Microsolvation of Salts in Water

Cheng-Wen Liu, Yi Qin Gao*

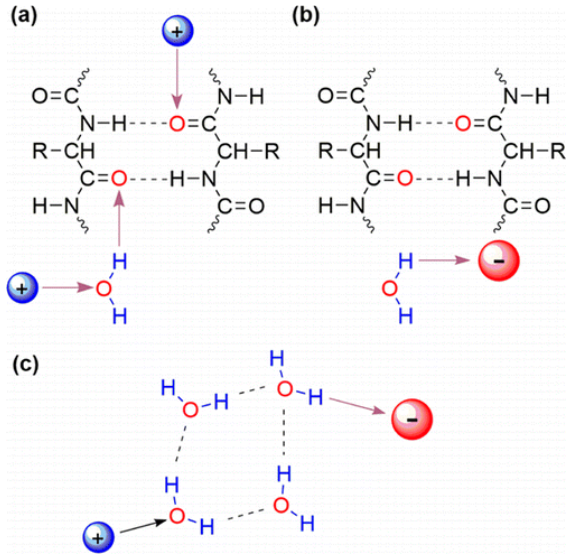
09/11/2015

Outline

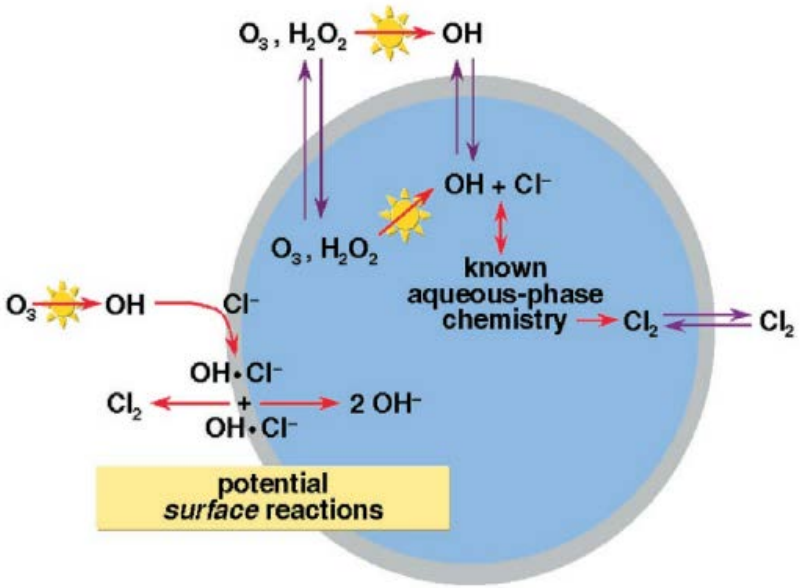
- Introduction
  - Study Motivation
  - Model Systems
  - Methodology
- Contents
  - Method validation on water clusters
  - Microsolvation of iodide salts in water
  - Microsolvation of NaCl in water
- Conclusions
- Acknowledgements

