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Aqueous Micro-hydration of $\text{Na}^+(\text{H}_2\text{O})_{n=1-7}$ Clusters: DFT Study

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Abstract: Sodium ion micro-solvated clusters, $[\text{Na}(\text{H}_2\text{O})_n]^+$, $n = 1-7$, were completed by (DFT) density functional theory at B3LYP/6-311+G(d,p) level in the gaseous phase. At the ambient situation, the four, five and six micro-solvated configurations can convert from each other. The investigation of the sequential water binding energy on Na^+ obviously indicates that the influence of Na^+ on the neighboring water molecules goes beyond the first solvation layer with the hydration number of 5. The hydration number of Na^+ is 5 and the hydration space ($r_{\text{Na-O}}$) is 2.43 Å. The current study displays that all our simulations have an brilliant harmony with the diffraction result from X-ray scattering study. The vibration frequency of H_2O solvent was also determined. This work is important for additional identification of the $\text{Na}^+(\text{H}_2\text{O})_n$ clusters in aqueous medium.

Keywords: Micro-hydration; RDF; DFT; Sodium Ion.

1 Introduction

Micro-hydration studies of charged and neutral chemical ions and molecules are an important tool to interpret mechanisms, energetic, structural and spectroscopic properties of hydration at atomic levels. As the dissolved solute is placed in water solvent, there is an arrangement of the vicinity water molecules to form hydrogen bonds between the solute and solvent. As a result strong hydrogen bonded H_2O mesh is formed around the dissolved solute due to the electron arrangement of the solute. Recently, information of solvation sphere

structure have been determined by several techniques like first principal quantum chemical calculations and cluster spectroscopy. The interaction between solute and surrounding solvent molecules is interpreted on the basis of information obtained about the structural properties of these hydrated clusters. The interaction between solute and its surrounded solvent molecules is the main reason of the solvation phenomenon [1-5].

The construction and binding energy of fine ion-water clusters have a consideration in the last years [6–8] due to their consequence in interpreting the manner of separate ions in chemical and biological systems. Sodium ion aqueous solutions have an abundant portion of contemplation due to their consequence in many fields: manufacture, electrochemistry, biology, and pharmaceutical. Many trial and ideal algorithms have been estimate for the contemplation of sodium ion aqueous solutions. Many trial techniques contain X-ray scattering, neutron diffraction, EXAFS and NMR [9] which recognize the coordination number (CN) and solvation distance ($r_{\text{Na-O}}$) of $\text{Na}^+(\text{H}_2\text{O})_n$, in which the $r_{\text{Na-O}}$ is around 0.243 and the CN is from 4 to 8. The difference of CN is found to be hanging on the concentration of sodium salt. Though, the outcome of sodium ion concentration on the CN is not studied until now. Theoretical studies of sodium ions in water have been achieved with different methods which propose a smaller $r_{\text{Na-O}}$ from 2.24 to 2.39 Å [10,11]. With a larger uncertainty, the second solvation shell of Na^+ ion in aqueous solution is also calculated [12]. In this effort, the structure of $\text{Na}^+(\text{H}_2\text{O})_n$ with $n = 1-7$ are calculated with DFT calculations so as to recognize the correct CN of sodium ion in water. The greatest contestants for every important configuration size are expected. Agreeing to the structural analysis results, authors suggest information around hydration structure, for example coordination number (CN), $r_{\text{Na-O}}$ and energy for different hydrated clusters of sodium ion.

