The effects of charge density distributions of metal ions on single water molecule dissociation of $[\text{M(H}_2\text{O)}_6]^{3+}$ systems

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Abstract

Some effects of cationic charge density distribution on single water molecule dissociation of $[\text{M(H}_2\text{O)}_6]^{3+}$ clusters with $\text{M}=$Cr, Mn, Fe, Co, and Ni have been investigated using first-principles study. The molecular structures, molecular binding energies, hydration enthalpies, cation and water molecules orbitals, infrared vibrational frequencies, and potential energy surfaces/crives had been computed to fulfill the purpose of research. Our investigation results have revealed that the hollow shape of charge density of central Cr(III) makes the Cr-O bonds rigid as indicated by a higher activation energy for releasing one water molecule from $[\text{Cr(H}_2\text{O)}_6]^{3+}$. The isotropic charge density of Fe(III) affects in lowering water rotational rigidities which is responsible for augmenting the activation energy, while the cones-shape charge density of Ni(III) weakens the ion-dipole interactions by increasing interactions between nearest neighbour water molecules.

1. Introduction

The dehydration has been acknowledged as an essential molecular interaction for water-ion exchange reaction, since some experimental evidences have shown that ion attack at surfactants and polyelectrolyte is followed by its partial interaction of the counter-ions [1, 2]. A recent study on counter ion-binding (aqueous Al(III) and Cr(III)) related to the ion attack at electrolyte polyvinyl sulphate (PVS) has brought up that hydration enthalpy from coordinated water release within the primary hydration sphere plays a key role in driving binding to PVS [3]. Similar reactions possibly happen in a humid membrane of fuel cell, when contained water is starting dehydrated at working temperature. The residues of dehydrated cations (e.g. Al(III) and Fe(III)) may attack and deactivate the proton hopping supports in the membrane (SO$_3$ end). Such interaction can impair the functionality of membranes through protons migration.

It has been stated that hydration enthalpy of $[\text{M(H}_2\text{O)}_6]^{3+}$ clusters with $\text{M}=$ central metal ions influences the amount of reaction product in water and ion exchange reactions, nevertheless, theoretically, the activation energy should be more significant on determining the success of a reaction. A clarification is essential to elucidate the dehydration mechanism and cationic effect in which they strongly affect to the ion attack interaction. The activation energy decides also the amount of dehydration products which are reckoned with the enthalpy calculations. The study will be addressed to respond previous clarification need by considering the charge density distribution as one intrinsic property of metal ions, particularly in the first-row transition metal ions.

2. Computational method

Our theoretical studies were carried out with the help of the Gaussian 03 software package (based on Gauss-type orbitals) which has advantages in computing the total electronic energies and atomic structure optimizations for...
simple molecular models, such as a small water molecules cluster. In this case, Gaussian orbital has no energy cut-offs and k-points as in the use of plane wave to expand crystal orbitals.

The models of transition metal ion M(III) surrounded by the first hydration sphere of water molecules (figure 1) are optimized using uB3LYP theory level with separated basis set; 6–311++G(d,p) for atoms of water and DGDZVP for the central metal ion. All [M(H₂O)₆]³⁺ systems had optimized using limits criteria of maximum force 0.00045 Hartree/Bohr and maximum displacement 0.0018 Ångström. The selected theory level was proven to be accurate in computing spatial electron density distributions and atomic structure properties [3]. However, the method has some weakness in the accuracy of computing electronic (energy) structures and the cost of computational time. Hence, electronic spin structures such as the spin polarization properties are not discussed here. Instead, the basis set superposition errors was proven to be accurate in computing spatial electron density distributions and atomic structure properties [5].