Significance of salt-water systems: two examples

In biology

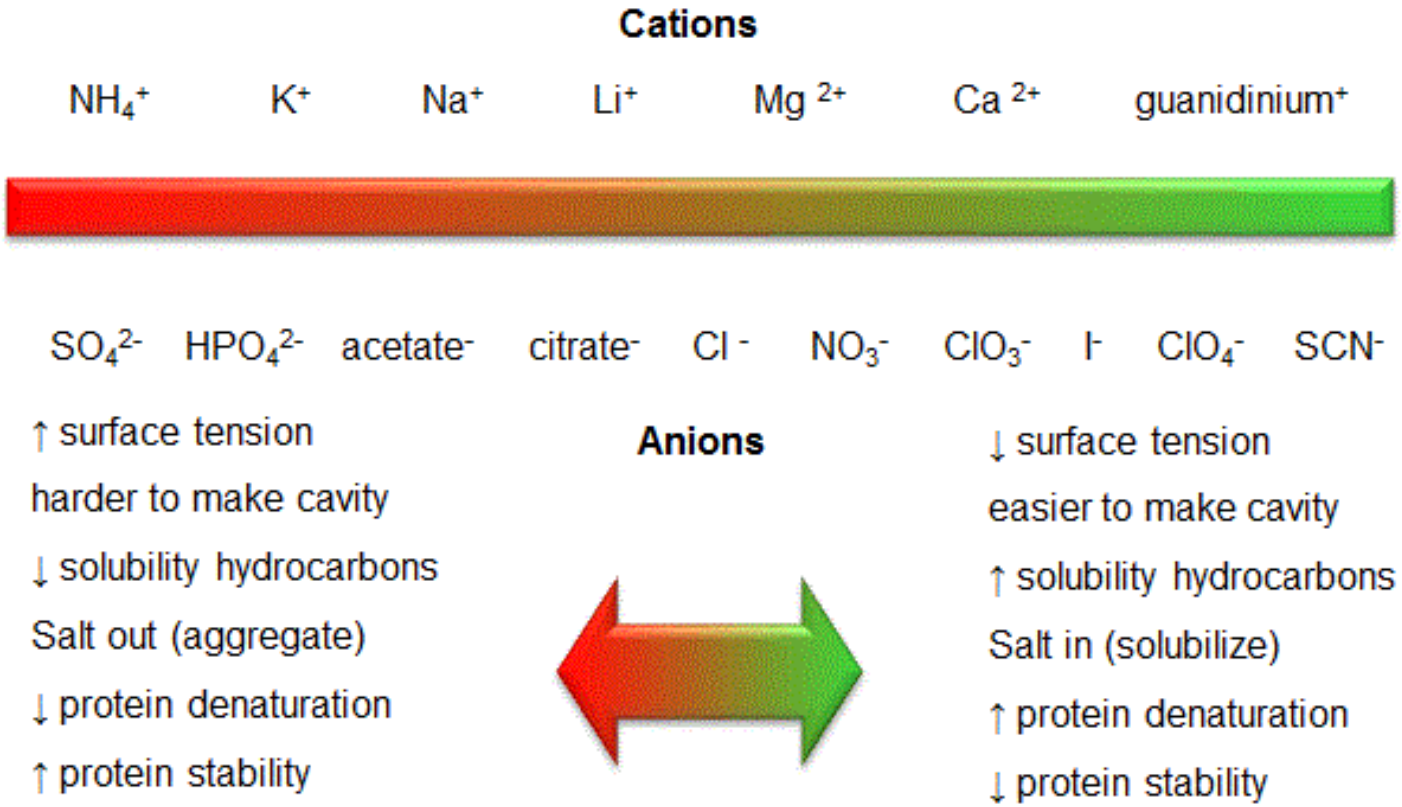


In atmosphere



Xie W.J., Gao Y.Q., ***J. Phys. Chem. Lett****., 4, 4247 (2013)*
Knipping E.M., Lakin M.J., Foster K.L., et al. ***Science****, 288, 301 (2000)*