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2 Computational protocol

Geometry optimizations of $\text{Na}^+(\text{H}_2\text{O})_n$ were captured using DFT calculations at B3LYP [13,14] and the 6-311+G(d,p) base set level [15]. The starting configuration of the $\text{Na}^+(\text{H}_2\text{O})_{1-2}$ configurations were met via changing the position of H_2O solvent with consideration to Na^+ . The form of the larger clusters were reproduced from the smaller ones by joining water molecules to the Na^+ through Na–O interaction and other water molecules through OH–O(H_2O) hydrogen bonds at different place. The optimized lowest energy geometry is reached by changing the initial geometry and confirming that convergence to the similar energy was reached within 10^{-6} H also confirming that there were no imaginary frequencies.. The RMS internal forces for optimized geometries were 17×10^{-5} , 11×10^{-6} , 11×10^{-6} , 25×10^{-6} , 62×10^{-7} , 13×10^{-6} and 39×10^{-6} for $\text{Na}^+(\text{H}_2\text{O})$, $\text{Na}^+(\text{H}_2\text{O})_2$, $\text{Na}^+(\text{H}_2\text{O})_3$, $\text{Na}^+(\text{H}_2\text{O})_{4b}$, $\text{Na}^+(\text{H}_2\text{O})_{5b}$, $\text{Na}^+(\text{H}_2\text{O})_{6c}$ and $\text{Na}^+(\text{H}_2\text{O})_{7a}$, respectively. In method to reproof the achievement of the B3LYP functional, the configuration of $\text{Na}^+(\text{H}_2\text{O})_{n=1-7}$ were also optimized using BLYP functional basis sets, which supply results concurring with those of the B3LYP functional [16-18]. All structures are completed by using the computational software package Gaussian09 [19]. Authors used the Material Studio 3.2 to perform MD simulation [20]. The number of H_2O molecules in the first solvation sphere for sodium ion is determined by MD simulation in the solution phase. Material Studio 3.2 (Accelrys, Inc.) is used for the construction of simulation system that is a periodic box with $18.786 \times 18.786 \times 18.786$ Å dimensions and containing two Na^+ and two Cl^- ions surrounded by 221 H_2O solvent molecules. Na^+ and Cl^- ions are enough separated from each other in very dilute solutions. 6.9 Å is the initial distance between two ions Na^+ and Cl^- for the simulation. 298 K is the used temperature for the simulation of the system while the period of MD simulation is 50 ps with 1 fs step size. Cycles of 50 ps are followed until the coordination number of Na^+ ion is reached. Optimization and dynamics of the system box were performed using UFF level and thermostat used was Nose'. Conductor-like polarizable continuum model (CPCM) is performed to clear the effect of macroscopic solvation.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Hydrated structures

The most proper functional for the current work is the hybrid B3LYP which plays a very important role to define different structural properties. The H_2O solvents are delivered to the middle sodium ion in a step wise method holding in opinion the termination goal to dissolve the consequence of solvent. The water molecule is added to the middle ion in dissimilar thinkable means and the full constructional optimization is complete with DFT at the B3LYP level of theory. The Cartesian coordinates of the stable $\text{Na}^+(\text{H}_2\text{O})_n$ clusters at DFT/B3LYP/6-311+G (d,p) level of theory are shown in Table S1 in the Supplementary Materials. The optimized configuration and structure parameters were showed in Figure 1 and Table 1. Now we will apportionment with the thermodynamics parameter, the Gibbs free energy change of hydration (ΔG_{hyd}), the enthalpy change of hydration (ΔH_{hyd}), energy change of hydration (ΔE_{hyd}) and entropy change of hydration (ΔS_{hyd}). These parameters are of universal attention beside there are experimentally calculated parameters for solute hydration. The obtained numbers of these parameters are shown in Table 2 at DFT/B3LYP/6-311+G (d,p) level of theory. The thermodynamic parameters of the $\text{Na}^+(\text{H}_2\text{O})_n$ clusters are calculated according to the next equations:

$$\Delta G_{\text{hyd}} = G_{\text{solute}-(\text{H}_2\text{O})n} - G_{\text{solute}} - nG_{\text{H}_2\text{O}} \quad (1)$$

$$\Delta H_{\text{hyd}} = H_{\text{solute}-(\text{H}_2\text{O})n} - H_{\text{solute}} - nH_{\text{H}_2\text{O}} \quad (2)$$

$$\Delta S_{\text{hyd}} = S_{\text{solute}-(\text{H}_2\text{O})n} - S_{\text{solute}} - nS_{\text{H}_2\text{O}} \quad (3)$$

$$\Delta E_{\text{hyd}} = E_{\text{solute}-(\text{H}_2\text{O})n} - E_{\text{solute}} - nE_{\text{H}_2\text{O}} \quad (4)$$

Where $G_{\text{solute}-(\text{H}_2\text{O})n}$, $H_{\text{solute}-(\text{H}_2\text{O})n}$, $S_{\text{solute}-(\text{H}_2\text{O})n}$ and $E_{\text{solute}-(\text{H}_2\text{O})n}$ are Gibbs free energy, enthalpy, entropy and energy of hydrated $\text{Na}^+(\text{H}_2\text{O})_n$ clusters respectively. G_{solute} , H_{solute} , S_{solute} and E_{solute} are the same parameters for a single sodium ion. $G_{\text{H}_2\text{O}}$, $H_{\text{H}_2\text{O}}$, $S_{\text{H}_2\text{O}}$, and $E_{\text{H}_2\text{O}}$ are the same parameters for water molecule.