Discussed here. Instead, the basis set superposition errors found as quartet, quintet, sextet, quintet, and doublet for Cr(III), Mn(III), Fe(III), Co(III), and Ni(III) clusters, respectively. A relevant quantity of molecular bindings and reliability of calculations will be introduced first. Recalling density functional theory (DFT) study, especially for electron population [6–10] and energetic analysis [11–13], the intermolecular binding and structural behaviour are substantially influenced by electron distributions inside the observed system [14, 15]. A cation–dipole (water) binding interaction can be simply expressed using a classical electrostatic formulation [15]:

$$E^{i-d}_{st}(R, \theta) = -k \frac{Q_{1} \mu_{2} \cos(\theta)}{R^2},$$

where $E^{i-d}_{st}$, $R$, $Q_1$, $\mu_2$, and $\theta$ represent the ion–dipole interaction strength, the distance between the ion and the center of the dipole, the ion charge, the monomer dipole moment (MDM), and the angle between the dipole orientation and R direction, respectively. Two indices (1, 2) are assigned to the metal ion and one water molecule, respectively. The $k$ is an arbitrary proportional coefficient. A maximum interaction can be obtained by setting $\theta$ equal to zero. In equation (1), it is assumed that the change of the other energy contributors such kinetic energies are negligible in the ion–dipole interaction. Another interaction (reaction) energy descriptor is given with total energies of reactants and products obtained by first-principles DFT calculations energy as follows [14]:

$$E_{\text{cat–wat}} = \frac{E[\text{Cation}] + 6E[H_2O] - E[\text{Cation(H}_2\text{O)}_6]]}{6}.$$  

Here $E_{\text{cat–wat}}$ is the average cation–water binding energy being calculated, $E[\text{Cation}]$ is the total energy of cation, $E[H_2O]$ is the total energy of single isolated water molecule, and $E[\text{Cation(H}_2\text{O)}_6]$ is the total energy of the cationic water cluster. Although (2) does not provide information about local ion–dipole interaction such as the electrostatic approach in (1), but by ignoring inter-neighbour water interactions, we may obtain an average value for binding energy between the water molecules and the metal ion. A more convenient index which is comparable with the experimental hydration enthalpy per water molecule can be written as [16]:

$$\Delta H^o_h = -E_{\text{cat–wat}} + \frac{\Delta E_0 + \Delta E_{\text{sol}} + n\Delta H_{\text{vap}} + \Delta nRT}{n},$$

where $\Delta E_0$, $\Delta E_{\text{sol}}$, $n$, $\Delta H_{\text{vap}}$, $R$, and $T$ stand for the zero-point energy (ZPE), solvation energy, the number of water molecules, the vaporization energy, the gas constant, and the temperature, respectively. Using equation (2), one can evaluate original effects of the total electronic energies on the average intermolecular binding at equilibrium and by equation (3) one may compare and validate the used method with experiment data.

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Figure 1. Model of [M(H₂O)₆]³⁺ systems as the initial structure for single water molecule dehydration.
Table 1. Properties of [M(H₂O)₆]³⁺ systems obtained by the calculations together with experimental hydration enthalpies per molecule as references.

| M ions | 〈E_{rel}〉 (eV) | 〈E_{vib}〉 (kcal mol⁻¹) | ΔH°️ (kcal mol⁻¹) | calc. | exp. [18] | BSSEs (%) |
|--------|-----------------|--------------------------|------------------|-------|----------|----------|
| Cr     | 518             | 528                      | 812              | 760   | 3/2, 3.75| 6.53     |
| Mn     | 514             | 534                      | 824              | 757   | 2, 6.00  | 5.84     |
| Fe     | 523             | 524                      | 803              | 738   | 5/2, 8.75| 5.39     |
| Co     | 508             | 561                      | 878              | 775   | 3, 6.00  | 4.65     |
| Ni     | 264             | 616                      | 1029             | —     | 1/2, 0.75| 4.22     |
| Cu     | 215             | 625                      | 916              | —     | 1, 2.00  | 4.43     |

though using scaling procedures in some cases, equation (3) had worked well [17, 18], however, the second term still needs corrections for better agreements with the experimental data [19].

