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Study of Solvation of Fluoride and Chloride Ions in Water: A Theoretical Approach

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Abstract

Theoretical methods have been utilized to study the solvation of fluoride and chloride ions by water. The number of water molecules has been varied from one to four. Geometry optimization has been performed using B3LYP level employing two different basis sets, 6-311G++ and LanL2DZ and also HF method with 6-311G++ basis set. The results have been compared.

Keywords: salvation, fluoride, chloride, Ions

1. INTRODUCTION

Solvation effects play a significant role in different spheres of chemistry *viz.* reaction mechanism, spectroscopy and kinetics. Moreover, the physical and chemical properties of ions in water solution are of considerable importance in many biological and industrial processes.[1] On exploring the coordination shell of ions in solution,[2-4] it is observed that cations tend to bind to the oxygen atom of the water molecule with the hydrogen atoms pointing away. On the other hand, anion shows a tendency to bind to only one of the two hydrogen atoms of an adjacent water molecule in an asymmetric manner. This difference in the mode of binding of water to cations and anions is of considerable significance. Water molecules surrounding a cation will tend to avoid each other, where as in case of anion bound water, the free hydrogen is more favourably oriented to get associated with other surrounding water molecules leading to a network in hydration shell. Anion-water clusters, thus, form one of the typical solute-solvent models. Halide ions, particularly fluoride and chloride ions interact strongly with water molecules. Therefore, fluoride and chloride ions in aqueous solution have been studied employing experimental techniques[5,6] and theoretical approaches.[7-13] Many aspects remain unresolved regarding the structure of solvent shell surrounding simple ions and accompanying chemical consequences, despite several studies undertaken in the past.

In this study, the structure and binding energies of hydrated halide ion clusters have been investigated. Small water clusters (n = 1 – 4) are focused upon because of computational limitation. Although the electrostatic contribution is dominant in the total binding energy of these ionic clusters, the local structures are determined by anion-water and water-water interactions. The O–H stretching vibrations are used as probe to address the intermolecular rearrangement that is associated with solvation of halide ions. A comparison of structural and energy parameters of small $[X(H_2O)_n]^-$ clusters [X = F, Cl] obtained from such theoretical studies indicates a strong dependence on the method employed.

2. COMPUTATIONAL DETAILS

Here, geometry optimization has been performed at B3LYP using two basis sets, 6-311G++ and LanL2DZ, and for HF level, 6-311G++ basis set has been used. The energy of the optimized structure has been taken into consideration during calculation of total and differential binding energies for the different species. The fluoride and chloride ions have been selected for the present study and the number of water molecules has been varied from one to four. All the computation has been done using Gaussian 09 program package.[14]

3. RESULTS AND DISCUSSION

The schematic representation of optimized structures of $[X(H_2O)_n]^-$ species (n = 1 – 4) are depicted in Fig. 1 and Fig. 2 respectively.. In the present contribution, X denotes fluoride and chloride ions. Selected structural parameters obtained from geometry optimization are presented in Table 1.

