Monovalent ions dissolved in water

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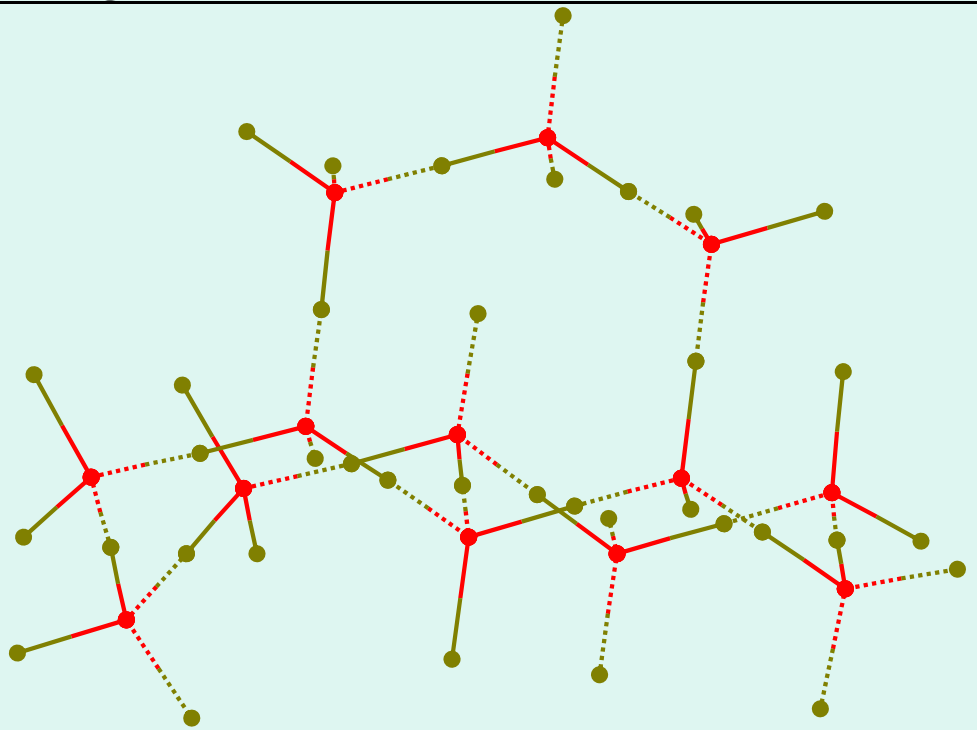
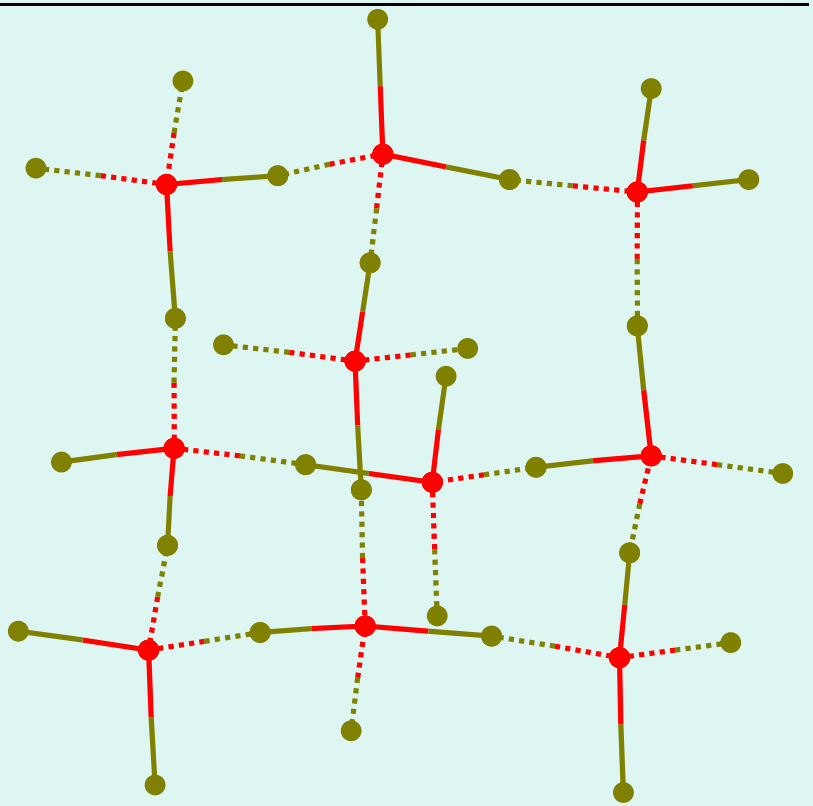
Introduction