Experimentally, it is arduous to produce infrared (IR) spectra for molecular system which has small total dipole moment values. In this study, the relative IR spectra for M–O symmetrical stretching have been computed using Gaussian 03 program [20]. The detailed theory and calculation method, one may refer to the study by Hess et al. [21]. Based on the same DFT theory level (uB3LYP) and separated basis set as mentioned previously in molecular structure optimization, the calculated M–O symmetrical stretching frequencies of each [M(H₂O)₆]³⁺ cluster from IR spectra computations are plotted in one relative vibrational diagram. By default, for frequency calculations in G03 program, the temperature was set at 298.15 K.

Analysis based on potential energy surfaces/curves is one of convenient method and analysis for obtaining a chemical reaction path which is comparable with a Monte Carlo study [22], especially for lesser number of constraint variables. The optimized structures of [M(H₂O)₆]³⁺ systems are used as the initial structures for dissociative dehydration scanning. Here, the M(III)–O distances were taken into account as the only one constraint variable. In this case, the Hessian matrix is updated using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [23]. The internal coordinates have been utilized for the next search direction which it has advantage on that the bond stretching second derivatives are transferable and can be easily parameterized in the Hessian matrix [24]. For dissociation processes, the M–O step distance is set at 0.1 Å with number of step about 50. The relaxed structure in each step has been optimized under standard criterions of maximum atomic force and maximum displacement; that are 3 × 10⁻⁴ and 1.2 × 10⁻² respectively in atomic units.

3. Results and discussion

Our theoretical studies were carried out with the help of the Gaussian 03 software package (based on Gaussian wave functions) which has advantages in computing the total electronic energies and spatial structure analyses for simple molecular models, such as a small water molecules cluster.

3.1. Enthalpy, dehydration and cationic charge density shape

Reviewing the molecular binding energy and hydration enthalpy is necessary because it can represent the average molecular bond strength of water molecules to the metal ion at the equilibrium structure which provides a good preliminary point of view for further analyses of water molecule dissociation processes.

The calculated hydration enthalpies per water molecule (ΔH°️) as shown in table 1 approximately reproduces the experimental data. The calculated spin contamination (〈S²〉) values [25] and BSSEs [26] have gained the reliability information of the used method based on the unrestricted B3LYP/6-311++G**. However, in detail, the ΔH°️ differences among metal ions are still not proportional as compared to experiment data (max. difference about 37 kJ mol⁻¹), which may leave some questions that could widen the study scope (under developing by the other research groups) [27]. Minor excess of the energies could be caused by the static (harmonic) approximation method from Gaussian 03 programs to obtain ZPEs contribution in equation (3) [20]. However, the method has taken into account vibrational temperatures in their ZPE correction as the effects of molecular vibrations which persist even at 0 K. Experimentally, the issue of ZPE extraction, up to now, is still lively discussed [28]. Therefore, we only focus on the electrons density distribution and single water molecule dissociation from total electronic energy which take about 70.85% part of experimental hydration enthalpies.

Contemplating a complete reaction, the amount and variety of reaction products is not only related with the hydration enthalpy, but they also depend on the activation energy [29] for dehydration reaction. If so, there is a possibility that both amount and variety of products estimated by recent enthalpy calculation [30] might be different from the results following the reaction path. This likelihood is reasonable, because the hydrated metal
ions have more than one dehydration reaction options. For example, let us consider the following dehydration reactions:

\[
[M(H_2O)_6]^{3+} \rightarrow [M(H_2O)_{6-n}]^{\text{I}^{\text{III}}} + n(H_2O), \tag{4}
\]
\[
[M(H_2O)_6]^{3+} \rightarrow [M(H_2O)_{3-n}]^{2+} + [n(H_2O)H]^+. \tag{5}
\]

The dehydration will produce \(n\) pure water molecules by equation (4) and mixed hydronium by equation (5). In case of \(n = 1\), both (4) and (5) denote dissociative reaction of single water molecule from \([M(H_2O)_{6}]^{3+}\) systems or \(M(\text{III})\) clusters. Substantively, previous average intermolecular binding in equation (2) comes from chemical equation (4) for \(n = 6\), nevertheless, as another choice of dehydration reaction, one can use equation (5), and possibly there still exist the other reactions as the options. To obtain a correct dehydration reaction, the minimum potential energy curves through the reaction coordinates can be utilized. Indeed, the interaction of metal ion with the primary shell of water molecules only involves a central cation and six water molecules. So, if each of all water molecules and the total charges of systems are identic in the sequence of \(M(\text{III})\) clusters then a hypothesis that the favourable reaction path might be controlled by charge density distributions of central metal ion becomes admissible.