The energy change of hydration (ΔE_{hyd}) is enlarged as presented in Table 1 by the accumulation of water molecules. The identical action is seen for further parameters ΔG_{hyd} , ΔS_{hyd} and ΔH_{hyd} . The hydration distance $r_{\text{Na-O}}$ is increasing with the increase of water

Figure 1: Optimized geometries of hydrated sodium ion clusters at DFT/B3LYP/6-311+G(d,p) levels of theory.

Table 1: Calculated values of different structural, energies and thermodynamic parameters of $\text{Na}^+ - n\text{H}_2\text{O}$ ($n = 1-7$) hydrated clusters at DFT/B3LYP/6-311+G(d,p) level of theory basis function.

System	$G_{\text{hyd}} / \text{kJ.mol}^{-1} \times 10^3$	$S_{\text{hyd}} / \text{cal.mol}^{-1} \cdot \text{K}^{-1}$	$H_{\text{hyd}} / \text{kJ.mol}^{-1} \times 10^3$	$E_{\text{hyd}} / \text{kJ.mol}^{-1} \times 10^3$
$\text{Na}^+(\text{H}_2\text{O})$	-626.407	58.471	-626.334	-626.336
$\text{Na}^+(\text{H}_2\text{O})_2$	-827.203	79.728	-827.103	-827.106
$\text{Na}^+(\text{H}_2\text{O})_3$	-1027.644	91.942	-1028.043	-1028.046
$\text{Na}^+(\text{H}_2\text{O})_{4a}$	-1228.731	120.630	-1228.581	-1228.587
$\text{Na}^+(\text{H}_2\text{O})_{4b}$	-1228.744	128.438	-1228.584	-1228.587
$\text{Na}^+(\text{H}_2\text{O})_{4c}$	-1228.705	127.867	-1228.216	-1228.219
$\text{Na}^+(\text{H}_2\text{O})_{5a}$	-1429.472	137.263	-1429.301	-1429.303
$\text{Na}^+(\text{H}_2\text{O})_{5b}$	-1429.479	133.420	-1429.314	-1429.317
$\text{Na}^+(\text{H}_2\text{O})_{5c}$	-1429.469	123.961	-1429.282	-1429.288
$\text{Na}^+(\text{H}_2\text{O})_{6a}$	-1630.202	139.221	-1630.028	-1630.033
$\text{Na}^+(\text{H}_2\text{O})_{6b}$	-1630.204	142.709	-1630.028	-1630.031
$\text{Na}^+(\text{H}_2\text{O})_{6c}$	-1630.220	142.783	-1630.041	-1630.044
$\text{Na}^+(\text{H}_2\text{O})_{6d}$	-1630.175	130.762	-1630.012	-1630.015
$\text{Na}^+(\text{H}_2\text{O})_{7a}$	-1830.931	152.735	-1830.740	-1830.742
$\text{Na}^+(\text{H}_2\text{O})_{7b}$	-1830.931	156.903	-1830.737	-1830.740
$\text{Na}^+(\text{H}_2\text{O})_{7c}$	-1830.947	159.230	-1830.750	-1830.753
$\text{Na}^+(\text{H}_2\text{O})_{7d}$	-1830.950	158.518	-1830.753	-1830.756

Table 2: Calculated values of the Gibbs free energy change of hydration (ΔG_{hyd}), the enthalpy change of hydration (ΔH_{hyd}), energy change of hydration (ΔE_{hyd}), entropy change of hydration (ΔS_{hyd}) and bond length of $\text{Na}^+(\text{H}_2\text{O})_{n=1-7}$ hydrated clusters at DFT/B3LYP/6-311+G(d,p) level of theory basis function.

