step ($\Delta t = 7$ a.u) and fictitious mass ($\mu = 1100$ a.u.) in Car - Parrinello dynamics.

3 Results and discussion

The acidity of a hydrated metal ion depends on the strength of the coordination bond between cation and the oxygen atoms of the first hydration shell water molecules. If this coordination bond is strong, the OH bond in the solvating water molecules of the first coordination shell are strongly polarized. These polarized bond can dissociate in a polar solvent to form hydrolyzed species such as $\text{Al(H}_2\text{O)}_5(\text{OH})^{2+}$. This process is important to many aspects of aluminum solvation and is complicated by the many interactions that determine the structure of the coordination shell. In the following, we will show that the polarization of the solvating molecules is a function of the coordination number of the first solvation shell. This leads to a cooperative relation between mobility of the protons in the first solvation shell and the coordination structure.
3.1 Structure of aqueous Al$^{3+}$

The formation of a stable coordination cell around Al$^{3+}$ occurs on the subpicosecond time scale and hence well within the range of an *ab initio* molecular dynamics (AIMD) run. Our AIMD runs were initiated by placing one aluminum ion in the middle of the cluster of 16 randomly oriented water molecules in a cubic simulation box with a length of 20 a.u. On the time scale of about 0.25 ps, dramatic rearrangement of water cluster took place with the formation of an almost perfect octahedra complex of Al(H$_2$O)$_6^{3+}$ surrounded by the 10 remaining water molecules. This octahedral structure appears to be very stable and remained intact during the 1 ps run at ambient conditions. During this run no exchange of water molecules between first and second solvation shell was observed.

To check the structural parameters of the hexa-hydrate complex as calculated by our method, we performed AIMD simulations on isolated Al(H$_2$O)$_6^{3+}$ (by removing 10 remaining waters from the structure obtained in our first run) and also small clusters of [Al(H$_2$O)$_n$]$^{3+}$ with $n = 1, 2, 3, 4, 5$. Since there are several possible low energy isomers of these clusters we have used simulating annealing, i.e., heating and cooling the system by reducing the kinetic energy, together with the steepest descent geometry optimizations to ensure that the lowest energy structures were obtained. In the present calculation we started from an initial temperature of 1000$^\circ$ K in the simulated annealing procedure. By performing short (on the time scale $\tau = 10$ fs) molecular dynamics runs followed by periodic quenching of the system, a rather fast effective cooling schedule was enforced. The geometrical parameters obtained in our calculations (see Table 2) are in good agreement with the second order Møller-Plesset perturbation theory (MP2) results [9].

For $n = 1, 2, 3$ planar structures were obtained. The $n = 4$ cluster was a tetrahedral complex. At $n = 5$, the structure of Al(H$_2$O)$_5^{3+}$ was a square-based pyramid (aluminum sits slightly above the center of the square formed by four waters with fifth water molecule along the line perpendicular to the square). This is different from Ref. [9], where Al(H$_2$O)$_5^{3+}$ was found to be a stable trigonal bipyramid (which can be viewed as distorted square-based pyramid) under $C_{2v}$ constrained optimization. We tried to find a $C_{2v}$ bipyramid structure but the system always went to the square pyramid on annealing. The minimum energy geometries of the trigonal bipyramid Al(H$_2$O)$_5^{3+}$ and octahedral complex Al(H$_2$O)$_6^{3+}$ are given in the Fig. 1.

Filling the first solvation shell of the aluminum cation by water molecules leads to gradual increase in the length of the coordination bond Al-O. At the same time the OH bond length of the waters in the first solvation shell approaches the value for free H$_2$O at $n = 6$. The intramolecular angle $<\text{HOH}$ for the
molecules in the first solvation shell is larger than in a free water molecule. As a function of coordination number the \(<\text{HOH}\) first decreases and then increases with the minimum at \(n = 3\). This trend is also observed in MP2 data but the numbers are smaller [9].