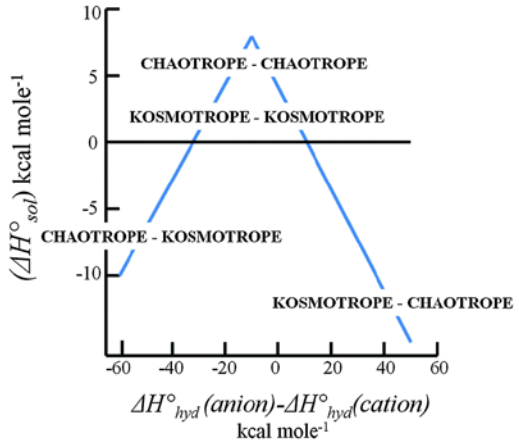
Hofmeister series



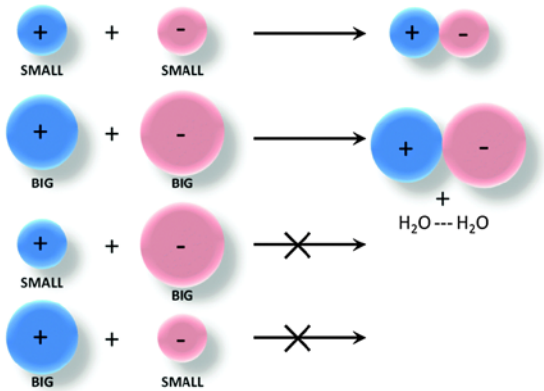
Hofmeister F. ***Arch. Exp. Pathol. Pharmakol.****, 24, 247 (1888)*
Flores, S. C., Kherb, J., Konelick, N., et al. ***J. Phys. Chem. C****, 116, 5730 (2012)*
Collins K. D., Neilson G. W., Enderby J. E., ***Biophys. Chem.****, 128, 95 (2007)*

Ion pairing and cooperativity

- **Law of matching water affinity**

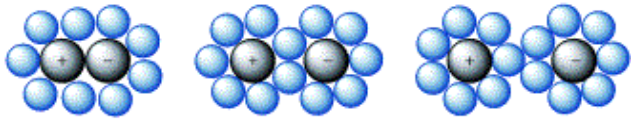


(A)



(B)

- **Categories of ion pair**



CIP **SIP** **SSIP**

Contact ion pair

Solvent-shared ion pair

Solvent separated ion pair

Collins K. D., ***Methods***, *34, 300 (2004)*

Salis A., Ninham B.W. ***Chem. Soc. Rev.,*** *43, 7358 (2014)*

Salt-water clusters

- **Cluster** is the bridge connecting isolated atoms or molecules and condensed phases

  - The hydration environments of ions.
  - How easily do different ion pairs become solvated by water molecules?
  - Does ion pairing follow the law of "matching water affinity"?
  - Does the ion cooperativity shown in bulk solutions also exist in clusters?

Model systems

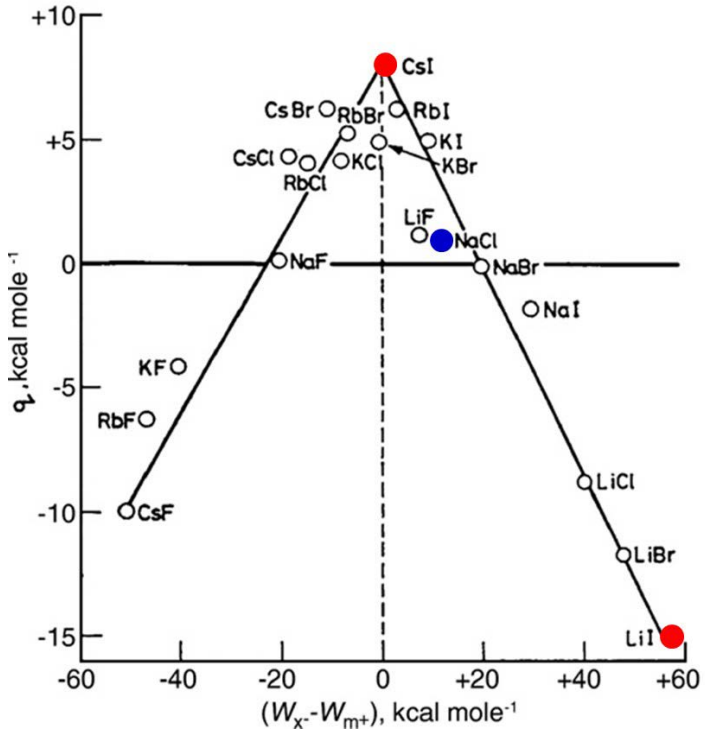
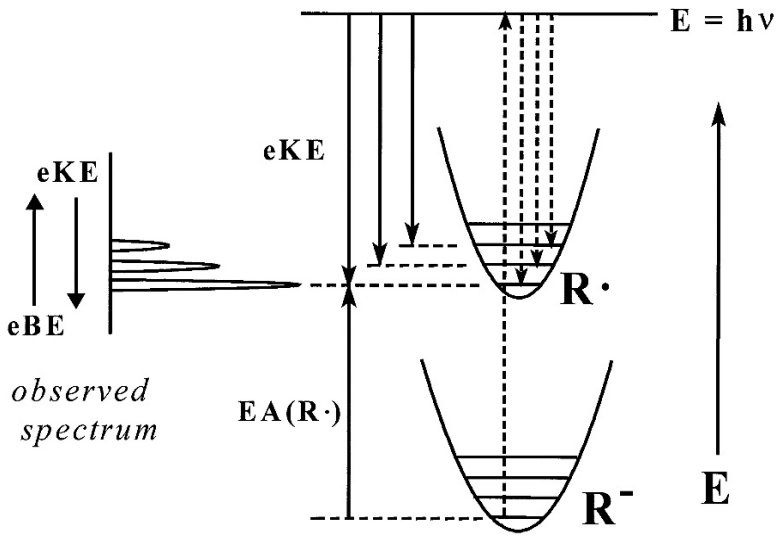