System	$\Delta G_{\text{hyd}} / \text{kJ.mol}^{-1}$	$\Delta S_{\text{hyd}} / \text{cal.mol}^{-1} \cdot \text{K}^{-1}$	$\Delta H_{\text{hyd}} / \text{kJ.mol}^{-1}$	$\Delta E_{\text{hyd}} / \text{kJ.mol}^{-1}$	Bond length / Å
$\text{Na}^+(\text{H}_2\text{O})$	-1294.372	-23.556	-1320.627	-1318.001	2.225
$\text{Na}^+(\text{H}_2\text{O})_2$	-2572.990	-48.990	-2630.751	-2630.000	2.248
$\text{Na}^+(\text{H}_2\text{O})_3$	-3497.166	-83.467	-4111.533	-4103.657	2.254
$\text{Na}^+(\text{H}_2\text{O})_{4a}$	-5067.22	-101.470	-5190.614	-5182.737	2.306
$\text{Na}^+(\text{H}_2\text{O})_{4b}$	-5080.343	-93.662	-5193.239	-5182.737	2.208
$\text{Na}^+(\text{H}_2\text{O})_{4c}$	-5040.96	-94.233	-4825.669	-5148.606	2.108
$\text{Na}^+(\text{H}_2\text{O})_{5a}$	-6290.698	-131.528	-6450.854	-6437.726	2.294
$\text{Na}^+(\text{H}_2\text{O})_{5b}$	-6298.575	-135.371	-6463.981	-6450.854	2.307
$\text{Na}^+(\text{H}_2\text{O})_{5c}$	-6288.073	-144.830	-6432.48	-6421.973	2.282
$\text{Na}^+(\text{H}_2\text{O})_{6a}$	-7503.68	-176.261	-7718.97	-7705.843	2.279
$\text{Na}^+(\text{H}_2\text{O})_{6b}$	-7506.305	-172.773	-7718.97	-7703.218	2.303
$\text{Na}^+(\text{H}_2\text{O})_{6c}$	-7522.058	-172.699	-7732.098	-7716.345	2.298
$\text{Na}^+(\text{H}_2\text{O})_{6d}$	-7477.425	-184.720	-7703.218	-7687.465	2.263
$\text{Na}^+(\text{H}_2\text{O})_{7a}$	-8716.66	-209.438	-8971.334	-8952.96	2.379
$\text{Na}^+(\text{H}_2\text{O})_{7b}$	-8716.66	-205.270	-8968.709	-8950.33	2.329
$\text{Na}^+(\text{H}_2\text{O})_{7c}$	-8732.414	-202.943	-8981.836	-8963.458	2.313
$\text{Na}^+(\text{H}_2\text{O})_{7d}$	-8735.039	-203.655	-8984.462	-8966.083	2.292

molecules, number n . The first hydration space between Na^+ and oxygen of water molecular ($r_{\text{Na-O}}$) of $\text{Na}^+(\text{H}_2\text{O})$ is 2.189 Å. The greatest stable structure of $\text{Na}^+(\text{H}_2\text{O})_{n=2}$ is linear with hydration distance 2.210 Å, and for $\text{Na}^+(\text{H}_2\text{O})_{n=3}$ is trigonal planar with hydration space 2.216 Å. As n rises to 4, three categories of stable structures, including three-coordinated conformers in the interior shell ($\text{Na}^+(\text{H}_2\text{O})_{4a}$), tetrahedron ($\text{Na}^+(\text{H}_2\text{O})_{4b}$) and two-coordinated conformers in interior shell ($\text{Na}^+(\text{H}_2\text{O})_{4c}$).