Let us consider the cation-water interactions, since the charge density of central cation sterically holds the frontier orbitals of water molecules (at nucleophilic site) to get closer to the central cation, thus the surfaces shape of cation charge density may control the frontier orbitals distributions of water molecules around central cation. The unpaired \(d\)-orbital distribution of a metal ion (figure 2) determines the surfaces shape of total charge density of the metal ion which may influence its interaction with the surrounding water molecules.

For \(Cr(\text{III})\) ion, the hollows of the total charge distributions at \(x, y, z\) axes are formed by extremely low electron density distributions of the three \(t_2g\) unpaired electrons at the axes. In case of charge density shape of \(Mn(\text{III})\) ion, four hollows at \(x\) and \(y\) axes are occupied (removed) by an \(e_g\) unpaired electron distributions. For the next sequence from \(Cr(\text{III})\) to \(Ni(\text{III})\) ions, the unpaired electron distributions close the hollows so as to form the cone-shape distributions at \(x, y, z\) axes.

### 3.2. \(M(\text{III})\) ion-water interactions analyses

The influence of molecular orbital (MO) distributions on the structure determination of observed system can be described by frontier orbital theory [32]. The highest occupied—lowest unoccupied MOs (HOMOs-LUMOs) counter-pairs are close together will initiate a charge transfer among MOs to stabilize the formed bond [33]. In case of ion-dipole interactions, beside the bond forming, the induced charges may also result in spatially the shifted MOs toward the metal ion [34].

The HOMOs of water molecule, those are \(1b_2, 3a_1, \) and \(1b_1\) MOs [35], each of which has substantial effects on both interatomic distances and bond angles. The \(3a_1\) and \(1b_2\) MOs determine the internal structure of water molecules (\(\angle HOH\) angle and OH covalent bond), while the \(1b_1\) MOs determine the external configuration (e.g. an M–O coordination bond and also \(\theta\) in equation (1)). Correlating to figure 2, it is seen from figure 3(a) that reducing number of hollows as increasing the atomic number from Cr(III) to Fe(III) is accompanied by the elongations of M–O distances. They indicate that the electron charge of water molecules shift into the hollows of the cation charge density. On the other hand, in case of Co(III) and Ni(III) clusters, the distances shorten as
increasing the atomic number. This is because the charge density changes to anisotropic so as to form cones at the axes and hence to enhance interactions between nearest neighbour water molecules. In case of Co(III) with single water molecule, experimental study [36] had exhibited M–O stretching frequency about 410 cm$^{-1}$.

An analysis on symmetrical M–O stretching mode (figure 3(b)) reveals that vibrational frequencies of Cr(III) and Mn(III) clusters are relatively higher than the others. It has supported our belief that the orbital shifts from water into hollows have made M–O bonds rigid. A higher infrared intensity of Mn(III) cluster reflects an anisotropic nature of the M–O distances. The intensity is not related directly with the effect of temperature induced dynamics [37] but originates from dipole moments which affect the dielectric constant $\varepsilon$.

Unfortunately, further studies involving a complete Beer–Lambert intensity as in experimental vibrational spectra will require computational molecular dynamics which could not be discussed here in detail yet.

The optimized M–O distances (table 2) are in agreement with experimental data, especially for M–O distances of Mn(III) cluster. Since the charge density distributions could determine the structures, if so from the optimized structures, one may reversely predict the MOs distributions specifically for the HOMOs. As a reminder, beside the nuclei and electron attractive interaction, the Weizsäcker kinetic energy [38] (which represents a density volume pumping or steric effect [39]) is also related to the orbital shifts by its charge density gradient.