Fig. The locations of three systems

Collins K. D., ***Methods***, *34, 300 (2004)*

Approaches for small clusters

Anion photoelectron spectroscopy (APS) and QM calculations are combined



VDE = E(neutral) – E(anion)
(both at anion geometry)

Fig. Schematic potential energy surfaces depicting the anion photoelectron spectroscopy expt.

*P.G. Wenthold, W.C. Lineberger., **Acc. Chem. Res**., 32, 579 (1999)*

Difficulties for large clusters

- **Experimentally**

  Thermal motion

  ➢ Large clusters only exist in low temperatures.

- **Theoretically**

  Complexity of potential energy surface.

  ➢ If one H_2O adapts only four connection patterns, 2D2A, 2D1A, 1D2A and 1D1A, for $(H_2O)_{10}$, there would be 4^{10} configurations.

Integrated Tempering Sampling method

- Effective potential and force in ITS simulation

$$\mathrm{U_{eff}} = -\frac{1}{\beta_0} ln \sum_k n_k e^{-\beta_k U} \qquad \mathrm{F_{eff}} = -\frac{\partial \mathrm{U_{eff}}}{\partial r} = \frac{\sum_k \beta_k n_k e^{-\beta_k U}}{\beta_0 \sum_k n_k e^{-\beta_k U}} \mathrm{F}$$