The $r_{\text{Na-O}}$ of $\text{Na}^+(\text{H}_2\text{O})_{4b}$ is 2.269 Å, which is longer than that of $\text{Na}^+(\text{H}_2\text{O})_{4a}$ and $\text{Na}^+(\text{H}_2\text{O})_{4c}$. The most stable structure of $\text{Na}^+(\text{H}_2\text{O})_4$ is $\text{Na}^+(\text{H}_2\text{O})_{4b}$ and the minor stable structure is $\text{Na}^+(\text{H}_2\text{O})_{4c}$ with an energy variance of 8.157 kcal/mol parallel to that of $\text{Na}^+(\text{H}_2\text{O})_{4b}$. 5 water molecules are coordinated with Na^+ , which forms first hydration coat with the $r_{\text{Na-O}}$ 2.244 Å in $\text{Na}^+(\text{H}_2\text{O})_{5a}$. The second two structures; $\text{Na}^+(\text{H}_2\text{O})_{5b}$ has a tetrahedron interior shell and, $\text{Na}^+(\text{H}_2\text{O})_{5c}$ has a trigonal interior shell with the second shell water

molecules with each accepting two hydrogen bonds from the interior shell which creates a more dense and constant structure. The $r_{\text{Na-O}}$ of $\text{Na}^+(\text{H}_2\text{O})_{5b}$ and $\text{Na}^+(\text{H}_2\text{O})_{5c}$ is 2.259 Å and 2.182 Å, respectively. $\text{Na}^+(\text{H}_2\text{O})_{5b}$ is the most stable structure of five coordinated clusters. For six coordinated configurations, four types of stable conformers, $\text{Na}^+(\text{H}_2\text{O})_{6a}$, $\text{Na}^+(\text{H}_2\text{O})_{6b}$, $\text{Na}^+(\text{H}_2\text{O})_{6c}$ and $\text{Na}^+(\text{H}_2\text{O})_{6d}$, are obtainable. In this work, each configuration has a six-coordinated hydration configuration with $r_{\text{Na-O}}$ 2.238 for $\text{Na}^+(\text{H}_2\text{O})_{6a}$, 2.262 for $\text{Na}^+(\text{H}_2\text{O})_{6b}$, 2.261 for $\text{Na}^+(\text{H}_2\text{O})_{6c}$ and 2.245 for $\text{Na}^+(\text{H}_2\text{O})_{6d}$. $\text{Na}^+(\text{H}_2\text{O})_{6c}$ is the greatest stable configuration of six coordinated clusters. For seven water molecules ($n=7$), the greatest stable construction is $\text{Na}^+(\text{H}_2\text{O})_{7c}$ which has a five coordinated interior shell and two exterior water molecules connected to the inside molecules by hydrogen bonds. The slight stable configuration is $\text{Na}^+(\text{H}_2\text{O})_{7d}$ with energy variance 6.378 kcal/mol from $\text{Na}^+(\text{H}_2\text{O})_{7c}$. The further two configurations are $\text{Na}^+(\text{H}_2\text{O})_{7a}$ and $\text{Na}^+(\text{H}_2\text{O})_{7b}$ with seven and six coordinated water molecules in the interior shell. The obtained quantities of hydration free energy ($\Delta\Delta G_{\text{hyd}}$) of the hydrated clusters rise with the increasing of the H_2O molecules numbers, indicating the interaction between solvent and dissolved ion and additional interactions between solvent molecules by H-bonds [21-24]. When the H_2O solvent molecules are added, the hydration tends toward more exothermic and, in this way, the solvation energy per one H_2O solvent molecule finishes up remarkably smaller in magnitude. The previous tendency possibly appears due to H_2O – H_2O repulsion when the primary solvation shell is totally full by H_2O solvent. The zero value of incremental free energy of hydration could not be as it is essentially the variance among the electronic energy of the successive metal ion complex minus the energy of a single water molecule as set in the next eq.

$${}^{\circ}\Delta\Delta G_{\text{hyd}} = G_{\text{solute}-(\text{H}_2\text{O})n} - (G_{\text{solute}-(\text{H}_2\text{O})n-1} + G_{(\text{H}_2\text{O})}) \quad (5)$$

Hence, with a particular final aim to acquire a stronger representation, the free energy of hydration ($\Delta\Delta G_{\text{hyd}}$) that arises from the step wise addition of solvent molecules is shown in Figure 2. The value of ($\Delta\Delta G_{\text{hyd}}$) for the hydrated clusters, $\text{Na}^+(\text{H}_2\text{O})_n$, grows meaningfully as the length of the individual water particle ties to the solute particle. The polarization of the Na^+ drives outside the solvation primary shell though it is difficult to expect the sodium metal ion solvation number from this figure. Figure 2 shows that ($\Delta\Delta G_{\text{hyd}}$) with uncertain behavior with increasing the water molecules until $n=5$. After $n=5$, ($\Delta\Delta G_{\text{hyd}}$) has a perfect behavior. These features not only provide that the sodium ion mostly cooperates with its adjacent water molecules,