In case of Cr(III) cluster, the $3a_1$ MO of a water molecule has been directly shifted into the hollows of the cation charge density. Oppositely, the $1b_1$ and $1b_2$ MOs of the water molecules are repulsively restrained by cationic charge density distribution around hollow edges. Even though the $1b_1$ MOs have minor effects on OH bonds, the $1b_2$ MOs have a substantial contribution to the bonds. The OH distances in Cr(III) cluster are shorter than the others (figure 4(a)). They are due to the less volume compression for $1b_1$ and $1b_2$ MOs which conserve the OH distances. Contrary, by increasing the atomic number toward Ni(III), the $1b_1$ and $1b_2$ MOs of a water molecule interact with MOs of the nearest neighbour water molecules and hence elongate the OH distances. The HOH bond angles in Cr(III) and Mn(III) clusters are wider than the Fe(III) one (figure 4(b)), since their charge density hollows have made room for the $3a_1$ MO shifting of an approaching water molecule. Just in case of the Ni(III) cluster, the interactions between nearest neighbour water molecules are accountable for the $\angle$HOH widening.

The $3a_1$ MOs shiftings of water molecules into the hollow region of cation charge density can be clearly observed in Mn(III) cluster (figure 5(a)) in which they affect anisotropic distances at $z$ (hollow region) and x (non-hollow region) axes. The $3a_1$ MOs are prohibited to shift (figure 5(b)) by repulsive interaction with $d_{x^2-y^2}$ cation orbital. Each of Co(III) and Ni(III) clusters has an unique property on determining the relations of the nearest neighbour water molecules. Water molecules around Co(III) seem to be isolated from neighbour water molecules because their $1b_1$ MOs tend to interact with $d_{x^2-y^2}$ orbital of central cation which limiting the

Table 2. Calculated M–O distances of [M(H$_2$O)$_3$]$^{3+}$ systems projected onto x, y, and z axes and related experimental data.

| Central metal ions | Calc.        | Expt.        |
|-------------------|--------------|--------------|
|                   | X ($\AA$) | Y ($\AA$) | Z ($\AA$) | M–O distances ($\AA$) |
| Cr                | 2.006      | 2.006      | 2.0065    | 1.99 [40, 41] (XRD) 2.01 [42] (EXAFS) |
| Mn                | 1.965      | 1.982      | 2.153     | x = 1.92, y = 1.93, z = 2.13 [43] (EPR) |
| Fe                | 2.049      | 2.049      | 2.049     | 1.99–2.05 [44] (XRD, EXAFS, ND), 2.02 [45] (EXAFS) |
| Co                | 2.034      | 2.033      | 2.032     | — |
| Ni                | 1.933      | 1.938      | 2.084     | — |

Figure 3. (a) Average M–O distances, and (b) relative vibrational frequencies for symmetrical M–O stretching mode.
interactions between water molecules. While the water molecules are isolated from each other by the water-
cation correlation in Co

\(\text{III}\) cluster (figure 5(c)), the nearest neighbour relations are strengthened in the Ni

\(\text{III}\) cluster by the 3\(\text{a}_1\)–1\(\text{b}_1\) MOs interactions among water molecules (figure 5(d)).

3.3. Mechanisms of single water molecule dissociation

Preceding optimized structures of \([\text{M}(\text{H}_2\text{O})_6]^3^+\) systems are used as the initial structures for dissociative dehydration scanning. We have obtained a surprising result that all but the Co

\(\text{III}\) cluster had shown single dehydration reactions by following equation (5) while only the Co

\(\text{III}\) cluster has followed equation (4). This means that we have to go beyond the assumption which had used equation (4) as a basis for the hydration enthalpy calculation.