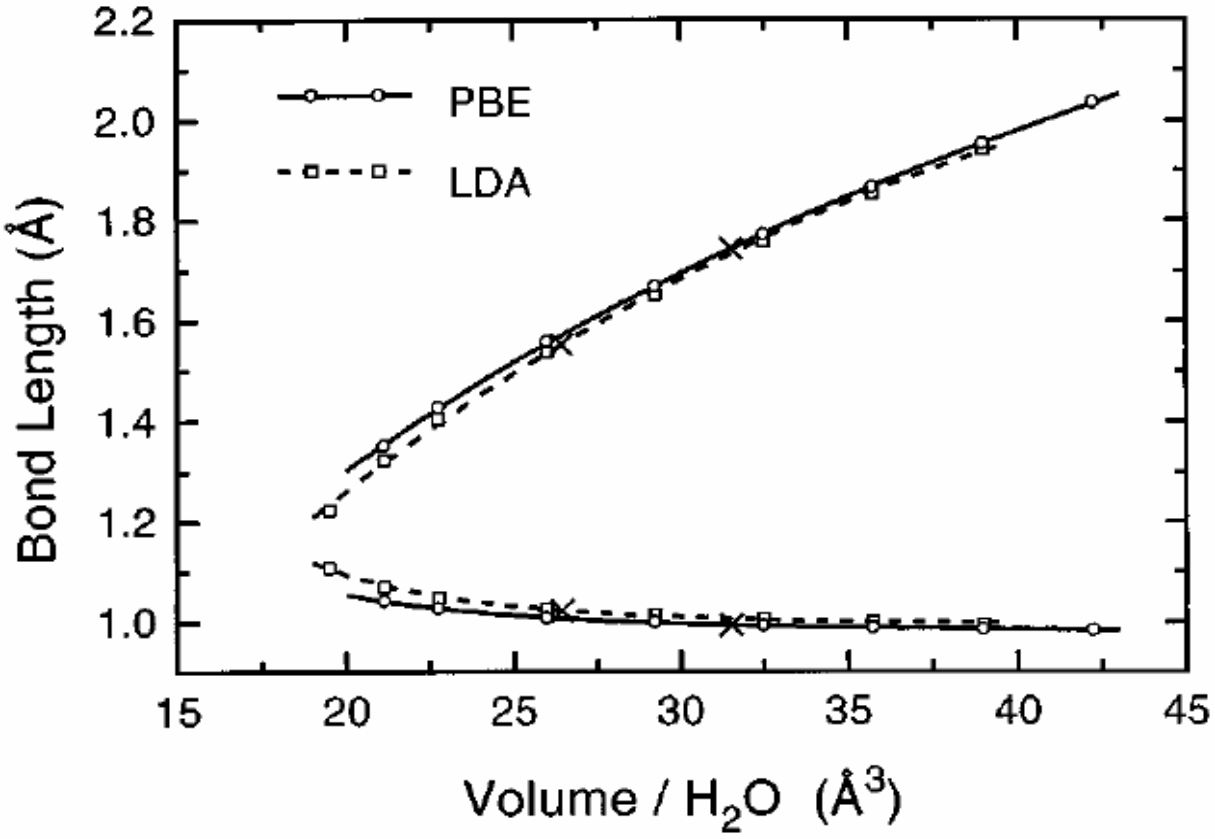
- Structure of the water is a subject of theoretical physics [[1]], and it differs significantly from gaseous state (here 'in-vitro' simulations working well) and solid state (ice, at which 'frozen' simulations working well) to liquid state (where is known the lack of geometrical symmetries which make more difficult the analysis).
  [1] Kjartan Thor Wikfeldt, 2011. Structure, Dynamics and Thermodynamics of Liquid Water: Insights from Molecular Simulations, Thesis for the Degree of Doctor of Philosophy in Theoretical Physics. Department of Physics, Stockholm University, Stockholm.

Ice

hexagonal	cubic
	

Were found no less than 15 phases of ice. At pressures till up about 1000 atm. and for temperatures till down about -200°C ice adopts two structures, both “close-packed”: hexagonal (at upper temperatures) and cubic (at lower temperatures).

O-H bond lengths



Theoretical (see figure): D. R. Hamann, 1997. H2O hydrogen bonding in density-functional theory. Phys Rev B 55(16):R10157-60

Experimental (see previous slide): d(O—H)=100pm; d(O…H)=175pm [1]

[1]: E. D. Isaacs, A. Shukla, P. M. Platzman, D. R. Hamann, B. Barbiellini, C. A. Tulk, 1999. Covalency of the Hydrogen Bond in Ice: A Direct X-Ray Measurement. Phys Rev Lett 82(3): 600-603

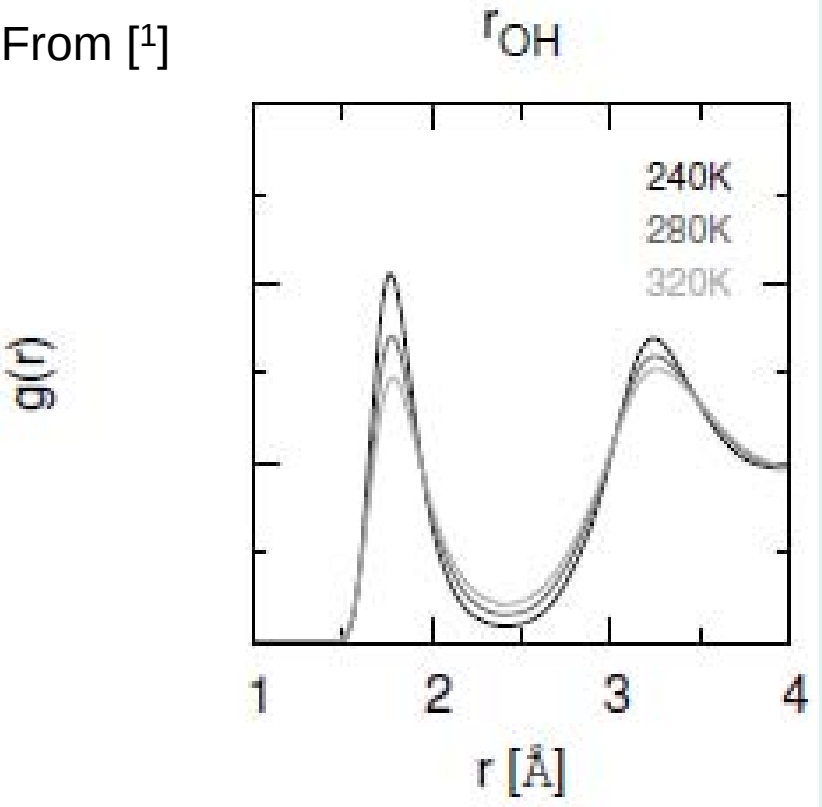
Molecular modeling

method	d(O-H)
MP4/6-31G*	97.03pm
MP3/6-31G*	96.68pm
MP2/6-31G*	96.89pm
M06-2X/6-31G*	96.56pm
HF/6-31G*	94.73pm
HF/3-21G*	96.65pm
HF/STO-3G	98.92pm
Experimental	95.78pm

http://cccbdb.nist.gov/alldata2.asp?casno=7732185

Maxwell–Boltzmann statistics

From [1]



