

Comparative Study of Interaction of Lithium, Sodium and Potassium Ions with Water Molecules

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Abstract

The study of ion-water interaction employing theoretical models is of significant interest in various research fields. In the present study, structural features and energies for three series of ion-dipole clusters have been investigated, namely, $\text{Li}(\text{H}_2\text{O})^{n+}$, $\text{Na}(\text{H}_2\text{O})^{n+}$ and $\text{K}(\text{H}_2\text{O})^{n+}$ ions ($n = 1-3$). The results reveal that the influence of lithium ion on water is comparatively greater than sodium and potassium ions.

Key words: Alkali metal ions, water, theoretical study

1. Introduction

The ion-water cluster systems provide an effective route to extract interaction information that is difficult to obtain directly from bulk solution. Ions influence properties of water, particularly liquid-air surface tension and the solubility of proteins.¹⁻⁴ Alkali metal ions form a set of important metal ions in biological and industrial systems. Particularly, sodium and potassium ions are present in appreciable amounts in aqueous solution of living systems and are essential in transmission of nerve signals.⁵ Lithium is gaining significance in the sphere of rechargeable batteries,⁶ in glass and porcelain industry and its applications in psychiatric treatment is on the rise.⁷

Several studies, both theoretical⁸⁻¹² and experimental,¹³⁻¹⁵ have been carried out, but the spread in the data is very large and interpretation is very difficult, especially in case of X-ray diffraction due to very weak scattering effect. Consequently, understanding about structure and bonding properties of hydrated ions demands more exploration. Three alkali metal ions (Li^+ , Na^+ and K^+) have been selected in the present study and their successive energies of hydration have been calculated. The investigation aims to compare the effect of variation of both the metal ion and the number of water molecules. The paper explores various characteristics of small water-clusters (including optimal structures, structural and energy

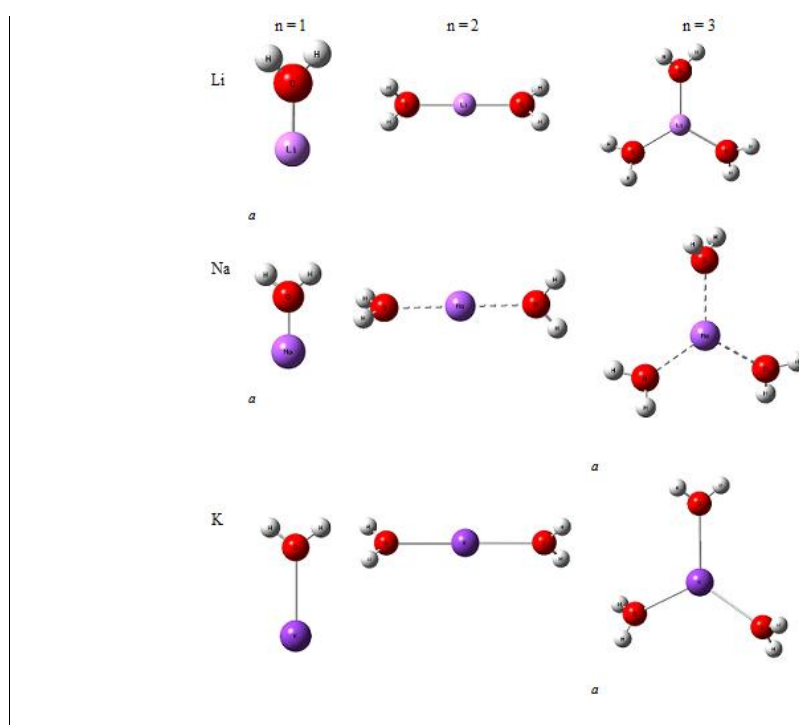
related parameters) employing density functional theory.

2. Computational Details

The DFT calculations were performed employing Gaussian 09 suite of programs¹⁶. The geometry optimization was performed at B3LYP level with 6-31+G (d, p) basis set for all calculations. The alkali metal ions under consideration are that of Li^+ , Na^+ and K^+ respectively and the number of water molecules, n , is varied from one to three.