- Distribution function and reweighting factor

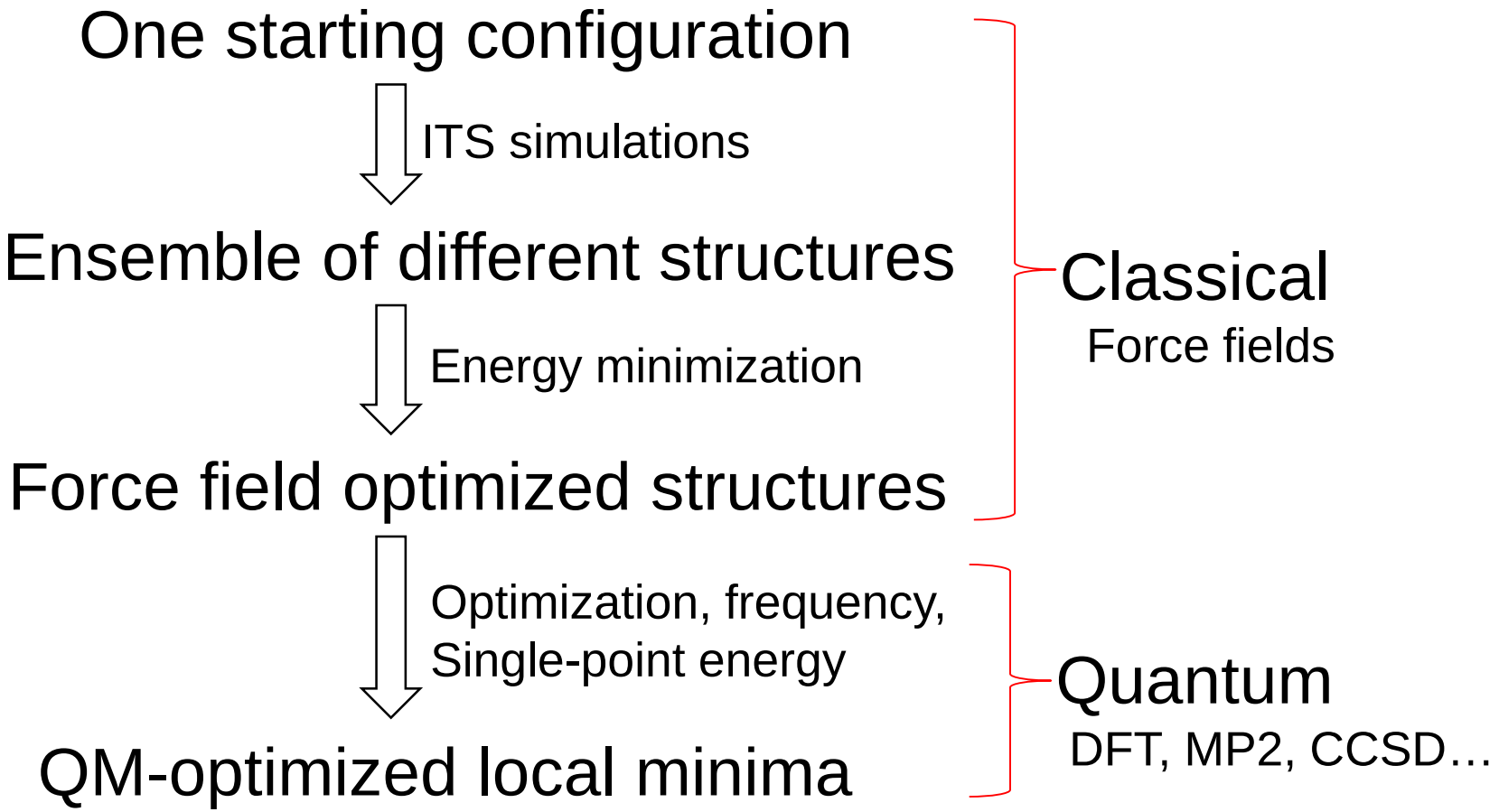
$$\rho(\mathrm{r}) = \rho_{\mathrm{eff}}(r) e^{-\beta_0 [U(r) - U_{eff}(r)]} \qquad e^{-\beta_0 (U - U_{eff})} = \frac{e^{-\beta_0 U}}{\sum_{k=1}^{N} n_k e^{-\beta_k U}}$$

- Applications: protein folding, peptide aggregations, chemical reactions and protein-DNA interactions