g_i: number of single-particle states with energy ε_i

$$N_i = g_i \cdot e^{-(\varepsilon_i - \mu)/k_B T}$$

ε_i: energy of the i^{th} level

μ: chemical potential

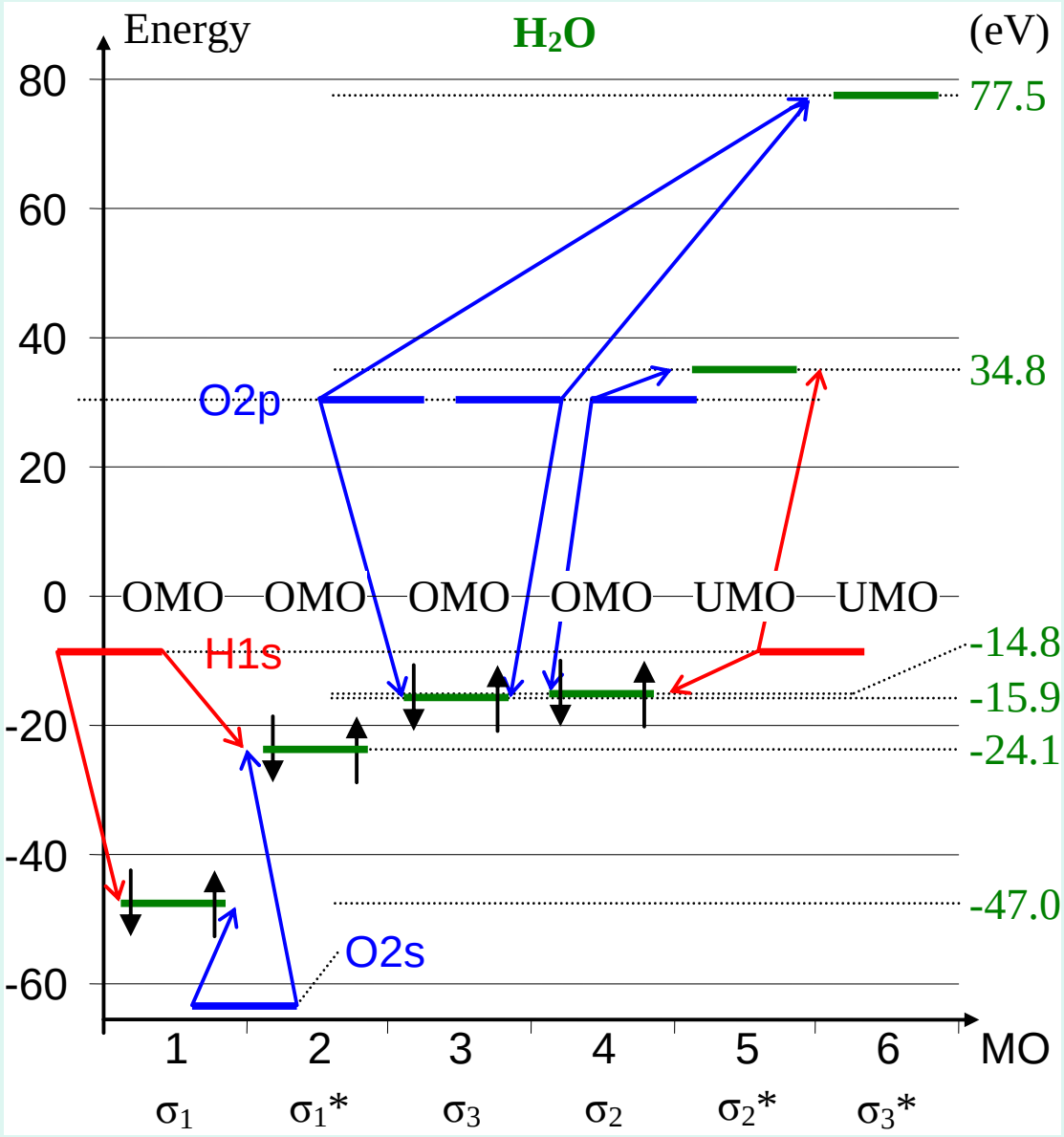
k_B: Boltzmann's constant

T: temperature

N_i: number of particles with energy ε_i

[1]: D. Prada-Gracia, R. Shevchuk, F. Rao, 2013. The quest for self-consistency in hydrogen bond definitions, J. Chem. Phys. 139: 084501

H_2O in vitro (LCAO - MO)



Parameters for ion solvation

Ion	r_i (pm)	$\Delta_s G_i$ [kJ·mol^{-1}]
Li^+	88	-529
Na^+	116	-424
K^+	152	-352
Rb^+	163	-329
F^-	119	-429
Cl^-	167	-304
Br^-	182	-278
I^-	206	-243
NH_4^+	153	-340

From [1]:
The Born model fails because it does not recognize the disruption of solvent structure which occurs in the immediate vicinity of the ion. In addition, it does not deal with the fact that the molecular mechanism involved in cation solvation is different from that for anions. In water cations are solvated by the electron density on the oxygen atom, whereas anions are solvated by hydrogen bonding with the water molecules.

[1]: W. R. Fawcett, 2005. Charge distribution effects in the solution chemistry of polyatomic ions. Cond Mat Phys 8(2): 413-424

Optimization methods

From [1]:

- We have compared several computational techniques with the aim to compute the radial distribution function (RDF) as a good characterization of water structure. In particular, we have used molecular mechanic (AMBER99), semi-empirical (AM1, PM3, PM6) and ab initio (DFT) technique.
- In conclusion, our results indicate advantage of “middle road” semi-empirical approach with PM6 parameterisation over AM1, PM3 and ab initio DFT approach.

[1] R. Staník, P. Ballo, I. Benkovský, 2012. Comparison of different computational methods for water structure optimization. Acta Facultatis Pharmaceuticae Universitatis Comenianae LIX: DOI 10.2478/v10219-012-0019-3

SM8 water model

- Proposed in: Marenich A. V., Olson R. M., Kelly C. P., Cramer C. J., Truhlar D. G., 2007. Self-Consistent Reaction Field Model for Aqueous and Nonaqueous Solutions Based on Accurate Polarized Partial Charges. J Chem Theory Comput 3: 2011-2033
- The most reliable implementation of the SM8 model predicts solvation free energies for a test set of 17 molecules with an RMSE of 1.08 kcal mol-1, which is as good as or better than other implicit and explicit solvation models previously reported [Chamberlin A. C., Cramer C. J.,Truhlar D. G., 2008. Performance of SM8 on a Test To Predict Small-Molecule Solvation Free Energies. J. Phys. Chem. B 112: 8651-8655]