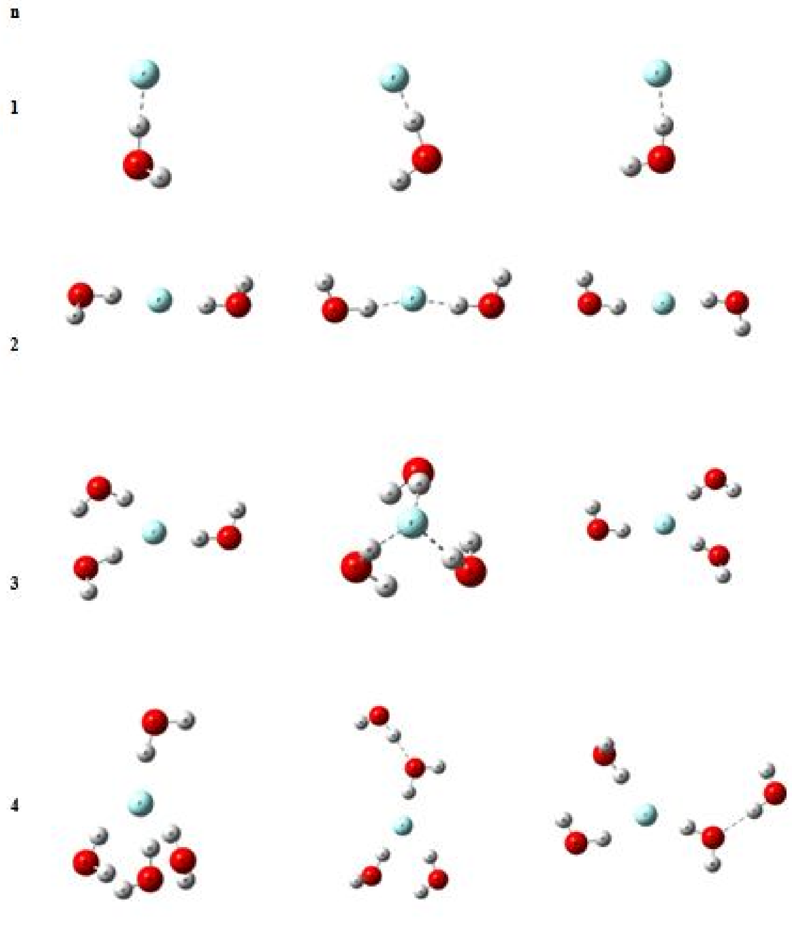

Figure 1: Optimised structures for $F^-(H_2O)_n$ cluster (n = 1 - 4). The first column represents geometry from 6-311g++ basis set and second column represents that from LANL2DZ basis set at B3LYP level of calculation. The third column displays the geometry obtained from HF level of calculation.

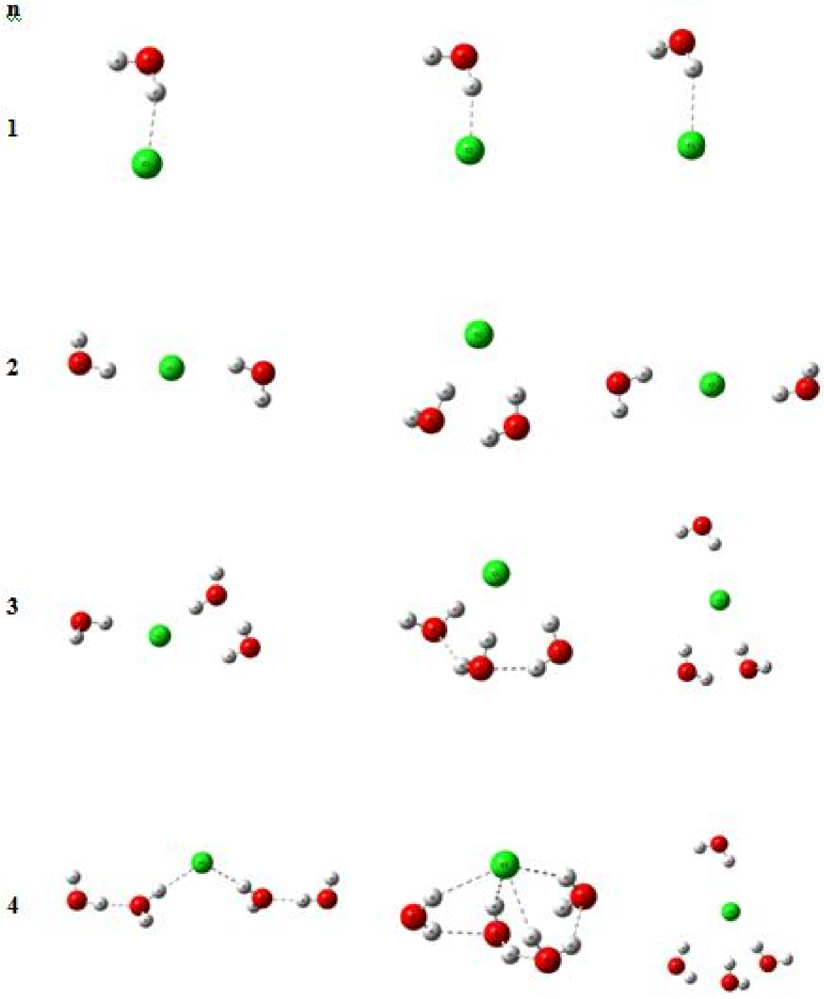

Figure 2: Optimised structures for $Cl^-(H_2O)_n$ cluster (n = 1 - 4). The first column represents geometry obtained from 6-311g++ level and second column represents that from LANL2DZ level of calculation.