The uppermost curve figure 6 is a relative potential energy curve of Cr

\(\text{III}\) cluster for dehydration reaction of single water molecule. The highest peak of this curve at step of \(\text{③}\) represents the activation energy for the dehydration about lesser than 100 kJ mol

\(^{-1}\), followed by Al

\(\text{III}\), Fe

\(\text{III}\), Co

\(\text{III}\), Mn

\(\text{III}\), and Ni

\(\text{III}\). The activation energies for Mn

\(\text{III}\) and Co

\(\text{III}\) clusters are almost equal. The activation energies of dehydration for both directions are extremely equal. However, both values are underestimated as predicted from the vibrational frequencies (figure 3(b)). It is due to the hollow capacity of cation charge density which provides more space for 3\(\text{a}_1\) MOs shifting of faced water molecules at region \(\text{①}\). It then reduces the activation energy. Oppositely, for the Fe

\(\text{III}\) cluster, the activation is overestimated from the vibrational frequencies (figure 3(b)). Their isotropic charge density of central cation has decreased the water rotational rigidity [13] which has relaxed two neighbour water molecules to gain two H-bonds forming. The formed H-bond coordinations have conserved the dipole moment and angle \(\theta\) of the constraint water molecule. Except for Co

\(\text{III}\) cluster, the steps of \(\text{⑥}\), \(\text{⑤}\), \(\text{④}\), and \(\text{③}\) represent two-coordination bond elongation, one-coordination bond breaking, transferring proton to the constraint water, hydronium forming (\(\text{H}_3\text{O}^+\)), and hydronium releasing, respectively. Some clusters have incomplete single water molecule dehydration steps. In case of Co

\(\text{III}\) cluster, the dehydration reaction produces a pure water molecule, since the water molecules are isolated from each other.
We believe that the activation energies of the dehydration reactions should be relevant to water and ion exchange reactions, particularly for exemplified metal ion attack at polyelectrolyte. To convince our computational results, the single dehydration of Al\(^{III}\) cluster has been evaluated to obtain comparable stabilities with the Cr\(^{III}\) and Fe\(^{III}\) clusters. Based on the activation energies (figure 6), we have found that Cr\(^{III}\) cluster is more stable than Al\(^{III}\) cluster. These results do not only explain the higher number of Al\(^{III}\) binding to PVS than Cr\(^{III}\)\(^3\)[3], but they also provide another reasonable explanation for higher membrane degradation level by Fe\(^{III}\) than that of Al\(^{III}\)\(^4\) metal ion. Another experimental study\(^{46}\) on the ion exchange reaction of Al\(^{III}\) with Fe\(^{III}\) also supports our results.

4. Conclusions

The different activation energies and reaction paths on single water dehydration of \([\text{M}(\text{H}_2\text{O})_6]^{3+}\) clusters are significantly influenced by the charge density distribution of central metal ion. While the hollow-shaped distribution of Cr\(^{III}\) has increased the activation energy of single water dissociation reaction, the cones-shape distribution of Ni\(^{III}\) reduces the ion-dipole strength which enhances interactions between nearest neighbour water molecules. The isotropic charge density of Fe\(^{III}\) affects in lowering water rotational rigidities which is responsible for augmenting the activation energy. Our computational results have also exhibited that all of the dissociative reaction paths of \([\text{M}(\text{H}_2\text{O})_6]^{3+}\) clusters follow equation (5), except for the Co\(^{III}\) one.

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References

[1] Sinn C G, Dimova R and Antonietti M 2004 Macromolecules 37 3444
[2] Ohki T, Harada M and Okada T 2008 J. Phys. Chem. B 112 11863
[3] Burrows H D, Costa D, Ramos M L, Miguel M G, Teixeira M H, Pais A A C C, Valente A J M, Bastos M and Bai G 2012 Phys. Chem. Chem. Phys. 14 7950
[4] Li H et al 2010 J. Power Sources 195 8089
[5] Chegerev M, Piskunov A, Tsyis A V, Starikov K V, Jurkschat A G, Baranov K, Stash E V, Fukin A I and Georgy K 2019 Euro. J. Inor. Chem. 6 875–84
[6] Mulliken R S 1953 J. Chem. Phys. 23 1833