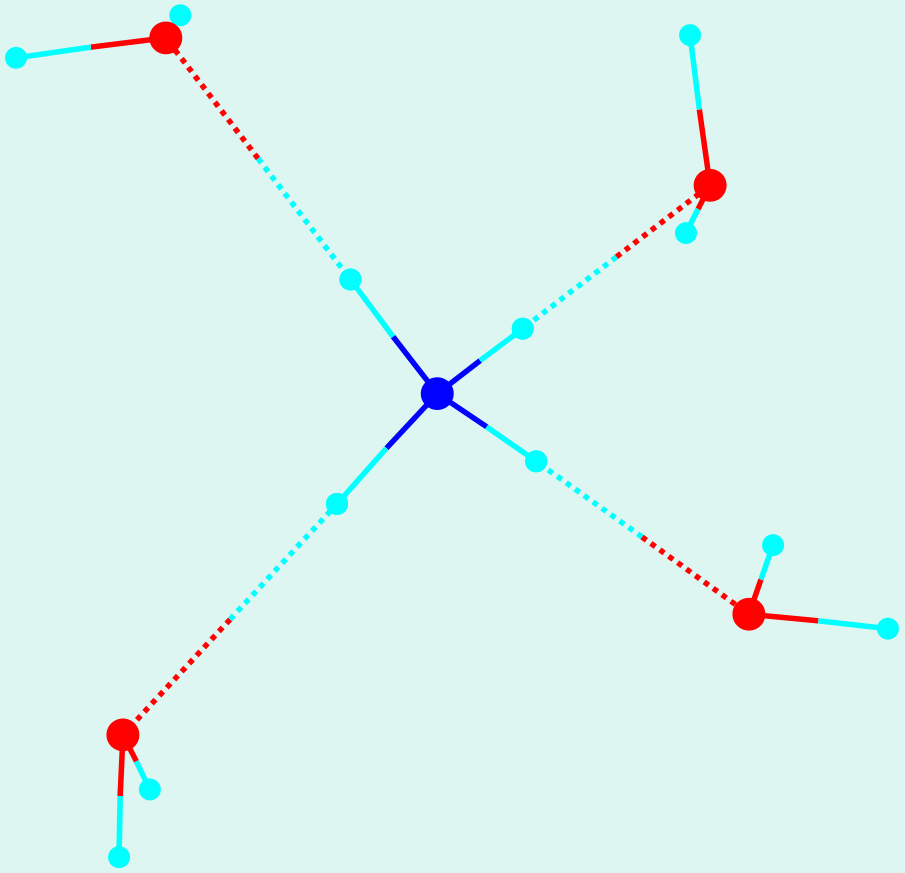
Research aim (1)

- To obtain ‘natural’ angles between bonds for a series of ions dissolved in water as well as ‘natural’ number of bonds as these can result from applying of the current methods of quantum calculations

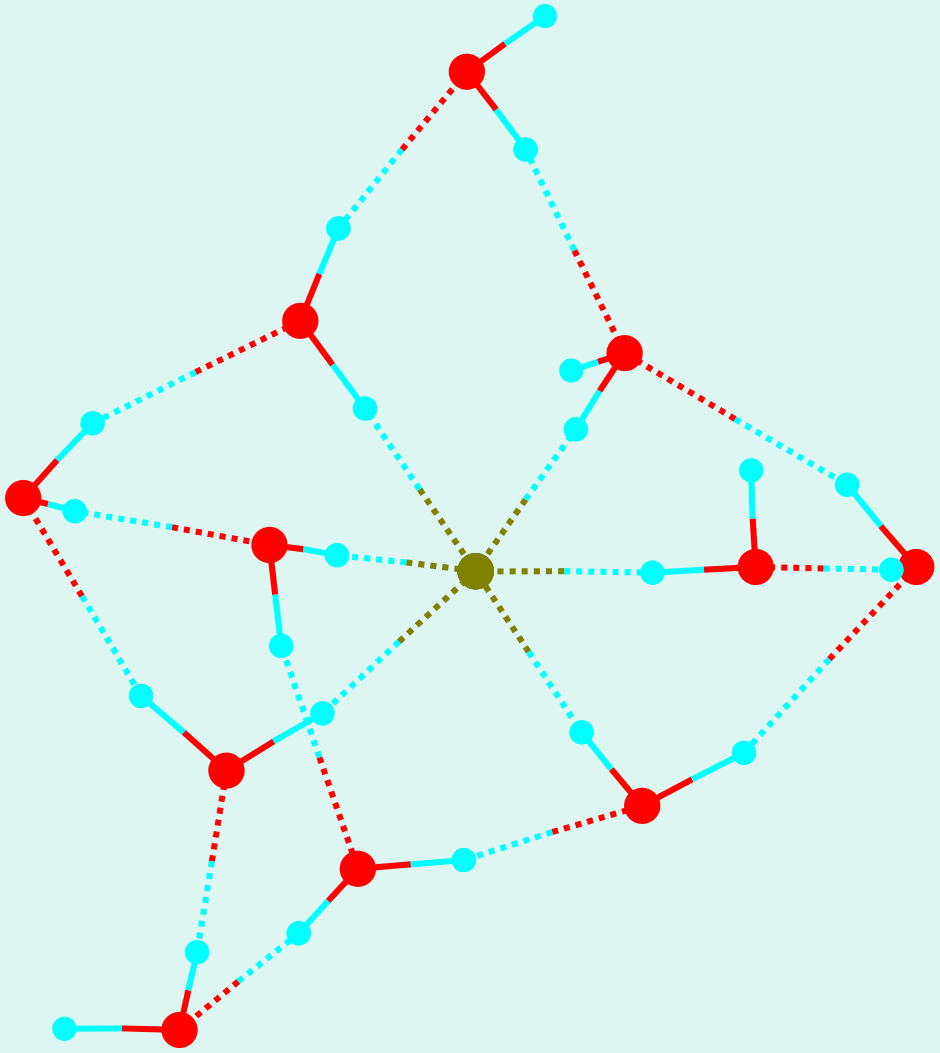
Material and method

- $NH4^+$, F^-, Cl^-, Li^+, Na^+, K^+ were subject to investigation
- Spartan'10 with SM8 environment is involved in the calculations
- HF 6-31G* was selected
- General procedure:
  - a number of water molecules were placed in the vicinity of the ions
  - geometry optimization was conducted
  - other water molecules were added in the empty spaces in the vicinity of the ions
  - last two steps were repeated till the moment when no chances were observed in the arrangement of the water molecules surrounding the ions in the first layer