The cohesive energies per coordination bond for \(\text{Al(H}_2\text{O)}^{3+}\) \((n = 1 - 6)\) clusters have been calculated according to the formula

\[
\Delta E_n = (E(\text{Al}^{3+}(\text{H}_2\text{O})_n) - E(\text{Al}^{3+}) - nE(\text{H}_2\text{O}))/n \tag{1}
\]

using PBE96 functional (PBE96 results differed by a few percent from the magnitude of the LDA results). The cohesive energies per coordination bond \(\Delta E_n\) as well as total cohesive energies \(\Delta E_n \times n\) for each of these clusters are reported in the Table 2 and are in close agreement with MP2 results [9].

To characterize the strength of polarization of the hydrated water molecules, in addition to the geometrical parameters of the optimized structures of \([\text{Al(H}_2\text{O)}_n]^{3+}\) we also determined the approximate dipole moments of water molecules in these clusters. We found the centers \(\langle r_e\rangle\) of the electronic density for the particular water molecule according to the formulae

\[
\langle r_e\rangle = \frac{\int d\vec{r} \vec{r} \rho(\vec{r})}{\int d\vec{r} \rho(\vec{r})} \tag{2}
\]

where the integration is over a sphere of about 3 a.u. centered on the oxygen ions. We note that the electron density was well localized on the solvating waters. Using this procedure the dipole moment of isolated water molecule was found to be 1.838 D in good agreement with the experimental value of 1.855 D [21]. The average dipoles of the single hydrated waters in \([\text{Al(H}_2\text{O)}_n]^{3+}\) clusters with \(n = 1, 2, 3, 4, 5, 6\) decrease by almost 20\% from 5.9 D to 5.02 D as a function of coordination. These numbers represent a substantial increase from the dipole moments of water molecule in vacuum and in the bulk liquid which are 1.855 D [21] and 2.6 D [22], respectively.

The increase in the bond polarization as a function of hydration numbers plays an important role in the dynamical behavior of the systems as will be discussed below. To illustrate the reduction of energy in the transfer of a proton from water in the first solvation shell to vicinity of an oxygen in the second solvation shell in the presence of aqueous \(\text{Al}^{3+}\) we carried out the following calculation. In the low energy structure of \(\text{Al(H}_2\text{O)}^{2+}\), a proton was moved from the water in the first solvation shell to the nearest water molecule in the second solvation shell along hypothetical reaction path leading to the acid reaction

\[
\text{Al}^{3+}(\text{H}_2\text{O})_6 + \text{H}_2\text{O}(2\text{nd solvation shell}) \longrightarrow \text{Al}^{3+}(\text{H}_2\text{O})_5\text{OH}^- + \text{H}_3\text{O}^+. \tag{3}
\]
The procedure was done at the constant O-O separation of 2.403 Å. We kept O-H-O atoms collinear while moving the proton between oxygen atoms in steps of 0.02 Å. The potential energy calculated using the PBE96 functional along the path O-H-O is plotted in Fig. 2 as a function of the asymmetric stretch coordinate

\[ Q = \frac{|r_{O_1H}| - |r_{O_2H}|}{\sqrt{2}} \]  

where \( r_{O_1H} \) and \( r_{O_2H} \) are the distances between the transferring proton and oxygens of water molecules. The potential energy for the proton transfer process from the aqueous Al\(^{3+}\) to the near vicinity of the water molecule in the second solvation shell is represented by the broad potential well of 9 kcal/mol. We note that there is only a single minimum in the potential given in Fig. 2. To form a minimum corresponding to H\(_3\)O\(^{3+}\) species may require a more complex reaction coordinate \[23\]. This will be the subject of further research. A similar calculation for proton transfer in a water dimer was carried out. In this case the transfer of the proton from one water molecule to the other requires about 50 kcal/mol. This dramatic reduction in the potential energy landscape due to the presence of aqueous Al\(^{3+}\) contributes to high mobility of the protons in our molecular dynamics simulations of aluminum ion with \( n = 14 - 16 \) water molecules discussed below (see Section 3.3).

