

Ab Initio Molecular Dynamics Simulations of Aluminum Ion Solvation in Water Clusters

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ABSTRACT

The results of *ab initio* molecular dynamics simulations of the solvation of Al^{3+} and its hydrolyzation products in water clusters are reported. Al^{3+} ions in water clusters ($6 \leq n \leq 16$) form a stable hexa-hydrate $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex in finite temperature simulations. The deprotonated $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ complex evolves into a tetra-coordinated $\text{Al}(\text{OH})_4^-$ aluminate ion with two water molecules in the second cluster solvation shell forming hydrogen bonds to the hydroxyl groups consistent with the observed coordination in water solutions. At high temperature, protons in the first solvation shell of the $\text{Al}^{3+}(\text{H}_2\text{O})_{14}$ cluster are very mobile transferring easily to the second cluster solvation shell and leading to the formation of transient (1ps) hydrolysis species.

Keywords: ab initio molecular dynamics, atomic level simulations based on quantum mechanics, density functional theory

1 MOTIVATION

The aqueous chemistry of aluminum, the most abundant metal in the earth's crust, remains a subject of fundamental interest after many years of intensive research [1]. The aluminum hydrolysis products have many practical applications, ranging from pharmaceutical design [2] to purification of water [1].

We have used *ab initio* molecular dynamics (AIMD) [3] to study the solvation of Al^{3+} ion in clusters of water molecules ($n=1$ to 16). The results we present here show that the strong coordination interaction between the Al^{3+} ion and the neighboring water molecules results in highly polarized bonds in the water molecules in the first cluster solvation shell. When additional waters are added to form a second cluster shell the energy required to transfer protons from the first to the second is relatively small. At sufficiently high temperatures this leads to proton transfer between the first and second cluster solvation shell on a picosecond time frame. On a longer time scale this mobility may lead to the formation of stable hydrated hydroxide clusters as has been observed in recent cluster experiments [4].

2 TECHNICAL DETAILS

In the calculations reported here Vosko *et al.*'s parameterized form for the exchange-correlation energy was used to implement the local density approximation (LDA) [5]. To improve the energetics of the calculation, the Perdew-Burke-Ernzerhof 1996 (PBE96) generalized gradient approximation [6] was implemented in a post-processing 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 Hamann pseudopotentials [7]. The non-local part of the pseudopotentials were modified to a completely separable form as suggested by Kleinman and Bylander [8]. Since the original Hamann pseudopotential requires a very high cut-off energy for oxygen, a softer potential was constructed by increasing the core radii.

Because we are dealing with charged isolated clusters with strong dipoles and long-range Coulomb interactions, an aperiodic convolution method for solving Poisson's equations for free-space boundary conditions was used [9]. Hydrogen atoms were replaced 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]. Since the potential energy surfaces of small clusters usually have many local minima, dynamical simulated annealing was used. The system was first heated and then cooled by scaling the kinetic energy in a series of $\tau = 300$ fs runs starting from an initial temperature of 1000° K and cooling to a final temperature around 30° K. Finally, steepest descent geometry optimizations were used to choose the ground state energy structure from a pool of cooled clusters.

3 RESULTS AND DISCUSSION

3.1 Aqueous Al^{3+}

The acidity of the hydrated Al^{3+} ion in the water cluster results from the polarization of the bonds in the coordinating water ligands. This process is complicated by the many interactions that determine the structure of the coordination shell. Our AIMD runs were initiated

by placing one aluminum ion in the middle of the cluster of 16 randomly oriented water molecules. On the time scale of 0.25 ps, dramatic rearrangement of water cluster took place with the formation of a first octahedral solvation shell, $\text{Al}(\text{H}_2\text{O})_6^{3+}$. There is little electron exchange between the coordinating molecules in this first shell and the Al^{3+} ion. The 10 remaining water molecules formed hydrogen bonds to the strongly coordinated first shell molecules to form an incomplete second solvation shell. The hydrogen bonds in the second shell are not saturated. The octahedral first solvation shell structure appeared to be very stable and remained intact during the 1 ps run at ambient conditions. During this run no exchange of water molecules between the first and second solvation shell was observed.

To check the structural parameters of the hexa-hydrate complex as calculated by our method, we performed structural optimizations on isolated clusters, $\text{Al}(\text{H}_2\text{O})_n^{3+}$, $n=1, 6$. The geometric parameters obtained in our calculations are in good agreement with second order Møller-Plesset perturbation theory (MP2) results [10].