Table 1: Selected bond distances (Å) and bond angles (°).

n	$F^-(H_2O)_n$					
	B3LYP / 6-311g++		B3LYP / LANL2DZ		HF / 6-311g++	
	$F\cdots H_{near}$	$\theta(F\cdots H\text{-}O)$	$F\cdots H_{near}$	$\theta(F\cdots H\text{-}O)$	$F\cdots H_{near}$	$\theta(F\cdots H\text{-}O)$
1	1.447	172.6	1.317	175.5	1.539	170.0
2	1.526	170.5	1.457	171.3	1.584	169.6
	1.526	170.5	1.458	171.3	1.584	169.6
3	1.763	153.8	1.642	156.3	1.635	169.0
	1.574	171.1	1.643	156.2	1.754	158.4
	1.556	168.4	1.644	156.1	1.625	169.5
4	1.766	152.6	1.538	167.9	1.551	175.5
	1.737	154.8	1.731	154.1	1.751	160.9
	1.617	169.9	1.419	174.5	1.646	168.9
	1.761	153.9				

n	$Cl^-(H_2O)_n$					
	B3LYP / 6-311g++		B3LYP / LANL2DZ		HF / 6-311g++	
	$Cl\cdots H_{near}$	$\theta(Cl\cdots H\text{-}O)$	$Cl\cdots H_{near}$	$\theta(Cl\cdots H\text{-}O)$	$Cl\cdots H_{near}$	$\theta(Cl\cdots H\text{-}O)$
1	2.203	162.0	2.088	164.5	2.424	152.1
2	2.238	159.9	2.068	164.2	2.433	151.5
	2.239	159.7	2.379	148.5	2.433	151.5
3	2.254	161.3	2.089	162.7	2.298	160.7
	2.112	165.2	2.372	144.6	2.904	137.9
	2.914	133.3	2.486	148.9	2.444	151.9
4	2.099	171.5	2.496	150.9	2.447	153.8
	2.100	171.4	2.261	152.4	2.865	144.5
			2.412	141.7	2.788	132.5
			2.317	149.3	2.299	160.6

$[F(H_2O)_n]^-$ clusters: For $[F(H_2O)]^-$ species, the optimized structure takes the C_S symmetry for both methods of calculation. The F…H_{near} distance and the F…H-O angle are comparable in both methods of calculation. The ionic hydrogen bonded structure is also exhibited through the lowering of stretching frequency of the O-H bond linked to fluoride ion compared to that of unbound water molecule (Table 2). In case of $[F(H_2O)_2]^-$, the ion is optimized with C_1 symmetry for calculations involving 6-311g++ basis set (for both B3LYP and HF level), while it takes up C_S symmetry with LanL2DZ basis set. The structure is symmetrical considering the F…H_{near} distance and the F…H-O angle. The structures obtained from 6-311++ level possess a centre of inversion located on the fluoride ion. The optimized geometry for $[F(H_2O)_3]^-$ species takes up C_1 symmetry for all computation methods. At 6-311g++ level, the bond length r(F…H_{near}) is 1.556 – 1.763 Å (for B3LYP), 1.625 – 1.754Å (for HF) and the bond angle (F…H-O) varies between 153.8 – 171.1° (for B3LYP), 158.4° - 169.5° (for HF). The geometry assumes an isosceles triangle with F^- ion located above the plane (D = 173.8/ 179.3). However, in case of study with LanL2DZ basis set, the $[F(H_2O)_3]^-$ cluster is comparatively more symmetrical in geometry. The three water molecules form an equilateral triangle, with the anion placed slightly above the triangular plane (D = 84.1). The F…H_{near} distance is ~ 1.64 Å and the F…H-O angle is ~ 156°. Investigation employing both methods show that the $[F(H_2O)_4]^-$ anionic cluster assumes C_1 symmetry. The optimized geometry from 6-311g++ basis set shows that the fluoride ion is asymmetrically surrounded by water. At B3LYP level, three water molecules are almost equidistant (~ 1.7 Å) and the fourth water molecule is located marginally closer r(F…H_{near} 1.617 Å) to the central ion. The F…H-O angle is in the range 152.6 – 169.9°. It is interesting to note that three of the four water molecules are within hydrogen bonding distance (2.5 Å) of each other with r(O…H) 2.29 – 2.41 Å. The calculation using LanL2DZ basis set and at HF level also displays an asymmetric structure with three water molecules encircling the fluoride ion, r(F…H_{near}) 1.419 – 1.731 Å/ 1.551 – 1.751 Å. The fourth H_2O molecule at a distance of 3.747 Å/ 3.87Å from the F^- ion presumably forms a second hydration shell with O…H 1.59 Å/ 1.77Å and O-H…O 173°.

Table 2: Stretching frequency (in cm^{-1}) of O-H bond in free water and $X^-(H_2O)$ species:

$X^-(H_2O)$	B3LYP / 6-311g++		B3LYP / LANL2DZ		HF / 6-311g++	
	O-H (water)	$O-H_X$	O-H (water)	$O-H_X$	O-H (water)	$O-H_X$
$F^-(H_2O)$	3812.42	2311.67	3865.2	1941.22	4009.29	3081.70
$Cl^-(H_2O)$	3812.42	3260.69	3865.2	3148.89	4009.29	3872.47

X = F, Cl; $O-H_X$ refers to O-H bond linked to X^- ion.