Figure 2: The relation between incremental hydration energy ($\Delta\Delta G_{\text{hyd}}$) and the number of water molecules in $\text{Na}^+(\text{H}_2\text{O})_n$ clusters at DFT/B3LYP/6-311+G(d,p) level of the theory.

but also suggest that the saturated hydration sphere mainly occurs when $n=5.2$. This occurrence advises that structural properties of the approximate complete solvent shell for $\text{Na}^+(\text{H}_2\text{O})_n$ clusters would not actually differ with extra water molecules as $n > 5$. It is decided that the saturated hydration number is 5.2 in the first hydration coat for $\text{Na}^+(\text{H}_2\text{O})_n$. To determine the effect of macroscopic hydration on sodium ion, popular conductor-like polarizable continuum model (CPCM) are applied to find optimized geometries. It is observed that bulk hydration of sodium ion adopting macroscopic solvent models like the polarized continuum model (CPCM) at the DFT/B3LYP/6-311+G(d,p) level of electronic structure theory does not change the geometrical parameters significantly. The electrostatic interaction between the wave function of the solute and dielectric model of bulk solvent that is generated from a number of surface charges on a definite elements of the cavity is taken in consideration by PCM model. The O– Na^+ bond length of $\text{Na}^+(\text{H}_2\text{O})_n$ is calculated by applying the CPCM model, and there is an increase in its values (the bond become longer). The O – Na^+ bond length is found to be 2.317 Å, 2.328 Å and 2.334 Å for $\text{Na}^+(\text{H}_2\text{O})$, $\text{Na}^+(\text{H}_2\text{O})_2$ and $\text{Na}^+(\text{H}_2\text{O})_3$ respectively. The O – Na^+ bond length is found to be 2.387 Å, 2.377 Å, 2.379 and 2.386 Å for $\text{Na}^+(\text{H}_2\text{O})_4$, $\text{Na}^+(\text{H}_2\text{O})_5$, $\text{Na}^+(\text{H}_2\text{O})_6$ and $\text{Na}^+(\text{H}_2\text{O})_7$ respectively. The elongation of O– Na^+ may be as a result of solvent-solvent interaction which effect on the solute-solvent interaction and make the solute (Na^+)-solvent(O) bond become longer.

3.2 Radial distribution function (RDF)

The coordination number of the first solvation shell is found to be 5 according to the quantum electronic configuration

Figure 3: The relation between radial distribution function ($g(r)_{\text{Na-O}}$) and the distance (r) obtained from the UFF-based classical MD simulation.

for Na^+ solvated ion. The classical MD simulation has been performed to confirm this result for aqueous Na^+ solution to obtain a good image about the configuration and the coordination number of the solvation layers that surrounding the solvated ion. Usually the coordination number calculations in various solvents is done according to the partial radial distribution function, $g_{\alpha\beta}$. α and β are molecules of different sorts in which β molecule has a spherical width dr , with a separation r from α molecule and the $n_{\alpha\beta}$ is the coordination number which can be determined by the integration of the RDF [25], $g_{\alpha\beta}(r)$ with respect to r as

$$n_{\alpha\beta} = \rho_{\beta} \int_0^r g_{\alpha\beta}(r) r^2 dr \quad (6)$$

where, ρ_{β} is the number density of atom type β . The measured RDF acquired from the present recognized classical MD simulation is shown in Figure 3. The first solvation peak is located at 2.2 Å but a bit more than the value of gas phase specifies that the solvation produces a slight density of the first solvation layer. The sodium ion in the aqueous medium is rigid and stable as indicated from the high intensity behavior of the first solvation layer peak. The integrated value of the radial distribution function indicates that the primary hydration layer of sodium ion is satisfied by five H_2O molecules. Consequently, five H_2O molecules is the correct solvation number of designated ion in aqueous environment. Figure 3 shows the sequentially coordination number $n(r)$ of the hydrated sodium ion. From the figure, it is seen that, $n(r)$

integrates to five oxygens at around 2.2 Å. Therefore, the sodium ion first hydration layer is constructed to have five H_2O molecules as obtained from RDF.