For $n = 1, 2, 3$ planar structures were obtained. The $n = 4$ cluster was a tetrahedral complex. The structure of $\text{Al}(\text{H}_2\text{O})_5^{3+}$ 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 differs from the structure reported in Ref. [10], where the structure of $\text{Al}(\text{H}_2\text{O})_5^{3+}$ 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 an C_{2v} optimal bipyramid structure but the system always evolved to a square pyramid structure on annealing. The minimum energy geometries of the square-based pyramid $\text{Al}(\text{H}_2\text{O})_5^{3+}$ is given in the Fig. 1.

To characterize the strength of the polarization of the hydrated water molecules in the first solvation shell, the dipole moments of water the molecules in this shell were calculated as follows. The centers $\langle r_e \rangle$ of the electronic density for the particular water molecule were found according to the formulae

$$\langle r_e \rangle = \frac{\int d\vec{r} \vec{r} \rho(\vec{r})}{\int d\vec{r} \rho(\vec{r})}, \quad (1)$$

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 [11]. The average dipoles of the single hydrated waters in $[\text{Al}(\text{H}_2\text{O})_n]^{3+}$ 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

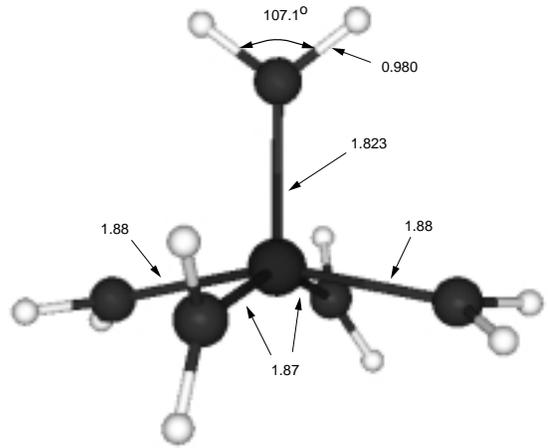


Fig. 1 a)

Figure 1: The minimum energy geometry of $\text{Al}(\text{H}_2\text{O})_5^{3+}$.

bulk liquid which are 1.855 D [11] and 2.6 D [12], respectively.

To illustrate the effect of the presence of the Al^{3+} on the energy required to transfer a proton from water in the first cluster solvation shell to vicinity of an oxygen in the second cluster solvation shell in the presence of aqueous Al^{3+} we carried out the following calculation. In the low energy structure of $\text{Al}(\text{H}_2\text{O})_7^{3+}$, 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. The procedure was done at the constant O-O separation of 2.403 Å, the O-O separation in the cooled $\text{Al}^{3+}(\text{H}_2\text{O})_7$ cluster. The O-H-O atoms were kept collinear while moving the proton between oxygen atoms in steps of 0.02 Å. The potential energy calculated using the PBE96 functional along the O-H-O beginning at approximately one OH distance from O_1 adjacent to the Al^{3+} ion and going to about one OH distance from O_2 in the second shell water is plotted in Fig. 2 as a function of the asymmetric stretch coordinate

$$Q = \frac{|r_{\text{O}_1\text{H}}| - |r_{\text{O}_2\text{H}}|}{\sqrt{2}} \quad (2)$$

where $r_{\text{O}_1\text{H}}$ and $r_{\text{O}_2\text{H}}$ are the distances between the transferring proton and oxygens of water molecules. Calculations performed with LDA functional without gradient correction differed by about 1 kcal/mol from those of the PBE96 functional.

Because of the strong polarization of the OH bond in the solvating water molecules the transfer of protons between the first and second solvation shell in this problem resembles the behavior calculated for the H_5O_2^+ system [13], [14]. In Fig. 2 there is only a single minimum. The OH bond length of the first solvation shell water is

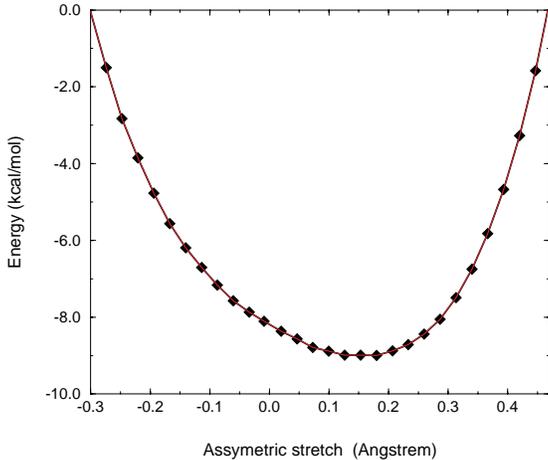


Fig. 2

Figure 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 $\text{Al}(\text{H}_2\text{O})_7^{3+}$ cluster. O-O separation is 2.403 Å. O-H-O atoms have been kept collinear. A and B mark the OH distances for isolated water molecules. Q is the asymmetric stretch coordinate (see text).

marked with arrow A. An OH bond distance from the second solvation shell oxygen is marked with arrow B. The position of the minimum energy in the in the OHO bond is close to the center as in the H_5O_2^+ system and considerably longer than the LDA OH bond length of .0953 Å. The energy required to move the proton from the lowest energy position in the first solvation shell to roughly one OH distance from the oxygen in the 2nd solvation shell is 9 kcal/mol. We have done similar calculations for the neutral water dimer. In this case the energy of transfer is of course quite high, ≈ 50 kcal/mol. This dramatic change 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). Since there is no maximum in the potential energy in Fig. 2, for the proton to be trapped in the second solvation shell, i.e. to form a separated H_3O^{3+} species a more complex reaction coordinate [14], [18], [16] may be required.