Table 3: Total binding energies and differential binding energies for $[F(H_2O)_n]^-$ clusters

n	Expt.[a] *B. E.* (kcal/mol)	*B. E.*			Expt.[a] ΔD_e (kcal/mol)	ΔD_e		
		B3LYP / 6-311g++	B3LYP / LANL2DZ	HF / 6-311g++		B3LYP / 6-311g++	B3LYP / LANL2DZ	HF / 6-311g++
1	- 23.3	- 30.7	- 44.1	-26.3	- 23.3	- 30.7	- 44.1	-26.3
2	- 42.5	- 55.5	- 73.9	-49.4	- 19.2	- 24.8	- 29.4	-23.1
3	- 57.8	- 75.0	- 100.3	-67.4	- 15.3	- 19.5	- 26.8	-18.1
4	- 71.7	- 92.5	- 117.7	-82.9	- 13.9	- 16.2	- 17.4	-15.6

[a] Experimental values taken from Ref. no. [15, 16]

Table 4: Total binding energies and differential binding energies for $[Cl(H_2O)_n]^-$ clusters

n	Expt.[b] *B. E.* (kcal/mol)	*B. E.*			Expt.[b] ΔD_e (kcal/mol)	ΔD_e		
		B3LYP / 6-311g++	B3LYP / LANL2DZ	HF / 6-311g++		B3LYP / 6-311g++	B3LYP / LANL2DZ	HF / 6-311g++
1	- 14.7	- 16.2	- 23.1	-13.6	- 14.7	- 23.1	- 23.1	-13.6
2	- 27.7	- 30.8	- 44.7	-26.5	- 13.0	- 14.7	- 21.6	-12.9
3	- 39.5	- 46.4	- 63.7	-39.7	- 11.8	- 15.7	- 19.1	-13.2
4	- 50.1	- 62.9	- 82.9	-52.1	- 10.6	- 16.4	- 19.1	-12.5

[b] Experimental values taken from Ref. no. [15]

$[Cl(H_2O)_n]^-$ clusters: At both levels of calculation, the optimized structure of $[Cl(H_2O)]^-$ ion takes the C_S symmetry. The lowering of O-H stretching frequency of the water molecule bound to chloride ion compared to that of free water molecule (Table 2) substantiates ionic hydrogen bonded nature of the $[Cl(H_2O)]^-$ species. The $[Cl(H_2O)_2]^-$ species assumes C_1 symmetry for geometry optimization following both methods of investigation. The chloride ion is symmetrically located between the two water molecules in the optimized structure obtained from 6-311g++ level with r(Cl…H_{near}) 2.238 Å/ 2.433 Å (B3LYP/ HF) and θ(Cl…H-O) 159°/ 151.5°. On the other hand, the $[Cl(H_2O)_2]^-$ ion takes up an angular structure when examined at LanL2DZ level. The $[Cl(H_2O)_3]^-$ ionic cluster is optimized with C_1 symmetry. The ionic species forms an almost planar triangle (D ~ 4.4/ -178.7) with Cl^- at the centre, for 6-311g++ route of investigation. The Cl…H_{near} distances and Cl…H-O angles are non equivalent. For study involving LanL2DZ basis set, the structure is pyramidal with chloride ion at the apex and nearest hydrogen atoms of the three water molecules forming the triangular base. The bond length Cl…H_{near} is in the range 2.089 – 2.486 Å and the bond angle Cl…H-O varies between 144.6 – 162.7°. The water molecules are possibly linked by O…H bond (O3…H5 1.928 Å and O2…H10 1.988 Å). For $[Cl(H_2O)_4]^-$ species, the optimized geometry takes up C_1 symmetry at both levels of calculation. Two of the four water molecules are in close proximity (r(Cl…H_{near}) ~2.09 Å) to the anion in the symmetrical structure obtained from B3LYP level using 6-311g++ basis set. The remaining two water molecules probably form a second shell of hydration with O…H 1.697 Å and O…H-O angle of 174.6°. The shortest Cl…H_{near} distance is observed in this structure. On the other hand, for HF level, the Cl^- ion is surrounded by four H_2O molecules with r(Cl…H_{near}) 2.299 – 2.865 Å and θ(Cl…H-O) 132.5 – 160.6°. Three water molecules are linked by O…H bonds (O10…H11 2.017Å and O8…H7 2.076Å). In case of LanL2DZ path, the chloride ion is bonded to all four H_2O molecules having r(Cl…H_{near}) 2.261 – 2.496 Å and Cl…H-O bond angle of 141.7 – 152.4°. The surrounding water molecules are hydrogen bonded (O…H is in the range 1.944 – 2.15 Å) to each other.