3.3 IR spectrum

IR can support in defining the time of proton transmission from the solute molecule to solvent water molecules, by the occurrence of aqueous proton creating new peaks in the IR band. Matching the simulated IR spectra with that of gas phase IR spectra of $\text{Na}^+ \cdot n\text{H}_2\text{O}$ clusters can aid in confirming the configurations expected. IR spectrum simulated is constructed on harmonic calculations. To account for the anharmonic nature of the chemical bonds, a scaling element requests be combined to the considered spectrum. The IR spectrum of $\text{Na}^+(\text{H}_2\text{O})_{n=1-7}$ clusters and single water molecule at DFT/B3LYP/6-311+G(d,p) level of theory is seen in Figure 4 and the frequencies are tabulated in Table 3. The symmetric stretching vibration (ν_{sym}) and asymmetric stretching vibration (ν_{asym}) of a single water molecule is at 3340.47 and 3409.39 cm^{-1} , respectively while the symmetric scissoring vibration is at 1437.19 cm^{-1} . These vibrations are adjacent to the experimental standards (3657 and 3756 cm^{-1}) [26]. When Na^+ attached with $n=1-3$ water molecules to form the first hydration sphere, the parallels ν_{sym} are 3798.56, 3806.76 and 3803.99 cm^{-1} and the ν_{asym} are 3883.20, 3893.60, 3887.67 cm^{-1} . It is obviously detected that these matching frequencies of $\text{Na}^+(\text{H}_2\text{O})_{n=1-3}$ parallel to that of

Figure 4: The IR spectrum of (a) H_2O ; (b) $\text{Na}^+(\text{H}_2\text{O})$; (c) $\text{Na}^+(\text{H}_2\text{O})_2$; (d) $\text{Na}^+(\text{H}_2\text{O})_3$; (e) $\text{Na}^+(\text{H}_2\text{O})_{4b}$; (f) $\text{Na}^+(\text{H}_2\text{O})_{5b}$; (g) $\text{Na}^+(\text{H}_2\text{O})_{6c}$; (h) $\text{Na}^+(\text{H}_2\text{O})_{7a}$.

Table 3: The vibration frequencies of $\text{Na}^+(\text{H}_2\text{O})_n$ at DFT/B3LYP/6-311+G(d,p) level of theory.

System	ν_{sym}
$\text{Na}^+(\text{H}_2\text{O})$	3798.56-333.63-342.25-455.83-3883.20-1676.43
$\text{Na}^+(\text{H}_2\text{O})_2$	28.21-35.74-240.54-302.02-317.47-377.69-419.40-444.30-1672.56-1673.83 3805.82-3806.76-3893.60-3893.89
$\text{Na}^+(\text{H}_2\text{O})_3$	17.15-20.86-93.29-244.61-317.24-323.94-332.80-389.02-422.56-449.87- 1555.29-1678.23-1680.23-3794.16-3802.99-3803.99-3887.67-3888.64- 3974.69
$\text{Na}^+(\text{H}_2\text{O})_{4b}$	38.41-43.87-47.42-47.49-65.70-91.17-92.23-100.42-163.14-216.39-228.52 231.05-267.17-279.90-280.25-291.85-353.47-380.72-380.83-396.10- 1659.45-1660.29-1660.33-1662.77-3815.97-3816.03-3816.09-3817.38- 3913.58-3913.68-3913.85-3914.06
$\text{Na}^+(\text{H}_2\text{O})_{5b}$	28.10-40.74-50.19-52.05-77.89-90.30-98.00-146.61-162.63-179.35-187.17 216.41-221.64-226.37-231.56-248.21-261.31-277.98-294.51-311.52-358.98 393.77-503.18-540.07-664.92-681.10-1640.58-1652.15-1656.04-1656.99- 1687.34-3648.52-3680.15-3790.33-3818.16-3818.73-3890.51-3892.99- 3895.37-3918.18-3918.20
$\text{Na}^+(\text{H}_2\text{O})_{6c}$	25.74-25.75-36.84-68.33-72.52-72.53-114.59-139.10-153.06-153.11-175.00- 175.06-199.24-208.06-221.83-226.31-273.97-251.07-251.78-278.41-278.43- 333.81-375.82-375.84-486.60-522.62-534.19-645.78-649.08-667.96-668.00- 1637.95-1638.75-1645.49-1645.50-1682.60-1683.06-3660.30-3660.32-3688.25 -3692.36-3792.32-3792.33-3893.47-3893.48-3896.88-3896.92-3899.31-3899.44
$\text{Na}^+(\text{H}_2\text{O})_{7a}$	58.94-68.28-80.80-90.75-104.53-111.78-128.81-139.49-143.40-168.90-188.43- 211.04-233.88-246.99-257.00-271.79-277.53-281.60-301.92-308.63-322.63- 346.35-349.80-368.23-370.70-408.84-434.49-474.48-488.88-531.15-534.17- 547.03-680.67-697.21-718.64-774.98-781.72-890.00-1611.72-1617.81-1623.81 -1638.26-1676.53-1679.92-1691.14-3475.54-3529.57-3562.58-3612.59-3635.33- 3689.58-3739.43-3864.42-3870.47-3872.19-3876.93-3883.93-3890.12 -3905.10