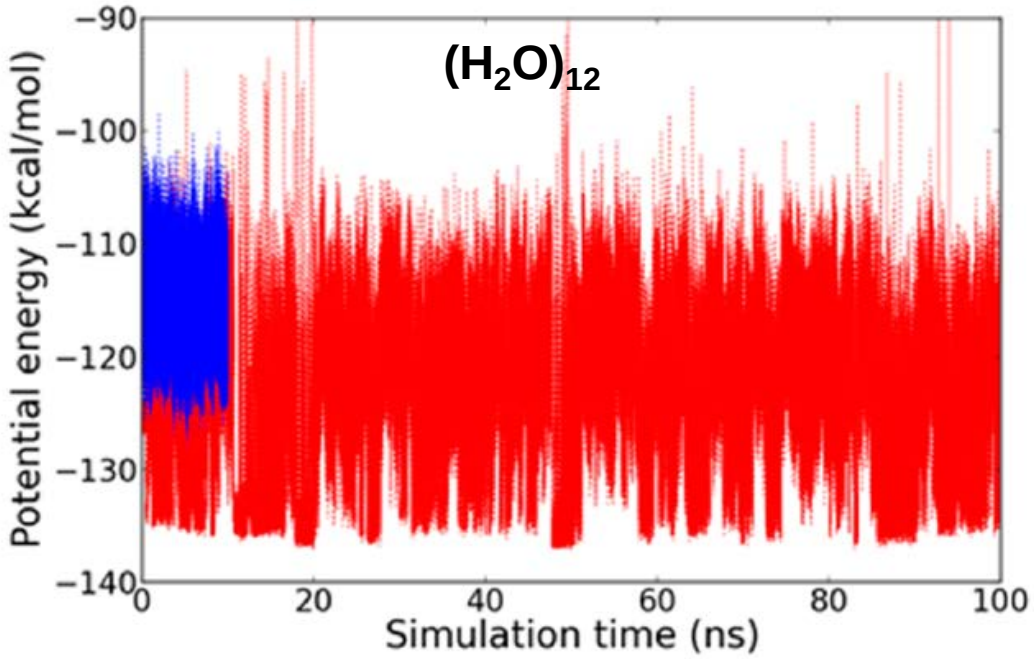
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Gao Y.Q., ***J. Chem. Phys.*** *128, 064105; (2008)*
Gao Y.Q., ***J. Chem. Phys.*** *128, 134111; (2008)*

ITS(MM)-QM framework



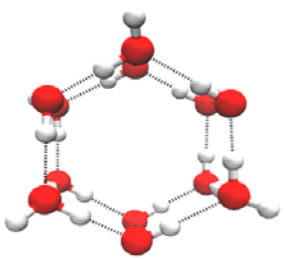
Potential energy evolution



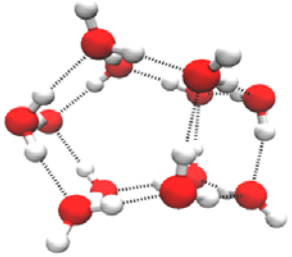
Blue: Standard MD simulation
Red: ITS enhanced sampling simulation

Structures of $(H_2O)_{12}$ & $(H_2O)_{20}$

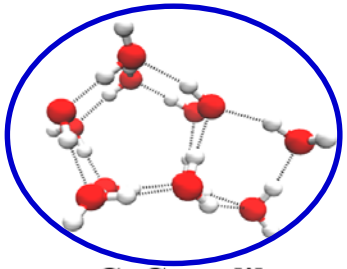
$(H_2O)_{12}$



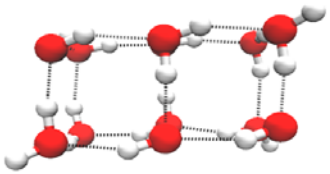
A. Prism
R.E.(BLYP-M2) 0.28
R.E.(LC-ωPBE) 0.00