3.2 Structure of aluminate ion, Al(OH)\(_4^-\)

Since the LDA geometry of aqueous aluminum ion, Al(H\(_2\)O\(_6\))\(^{3+}\) compared well with MP2 data and experimental X-ray diffraction results, we initiated a study of the formation of the most important hydrolysis product, Al(OH)\(_4^-\). To do this we started an AIMD run with the equilibrated Al(H\(_2\)O\(_6\))\(^{3+}\) structure but with 4 protons removed. The resulting deprotonated hexa-hydrate complex, Al(OH)\(_4^-\)(H\(_2\)O)\(_2\), after 0.1 ps readily evolved towards the equilibrium tetrahedral structure of aluminate ion, Al(OH)\(_4^-\), see Fig. 3. The two remaining water molecules were forced out of the first solvation shell and formed hydrogen bonds to the hydroxyl groups coordinated to the aluminate anion.

Since these simulations were done at the finite ionic temperature, it allowed us to test the thermal stability of this process. The resulting negatively charged fourfold coordinated structure has a negative highest occupied eigenvalue of \( \varepsilon = -2.07 \) eV. The tetrahedral structure of Al(OH)\(_4^-\) remained stable with no exchange in the following 0.5 ps of the AIMD run. Extensive MP2/6-311G ** and B3LYP/6-311G ** calculations of Al(OH)\(_4^-\) gave the average Al-O distance as 1.792 Å \[24\] which compares well with our LDA result, 1.750 Å. The Al-O bonds are strengthened in tetrahedral
Al(OH)$_4^-$ structure as compared to the Al(H$_2$O)$_6^{3+}$ octahedral complex, where the Al-O distance is 9% larger. As was discussed in Section 1, the change in coordination from six in Al(H$_2$O)$_6^{3+}$ to four in Al(OH)$_4^-$ is a unique feature of aluminum hydrolysis.

3.3 Beyond first solvation shell

The interaction between first and second solvation shells is an important issue in theoretical \cite{8,9} and experimental studies \cite{25,26} of the solvation of highly charged ions in water. As a first step to the understanding of these effects in bulk water, we report here results for the solvation of aluminum ion in the clusters of $n = 14 - 16$ waters.

The presence of hydrolysis (e.g. acid reaction of the form of Eq. 3) in the Al$^{3+}$ water system is well documented \cite{2}. However, our low temperature simulations with Al$^{3+}$ in the middle of cluster of water molecules did not show any proton mobility on the time scale of the simulations. Since the hydrolysis constants in the aqueous aluminum ion solutions are known to be four orders of magnitude higher at the temperature of 800$^\circ$ K than at room temperature \cite{27}, we also performed simulations with the Al$^{3+}$ inside cluster of 14 water molecules in this elevated temperature regime. Hydrolysis did occur in this heated system on the subpicosecond time scale. As the coordination bond of one of the six hydrated waters (with purple colored oxygen) lengthened two protons (green) on the remaining waters of the first solvation shell shuttled between hydrated waters and the incomplete second solvation shell. Snapshots showing the shuttling protons coordinated to second solvation shell water molecules are presented in Fig. 4.

In our calculations of the polarization of the OH bonds in the first coordination shell we have shown that the decrease in repulsive interactions in the solvation shell for low coordination led to shorter Al-O bond lengths and corresponding increase in polarization of the OH bonds. In a polarizable medium (e.g. water) this increase in polarization should lead to increased mobility of the protons. Evidence for this from our simulations is given in Fig. 5 where we show a cluster structure in which the Al$^{3+}$ ion is coordinated to only 3 waters. The extensive migration of the protons even at room temperature shown in this figure support the above conjecture. Neighboring waters of Al$^{3+}$ lose their protons shortly ($\sim 50$ fs) after the cation has been artificially moved into the 3-water coordination structure on the surface of the water cluster. After equilibration at room temperature, one proton was found to shuttle between hydrated water and the water in the second solvation shell, while two other protons left first solvation shell and became engaged in the hydrogen bonding network of the solvent. These three protons which showed high mobility are
colored green in Fig. 5. Although this ”surface” structure of aqueous aluminum is an artificial construction, it suggests the crucial role of the coordination of Al$^{3+}$ in hydrolysis.