the single water molecular have a red shift. Additionally, this occurrence was too stated in other arrangements $\text{Mm}^+(\text{H}_2\text{O})_n$ [26–27]. In the meantime, the ν_{sym} and ν_{asym} have a blue shift with growing the number of hydrated water molecules from 1 to 3. For $\text{Na}^+(\text{H}_2\text{O})_{4b}$ the ν_{sym} is at 3817.38 cm^{-1} and the ν_{asym} is at 3913.58 cm^{-1} . For $\text{Na}^+(\text{H}_2\text{O})_{5b}$ ν_{sym} and ν_{asym} are at 3818.16 and 3818.13, correspondingly. For $\text{Na}^+(\text{H}_2\text{O})_{6c}$ the ν_{sym} is at 3792.33 cm^{-1} and the ν_{asym} is at 3893.47 cm^{-1} . For $\text{Na}^+(\text{H}_2\text{O})_{7a}$ the ν_{sym} is at 3739.43 cm^{-1} and the ν_{asym} is at 3864.42 cm^{-1} . For the solvation phenomenon by five water molecules, significant changes with the intensity form and major peaks of H_2O are fundamentally repressed and numbers are blue shifted. Similarly, particular intensities for the main peaks are altered. This outcome may be predictable due to the formation of the first solvation sphere layer to the adding of water molecule to $\text{Na}^+(\text{H}_2\text{O})_4$. In conclusion, the results obtained by the current study can provide an

important vision for a thorough understanding of several chemical methods related to the hydration of sodium ion, particularly concerning ion concentration, in the wide area of chemical physics containing biological and atmospheric phenomena.

4 Conclusions

In the current study we scanned the progression of geometrical parameters and the sub-atomic level free energies of solvation for the optimized sodium ion aqueous clusters with $n = 1-7$ at DFT/B3LYP/6-311+G(d,p) basis sets of the theory. By the addition of an extra water molecule to central sodium ion, there is a decrease in the Na-O distance. There is an agreement between our geometry optimizations for sodium ion and previous experimental results. Both indicate that sodium ion has five water

molecules in the primary solvation sphere. There is no change in the coordination number due to solvation as approved by the calculated coordination number by force field classical MD simulation. The predictable equilibrium Na–oxygen space of 2.2 Å at the current level of theory is in bright covenant with the outcome of diffraction for the hydrated clusters. The correct prediction of sodium ion coordination number is obtained from the combination of results picked up from RDF and the quantum chemical DFT calculations of hydration free energy. DFT/B3LYP/6-311+G(d,p) basis sets is used for prediction of H₂O molecule and Na⁺(H₂O)_n clusters infrared bands. The matching frequencies of Na⁺(H₂O)_n paralleled that of the single water molecule have an affinity for red shift. The additional hydrogen bonds formed between water molecules showed the lesser vibration frequency seen in the IR bands. The consequence of the work could make progress in predicting the hydration progression of alkali metal ions that happens in biological and atmospheric sciences, and the work could be an excellent addition in the current scientific folder of chemical and physical investigations.

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