3.2 Aluminate Ion, $\text{Al}(\text{OH})_4^-$

Since the LDA geometry of cluster aluminum ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ compared well with MP2 data and experimental X-ray diffraction results for bulk water, we initiated a study of the formation of the most important hydrolysis product of Al, $\text{Al}(\text{OH})_4^-$. To do this we started an AIMD run with the equilibrated $\text{Al}(\text{H}_2\text{O})_6^{3+}$ struc-

ture, but with 4 protons removed. The resulting deprotonated hexa-hydrate complex, $\text{Al}(\text{OH})_4^-(\text{H}_2\text{O})_2$, after 0.1 ps evolved towards the equilibrium tetrahedral structure of aluminate ion, $\text{Al}(\text{OH})_4^-$. 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. starting from the deprotonated aqueous Al cluster.

In the finite temperature simulation ($T = 200^\circ$), the tetrahedral structure of $\text{Al}(\text{OH})_4^-$ remained stable with no exchange of protons from the expelled waters to the OH^- in the 0.5 ps of the AIMD run.

3.3 Proton Transfer Between The First and Second Cluster Solvation Shell

Hydrolysis reactions in water clusters containing Al^+ ions have recently been reported [4]. In these experiments, the aluminum water clusters exhibited higher reactivity than bulk systems, inducing intracuster reactions and charge transfer processes which provide new insights into ion solvation.

It is known that even in the bulk systems the time scale for aqueous proton transport is very short (1 ps) [15]. This anomalously high mobility of protons was explained by fluctuation-induced breakage of a hydrogen bond between the first and second solvation shell of hydronium cation H_3O^+ [16]. In the cluster simulations reported here the receiving water molecules are unsaturated with respect to hydrogen bond formation. Therefore, there is no requirement to break a solvent hydrogen bond to transfer protons. The transfer of protons in unsaturated systems such as proton wires can occur on a subpicosecond time scale [17]. This should facilitate the formation of transient hydrolysis species in the cluster.

Our low temperature simulations with Al^{3+} in largest water clusters did not show any proton mobility. At elevated temperature of about 800°K proton transfer did occur in on the subpicosecond time scale. Snapshots illustrating the migration of the protons in the water clusters are shown in Fig. 1. 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 the coordinating waters and the incomplete second solvation shell forming a transient (subpicosecond) hydrolysis species. Since the minimum potential energy position of the proton was close to the center of the O-H-O bond this is reminiscent the proton transfer step of the Grothuss mechanism [16], [18].

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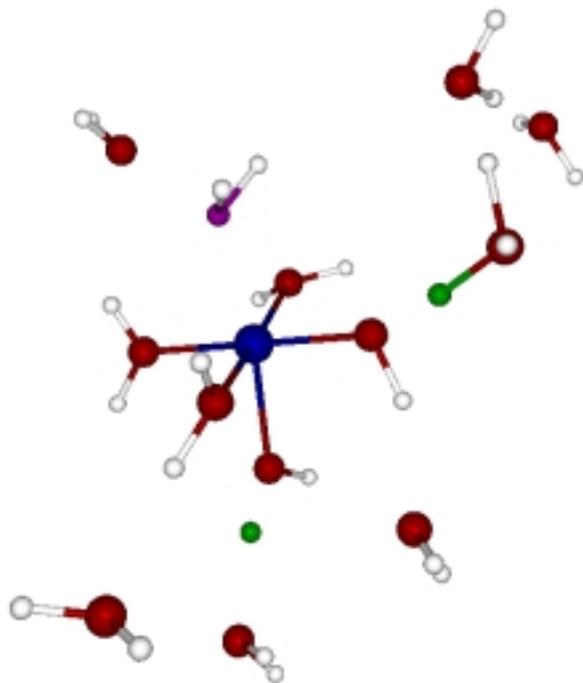


Fig. 4

Figure 3: Snapshot of the hydrated $\text{Al}(\text{H}_2\text{O})_6^{3+}$ at a temperature of about 800°K with the protons (green) shuttling between hydrated waters.