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Table 1
Intramolecular structural parameters for water monomer and hydrogen bond parameters for water dimer in comparison with known LDA results and experimental data (in Å and deg).

|                  | calculated results | Ref. [17] | experiment |
|------------------|--------------------|-----------|------------|
| **water monomer**|                    |           |            |
| r\textsubscript{OH} | 0.953              | 0.978     | 0.957\textsuperscript{a} |
| < HOH            | 104.8              | 104.4     | 104.5\textsuperscript{a} |
| **water dimer**  |                    |           |            |
| r\textsubscript{OO} | 2.713              | 2.710     | 2.98\textsuperscript{b} |
| < O – H\textsubscript{···}O | 170.8              | 171       | 174 ±10\textsuperscript{b} |

\textsuperscript{a) From Ref. [19]. \textsuperscript{b) From Ref. [20].}
Table 2
Global minimum geometries (in Å and deg) and average dipole moments of water molecules (in Debye) of $[\text{Al(H}_2\text{O)}_n]^{3+}$ complexes with $n = 1, 2, 3, 4, 5, 6$, obtained with the LDA density functional as described in the text. Total and per coordination bond cohesive energies (in kcal/mol), $\Delta E_n \times n$ and $\Delta E_n$ respectively, were calculated using PBE96 functional. For comparison, all electron MP2/cc-pwCVTZ results for $n = 1, 6$ and MP2/cc-pVDZ results for $n = 5$ from Ref.[9] are reported in parentheses. For the $n = 6$ the experimental X-ray diffraction result of Ref.[4] is given.

|       | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ | $n = 5$ | $n = 6$ |
|-------|---------|---------|---------|---------|---------|---------|
| $r_{\text{AlO}}$ | 1.724   | 1.751   | 1.751   | 1.815   | 1.870   | 1.880   | 1.920   |
|       | (1.723) | (1.795) | (1.901) | (1.949) | (1.911) |         |
| $r_{\text{OH}}$ | 1.031   | 1.011   | 0.999   | 0.989   | 0.980   | 0.976   |
|       | (1.018) | (0.984) |         |         | (0.972) |         |
| $< \text{HOH}$ | 106.9   | 106.5   | 106.2   | 106.7   | 107.1   | 107.6   |
|       | (106.54)| (106.01)|         |         | (106.56)|         |
| dipole | 5.9     | 5.51    | 5.26    | 5.06    | 5.02    | 5.02    |
| $\Delta E_n$ | -203.7  | -184.3  | -166.45 | -148.16 | -131.25 | -118.36 |
| $\Delta E_n \times n$ | -203.7  | -368.6  | -499.35 | -592.64 | -656.27 | -710.16 |
|       | (-201.3)| (-664.2)|         |         | (-723.7)|         |
Fig. 1. The minimum energy geometries of a) Al(H$_2$O)$_3^{3+}$ and b) Al(H$_2$O)$_6^{3+}$.

Fig. 2. Potential energy (in kcal/mol) for the proton moved between two water molecules in steps of 0.02 Å along a linear path O-H-O in Al(H$_2$O)$_3^{3+}$ cluster. O-O separation is 2.403 Å. O-H-O atoms have been kept collinear. Q is the asymmetric stretch coordinate (see text).

Fig. 3. Snapshots from ab initio molecular dynamics simulation starting from the deprotonated Al(OH)$_4^-$ (H$_2$O)$_2$ cluster. (a) Octahedral initial configuration; (b) after 0.025 ps; (c) after 0.05 ps; and (d) the final tetrahedral structure of Al(OH)$_4^-$ at 0.3 ps with two remaining water molecules forced out of the first solvation shell. Hydrogen bonds are illustrated by dashed lines.

Fig. 4. Snapshot of the hydrated Al(H$_2$O)$_3^{3+}$ at a temperature of about 800° K with the protons (green) shuttling between hydrated waters.

Fig. 5. Snapshot of the AIMD simulation of the artificial "surface" structure with a low coordinated aluminum ion on the surface of the water cluster and extensive hydrolysis. Protons which showed high mobility are colored green.
Fig. 1 a)
Assymmetric stretch (Angstrem)

Energy (kcal/mol)

Fig. 2
Fig. 3