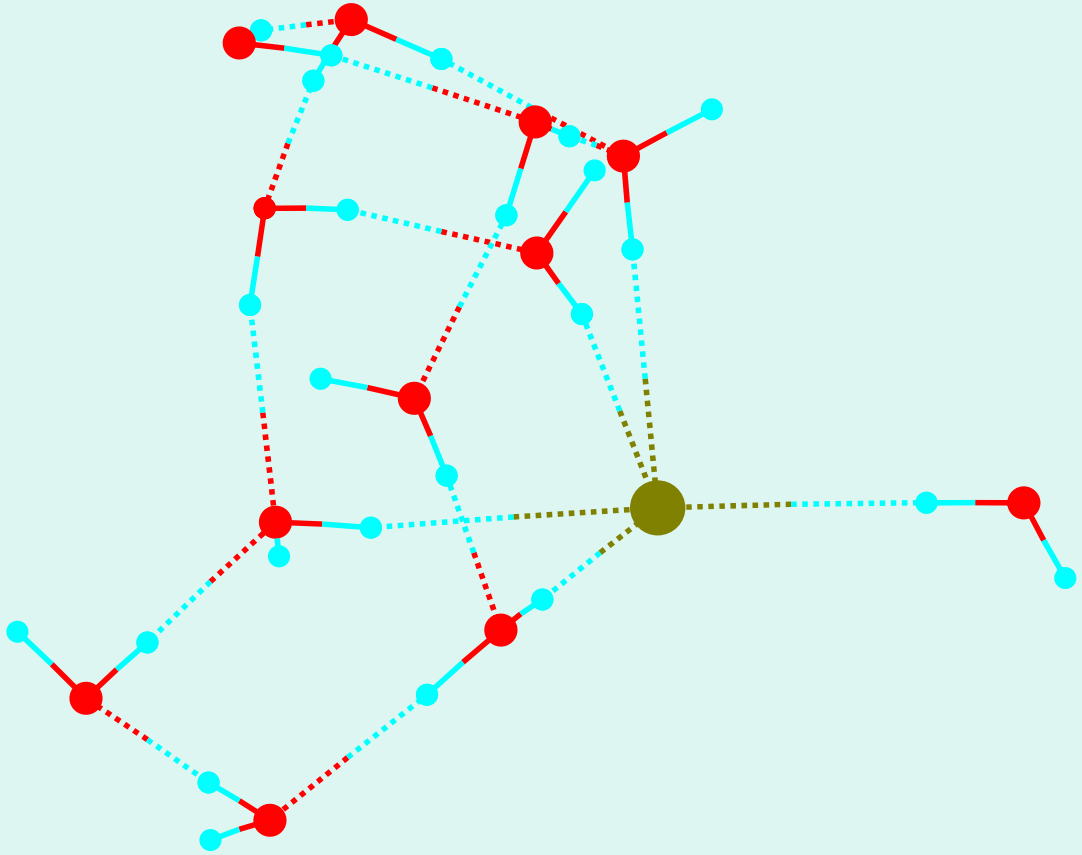
Results: $NH_4^+ \cdot 4H_2O$

Model, distances (pm) and angles (°)		
	O-H	95
	N-H	101
	O…H	208
	H-O-H	∠(95,95) = 105°
	H-N-H	∠(101,101) = 109°
	H-O…H	∠(95,208) = 113°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

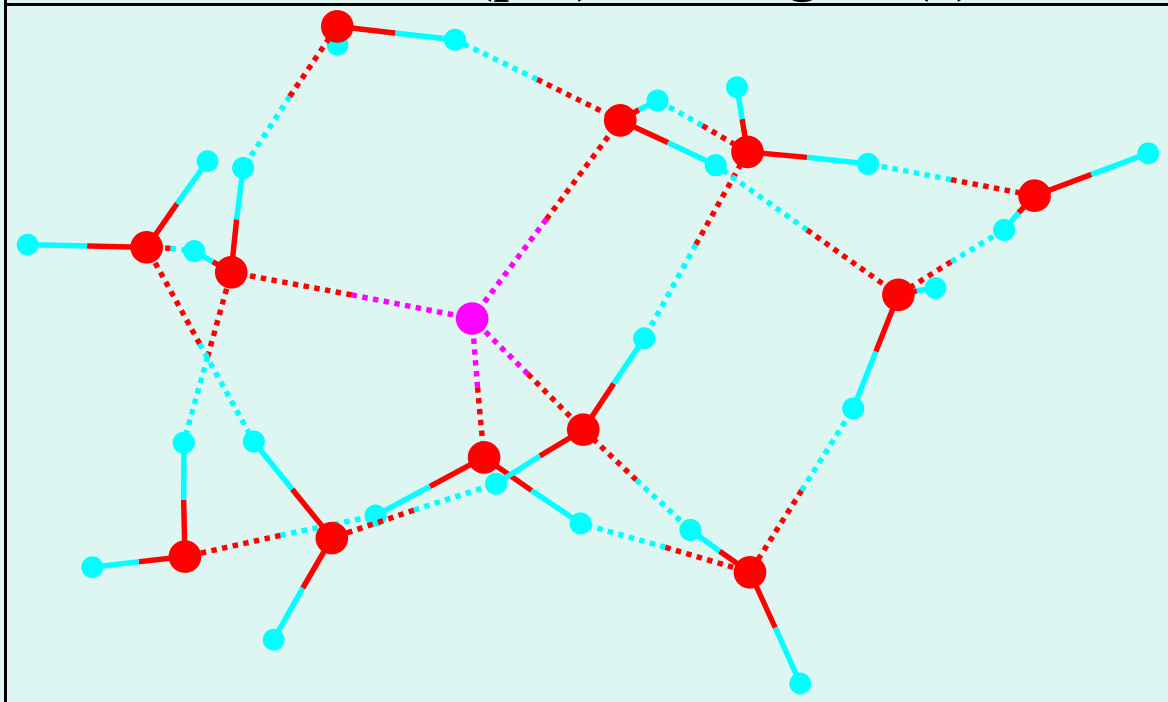
Results: $F^{-}\cdot 6H_2O$

Model, distances (pm) and angles (°)	H…F	H…F…H
	179	∠(179,184) = 77°
	182	∠(184,187) = 85°
	183	∠(182,183) = 85°
	184	∠(179,183) = 86°
	185	∠(185,187) = 87°
	187	∠(183,184) = 88°
		∠(179,182) = 89°
		∠(184,185) = 89°
		∠(179,185) = 90°
		∠(183,187) = 93°
		∠(182,185) = 98°
		∠(182,187) = 109°
		∠(179,187) = 162°
		∠(182,184) = 165°
		∠(183,185) = 177°
Restricted Hartree-Fock 6-31G* Charge=-1; Solvation=Water (SM8)		