B. Cage
R.E.(BLYP-M2) 0.00
R.E.(LC-ωPBE) 0.44

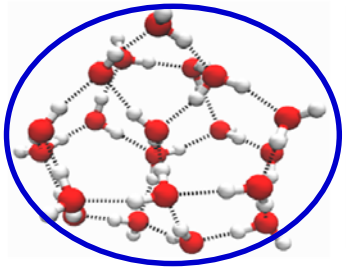


C. Cage-like
R.E.(BLYP-M2) 1.85
R.E.(LC-ωPBE) 2.41

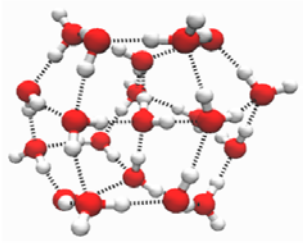


D. Fused Cube
R.E.(BLYP-M2) 0.31
R.E.(LC-ωPBE) 3.29

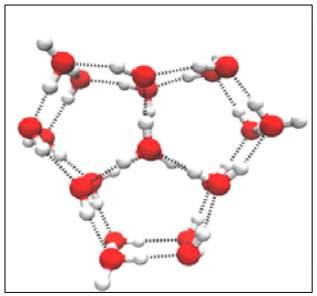
$(H_2O)_{20}$



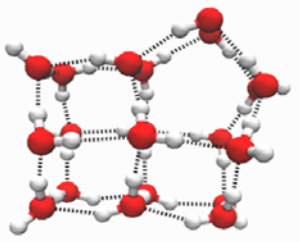
A. Fused-like
R.E.(BLYP-M2) 0.00
R.E.(LC-ωPBE) 0.00
R.E.(ωB97XD) 0.00
R.E.(B2PLYPD) 0.00



B. Clathrate-like
R.E.(BLYP-M2) 0.67
R.E.(LC-ωPBE) 1.38
R.E.(ωB97XD) 0.55
R.E.(B2PLYPD) 0.70



C. Edge-sharing
R.E.(BLYP-M2) 0.31
R.E.(LC-ωPBE) 2.20
R.E.(ωB97XD) 0.44
R.E.(B2PLYPD) 1.02



D. Cage
R.E.(BLYP-M2) 3.03
R.E.(LC-ωPBE) 2.61

All energies are in kcal/mol

High level calculations on $(H_2O)_{20}$

Table: Relative energies under BLYP-M2 functional-optimized structures. Energies are in kcal/mol

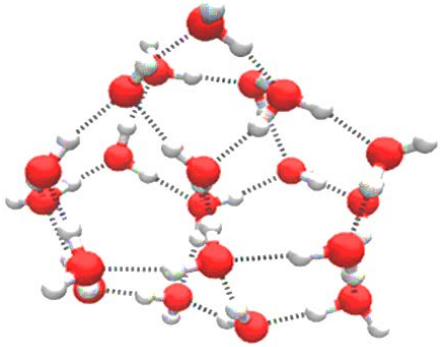
Structure	BLYP-M2/ACPD*		MP2/ACPD*
	[a]ΔE	[b]ΔE	[b]ΔE
20A	0.00	0.07	0.00
20B	0.67	1.30	0.99
20C	0.31	0.00	0.10
20D	3.03	3.18	3.36

*ACPD: aug-cc-pvdz

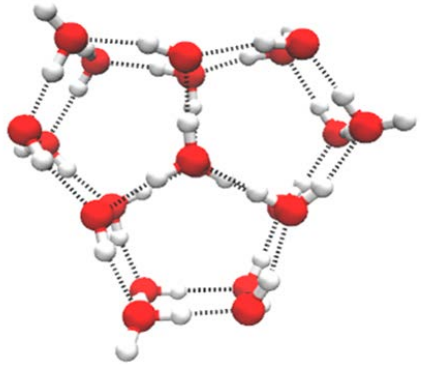
a) Zero-point energy corrections are included