3. Results and Discussion

Insight into the properties of small ion-water cluster can be obtained, qualitatively, from consideration of their shape and bonding. A schematic representation of the optimized geometries of $\text{M}(\text{H}_2\text{O})_n^+$ is shown in Figure 1. The $\text{M}(\text{H}_2\text{O})^+$ species belong to point- group Cs while $\text{M}(\text{H}_2\text{O})_2^+$ and $\text{M}(\text{H}_2\text{O})_3^+$ species are incorporated in C1 point-group.



|a: Geometries are less than optimized.

Figure 1: Optimized geometry structures of $\text{M}(\text{H}_2\text{O})_n^+$ clusters.

All M-O bond distances for $\text{M}(\text{H}_2\text{O})_n^+$ ($n = 2, 3$) cluster ions are almost the same for the same metal ion (Table 1). The M-O bond is lengthened with addition of water molecule. The Li-O bond length is of the order of 1.86 Å (for $n = 2$) and 1.90 Å (for $n=3$). The Na-O distance varies from 2.23 Å to 2.26 Å for $n = 2$ and 3 respectively. The corresponding bond distance for potassium ion clusters fall in the range 2.68 – 2.71 Å. These M-O bond lengths

corroborate well with reported values obtained from experimental and theoretical simulations performed earlier.¹⁷⁻²²

n	M-O Bond length in $M(H_2O)_n^+$ species		
	Li	Na	K
2	1.8665	2.2391	2.6828
	1.8665	2.2391	2.6827
3	1.9059	2.2651 ^a	2.7136 ^a
	1.9055	2.2660 ^a	2.7044 ^a
	1.9054	2.2655 ^a	2.7012 ^a

^a: Geometries are less than optimized.

Table 1: Bond lengths in Å

It is observed that O-H bond distances in the coordinating water molecules increases from 0.95 Å in free water molecule. The bond length is in the range 0.967 – 0.968 Å (0.9688 Å for $Li(H_2O)_2^+$, 0.9682 Å for $Na(H_2O)_2^+$ and 0.9677 Å for $K(H_2O)_2^+$ clusters respectively). The distance decreases for $M(H_2O)_3^+$ species.

The energy of $M(H_2O)_n^+$ ($n = 1, 2, 3$) ions (in a. u.) shows a steady decrease as the size of the cation increases from lithium to potassium. The energy (as $-E$) is plotted against atomic number, Z , Figure 2. This is in agreement with the experimental results. As the number of water molecules increase from one to three, the hydration energy records a fall (Table 2).

	n = 1	n = 2	n = 3
Li	-83.66577	-160.2616	-236.7336
Na	-238.2847	-315.0279	-391.4928
K	-676.1885	-722.6489	-829.106

Table 2: Energy of $M(H_2O)_n^+$ species in atomic units.

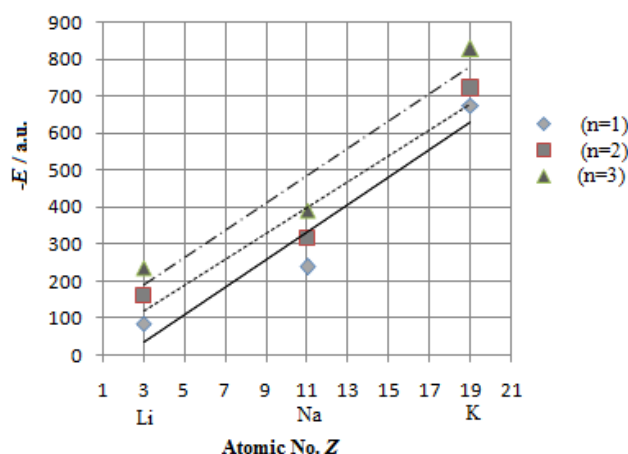


Figure 2: Energy of $M(H_2O)_n^+$ ions as a function of atomic number, Z . Dashed trend lines are shown for hydration numbers 1, 2 and 3.

4. Conclusion

In summary, the hydration behavior of the alkali metal ions is similar. A minute look at the results of theoretical investigation show that the lithium ion influences the coordinated water molecules to a greater degree and induces perceptible structural changes, compared to sodium and potassium ions. This is a consequence of its comparatively smaller size. The determination of accurate numbers of water molecules in the hydration sphere requires further studies in this area.

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