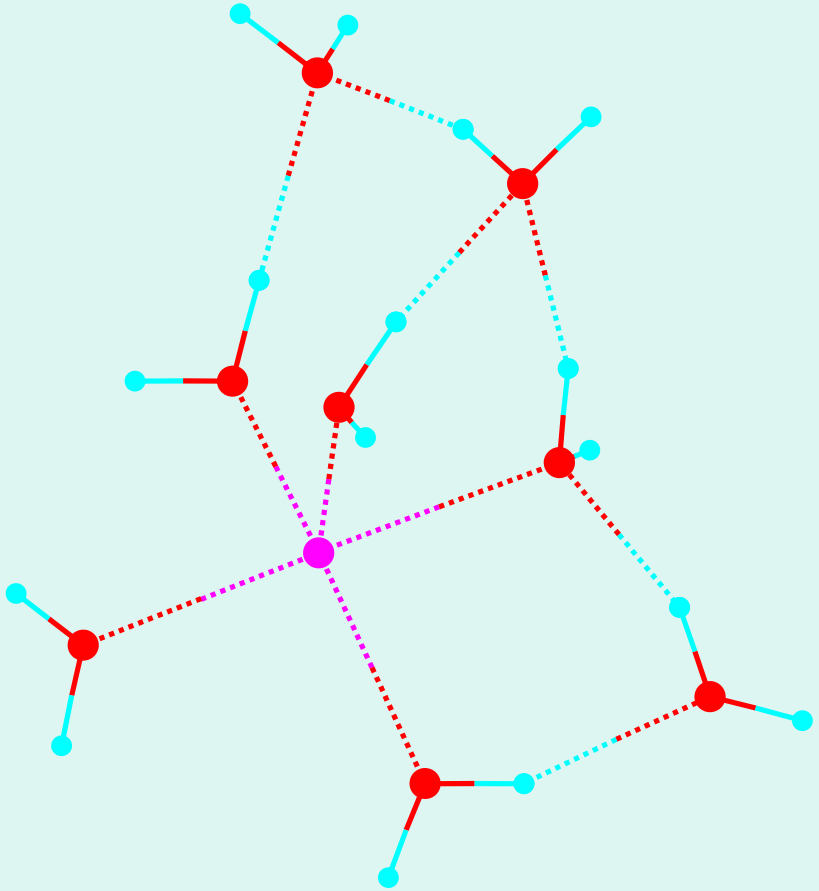
Results: $Cl^{-}\cdot 5H_2O$

Model, distances (pm) and angles (°)	H…Cl	H…Cl…H
	265	∠(281,307) = 67°
	274	∠(274,307) = 76°
	281	∠(281,284) = 82°
	284	∠(274,284) = 82°
	307	∠(265,307) = 89°
		∠(274,281) = 96°
		∠(265,274) = 101°
		∠(265,284) = 129°
		∠(284,307) = 140°
		∠(265,281) = 146°
Restricted Hartree-Fock 6-31G* Charge=-1; Solvation=Water (SM8)		

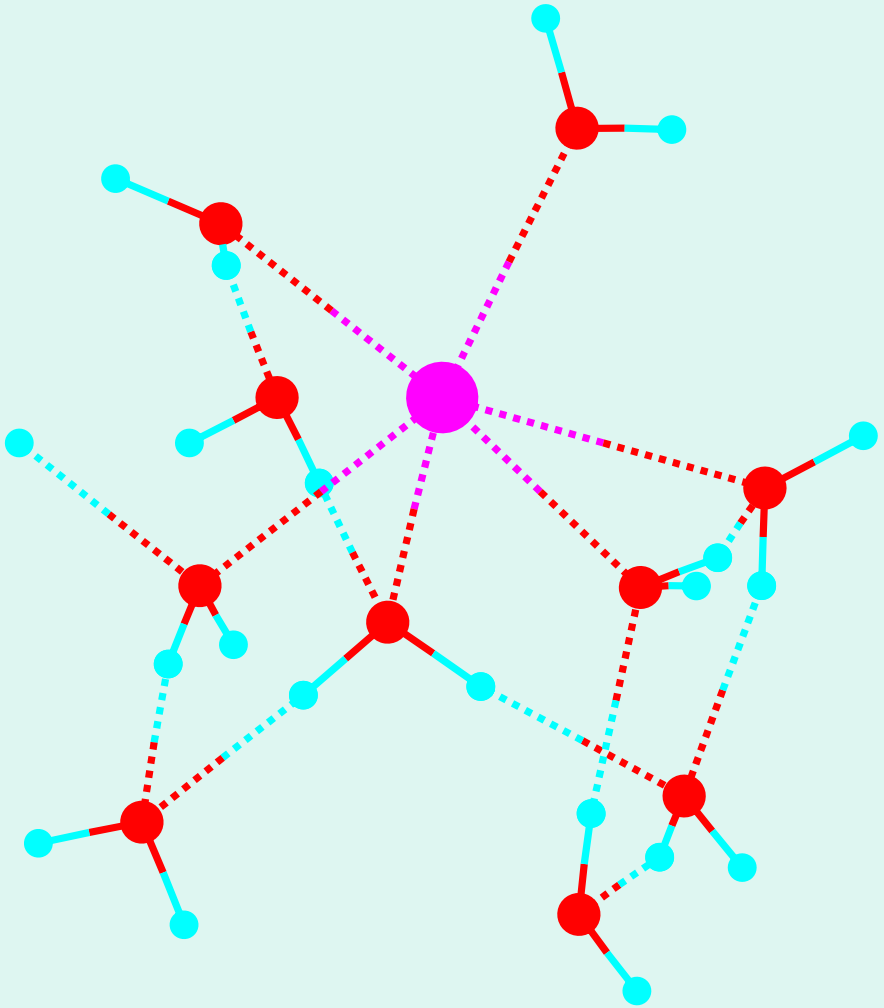
Results: $Li^{+}\cdot 4H_2O$

Model, distances (pm) and angles (°)	Li…O	O…Li…O
	193	∠(193,196) = 99°
	194	∠(194,200) = 104°
	196	∠(196,200) = 110°
	200	∠(193,200) = 111°
		∠(194,196) = 116°
		∠(193,194) = 117°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