The binding energies and differential binding energies are calculated for halide ion – water clusters. The total binding energy (*B. E.*) is defined as follows:

$$B.E. = E_{X(H2O)n} - (E_{X-} + nE_{H2O}) \quad (1)$$

where E refers to optimized energies of the following species, X^-, H_2O and $X^-(H_2O)_n$ respectively. The differential binding energy is the energy difference for the following process:

$$X^-(H_2O)_n + H_2O \rightarrow X^-(H_2O)_{n+1} \quad (2)$$

The differential binding energies (ΔD_e) are calculated by taking the energy for $X^-(H_2O)_{n+1}$ and subtracting it from the summation of the energies of $X^-(H_2O)_n$ and one water molecule. The energy values for $[F(H_2O)_n]^-$ and $[Cl(H_2O)_n]^-$ clusters are shown in Tables 3 and 4 respectively.

The differential binding energy values obtained from both experimental and computational pathways show a general decreasing trend. The outcome of HF route is well in agreement with the experimental results while that from B3LYP level is slightly overestimated. Some deviations in the trend are observed for the calculated ΔD_e for the chloride ion. The fluctuations are not sufficiently consistent to be explained by structural differences of the cluster anions. Both the experimental and calculated binding energies decrease with increasing n. The calculated *B.E.* employing HF method (particularly for Cl^- ion cluster) is in good agreement with the experimental values. The error following LanL2DZ basis set may reflect the underlying inadequacy of the method.

4. CONCLUSION

The solvation of F^- and Cl^- ions was examined by DFT methods using two different levels of calculation by varying the number of water molecules from one to four. The results suggest that the small clusters are surface anions, with the presence of intramolecular hydrogen bonding between the surrounding water molecules. The study provides insight into the subtle changes that take place in the water molecule in presence of halide ions. Both routes of investigation qualitatively predict the right trend in variation of total and differential binding energies. The results using HF method (6-311++g basis set) are more accurate when compared with the experimentally obtained values. However, extensive computational studies with more number of water molecules are required for analyzing complete solvation of anions.

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6. REFERENCES

1. Franks, F., Ed. *The Physics and Physical Chemistry of Water*, (Plenum Press: New York) 1972, Vol. 1
2. Marcus, Y. *Ion Solvation*, (Chichester: Wiley-Intersci.), 1985
3. Powell, D. H., Neilson, G. W., Endergy, J. E., *J. Phys. Condens. Mat.*, 5 (1993) 5723
4. Neilson, G. W., Mason, P. E., Ramos, S., Sullivan, D., *Philos. Trans. R. Soc. London Ser. A*, 359 (2001) 1575
5. Markovich, G., Giniger, R., Levin, N. Cheshnovsky, O., *Z. Phys. D: At., Mol. Clusters*, 20 (1991) 69
6. Markovich, G., Pollack, S., Giniger, R., Cheshnovsky, O., *J. Chem. Phys.*, 101 (1994) 9344
7. Hall, R. J., Hillier, I. H., Vincent, M. A., *Chem. Phys. Lett.*, 320 (2000) 139
8. Gora, R. W., Roszak, S., Leszczynski, J., *Chem. Phys. Lett.*, 325 (2000) 7
9. Choi, J., Kuwata, K. T., Cao, Y., Okumura, M., *J. Phys.Chem. A*, 102 (1998) 503
10. Lee, H. M., Kim, D., Kim, K. S., *J. Chem. Phys.*, 116 (2002) 5509
11. Yoo, S., Lei, Y. A., Zeng, X. C., *J. Chem. Phys.*, 119 (2003) 6083
12. Heuft, J. M., Meijer, E. J., *J. Chem. Phys.*, 119 (2003) 11788
13. Hagberg, D., Brdarski, S., Karlström, G., *J. Phys.Chem. B*, 109 (2005) 4111
14. Frisch, M. J., et al. (2009). *Gaussian 09*, Revision A.1 Gaussian, Inc. Wallingford CT
15. Hiraoka, K., Mizuse, S., Yamabe, S., *J. Phys. Chem.*, 1988, 92, 3943
16. Arshadi, M., Yamdagni, R., Kebarle, P., *J. Phys. Chem.*, 1970, 74, 1475