$Na^+ \cdot 5H_2O$

Model, distances (pm) and angles (°)	Na…O	O…Na…O
	231	∠(234,239) = 84°
	234	∠(236,239) = 85°
	235	∠(231,239) = 88°
	236	∠(231,235) = 93°
	239	∠(235,236) = 94°
		∠(234,235) = 97°
		∠(231,234) = 100°
		∠(234,236) = 123°
		∠(231,236) = 135°
		∠(231,235) = 178°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

$K^+ \cdot 6H_2O$

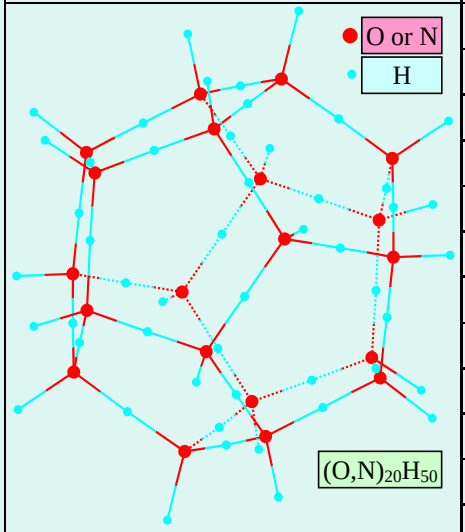
Model, distances (pm) and angles (°)	O…K	O…K…O
	278	∠(285,293) = 58.1°
	279	∠(281,285) = 79.0°
	281	∠(284,293) = 79.1°
	284	∠(278,281) = 80.8°
	285	∠(281,284) = 81.3°
	293	∠(279,293) = 86.2°
		∠(279,285) = 86.3°
		∠(278,279) = 92.5°
		∠(278,284) = 94.4°
		∠(281,293) = 100.5°
		∠(279,284) = 121.6°
		∠(284,285) = 127.8°
		∠(278,285) = 128.8°
		∠(279,281) = 157.1°
		∠(278,293) = 173.0°

Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)

Research aim (2)

- To assess the formation and/or stability of the dodecahedron clusters at the solving in water

Results: Ammonia in water

Pattern	Arrangements for $O_xN_{20-x}H_{50}$							
	Nr	Cluster	H_2O	NH_3	H_3O^+	HO^-	$[^+/^-]/H_2O$	Reaction of formation	N/(N+O) %
	1	O_2N_{18}	2	18	8	0	+(8)/(2+8)	$18NH_3 + 10H_2O \rightarrow O_2N_{18}H_{50} + 8H_3O^+$	18/28=64.3
	2	O_4N_{16}	4	16	6	0	+(6)/(6+4)	$16NH_3 + 10H_2O \rightarrow O_4N_{16}H_{50} + 6H_3O^+$	16/26=61.5
	3	O_5N_{15}	5	15	5	0	+(5)/(5+5)	$15NH_3 + 10H_2O \rightarrow O_5N_{15}H_{50} + 5H_3O^+$	15/25=60.0
	4	O_6N_{14}	6	14	4	0	+(4)/(4+6)	$14NH_3 + 10H_2O \rightarrow O_6N_{14}H_{50} + 4H_3O^+$	14/24=58.3
	5	O_8N_{12}	8	12	2	0	+(2)/(2+8)	$12NH_3 + 10H_2O \rightarrow O_8N_{12}H_{50} + 2H_3O^+$	12/22=54.5
	6	$O_{10}N_{10}$	10	10	0	0	(0)/(0+10)	$10NH_3 + 10H_2O \rightarrow O_{10}N_{10}H_{50}$	10/20=50.0
	7	$O_{12}N_8$	12	8	0	2	-(2)/(2+12)	$8NH_3 + 14H_2O \rightarrow O_{12}N_8H_{50} + 2HO^-$	8/22=36.4
	8	$O_{14}N_6$	14	6	0	4	-(4)/(4+14)	$6NH_3 + 18H_2O \rightarrow O_{14}N_6H_{50} + 4HO^-$	6/24=25.0
	9	$O_{15}N_5$	15	5	0	5	-(5)/(5+15)	$5NH_3 + 20H_2O \rightarrow O_{15}N_5H_{50} + 5HO^-$	5/25=20.0
	10	$O_{16}N_4$	16	4	0	6	-(6)/(6+16)	$4NH_3 + 22H_2O \rightarrow O_{16}N_4H_{50} + 6HO^-$	4/26=15.4
	11	$O_{18}N_2$	18	2	0	8	-(8)/(8+18)	$2NH_3 + 26H_2O \rightarrow O_{18}N_2H_{50} + 8HO^-$	2/28=07.1

t(°C)	$(N/(N+O))_{sat}$	K_b	K_w	pH
0	0.460	$1.37 \cdot 10^{-5}$	$1.14 \cdot 10^{-15}$	12.5
10	0.401	$1.57 \cdot 10^{-5}$	$2.93 \cdot 10^{-15}$	12.1
20	0.334	$1.71 \cdot 10^{-5}$	$6.81 \cdot 10^{-15}$	11.6
30	0.279	$1.82 \cdot 10^{-5}$	$1.47 \cdot 10^{-14}$	11.3
40	0.232	$1.86 \cdot 10^{-5}$	$2.92 \cdot 10^{-14}$	10.9
50	0.179	$1.89 \cdot 10^{-5}$	$5.48 \cdot 10^{-14}$	10.6

Calculus based on observed data

$w := 5.48\,10^{-14}$ $n := 1.89\,10^{-5}$ $f := 0.179$ $x := 10^{-3}$ $y := 10^{-12}$ Given

$$x \cdot (x + y) = n \cdot (1 - x) \cdot \left(\frac{1 - f}{f} - x - 2 \cdot y \right) \qquad y \cdot (x + y) = w \cdot \left(\frac{1 - f}{f} - x - 2 \cdot y \right)^2$$

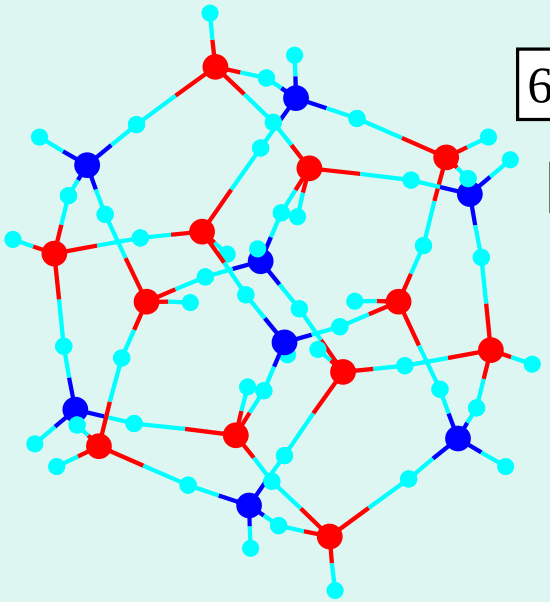
vec := Find(x, y)

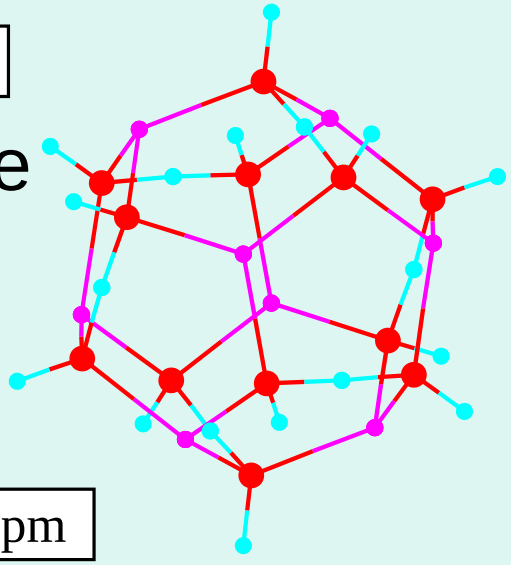
$$vec = \begin{pmatrix} 9.3 \times 10^{-3} \\ 1.2 \times 10^{-10} \end{pmatrix} \qquad z := \frac{\left(vec^T\right)^{\langle 0 \rangle} + \left(vec^T\right)^{\langle 1 \rangle}}{\frac{1 - f}{f} - \left(vec^T\right)^{\langle 0 \rangle} - 2 \cdot \left(vec^T\right)^{\langle 1 \rangle}}$$

$z = 2 \times 10^{-3}$ $pH := -\log\left(\frac{w}{z}\right)$ $pH = 10.6$

Most probable clusters of cations in water

6 O-H in & 6 O-H out





d(Li,O) = 179±1 pm

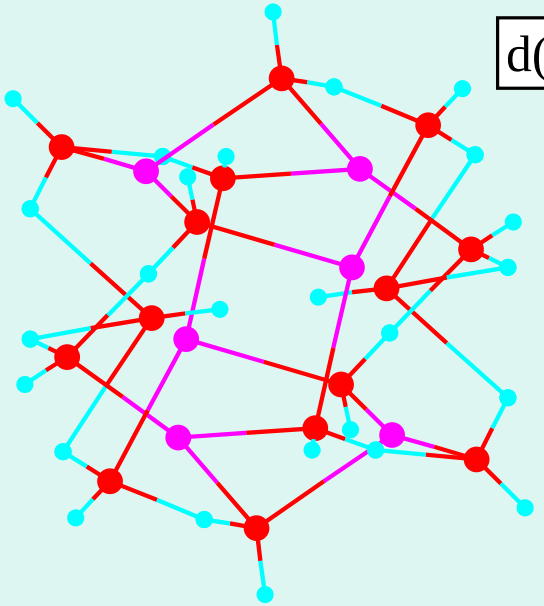
$O_{12}N_8H_{50}$; stable

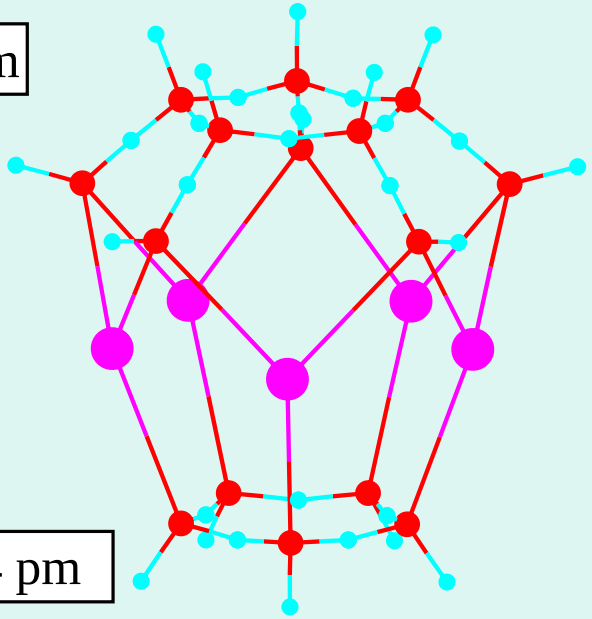
$O_{12}Li_8H_{18}$; stable

$O_{14}Na_6H_{26}$; instable

$O_{15}K_5H_{29}$; stable

d(Na,O) = 275±46 pm





d(K,O) = 270±4 pm

Conclusions

- ‘In vivo’ optimization can be conducted successfully with SM8 water model
- Were obtained a series of important results with regard to symmetry broken effects at energy levels of some monovalent ions at solvation due to the presence of water molecules
- The study can be further continued to assess the influence of temperature on solvation and to correlate observed values for solvation limits with estimated ones from applying iterative arrangements of the calculated models