b) Zero-point energy corrections are NOT included

An explanation for stability: balance



455+556

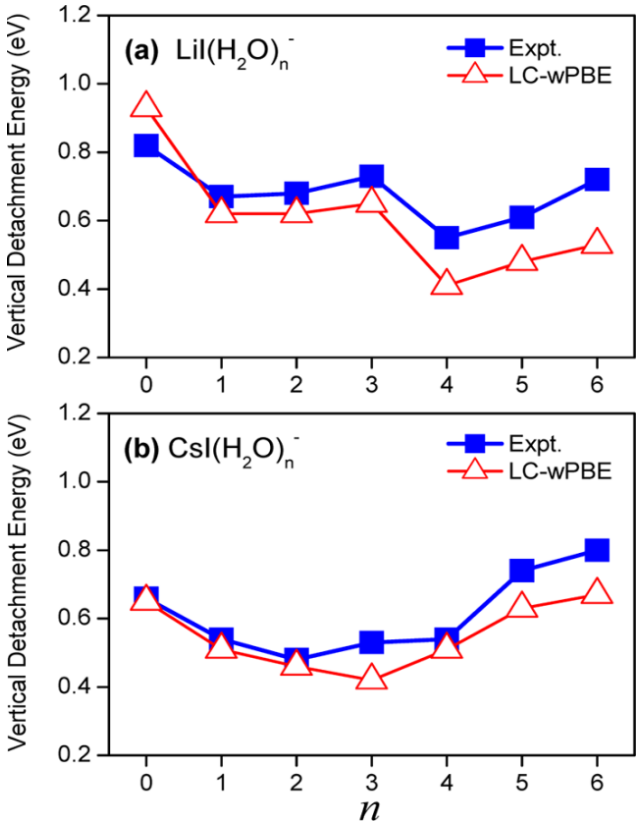


555+555

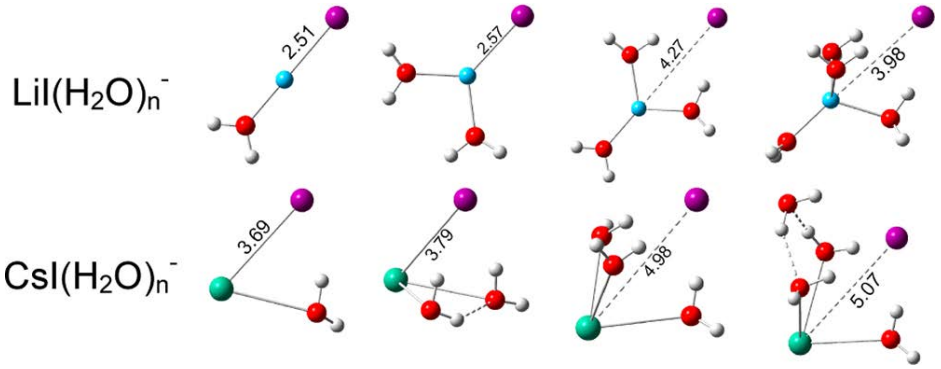
- Hydrogen bondings decrease the energy of the structures
- Four-membered rings bring angular strain caused energy penalty

VDEs and anion structures

VDEs



Structures



Other functionals: ωB97XD and M062X;

CCSD(T) single point energy.

Structures for neutrals

- LiI and CsI interact with water differently
- LiI ion pair becomes separated when n=5

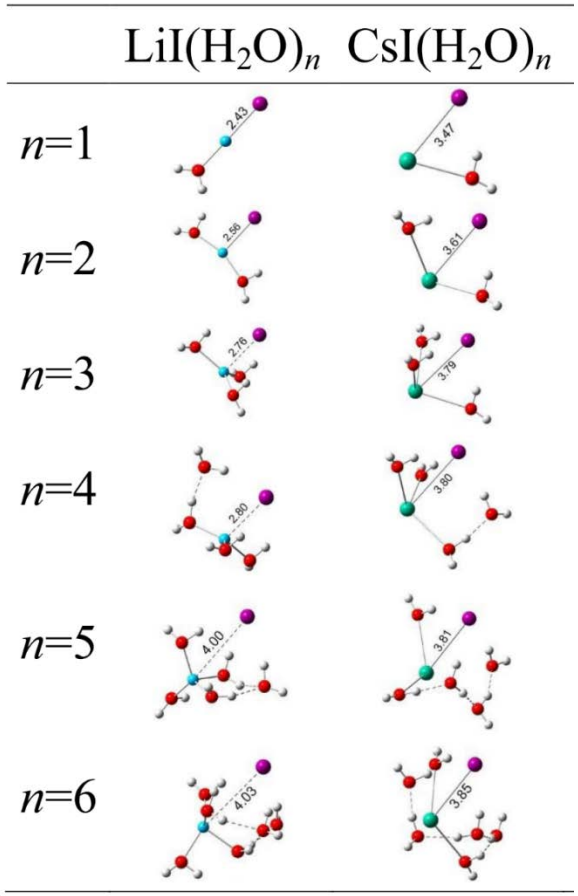
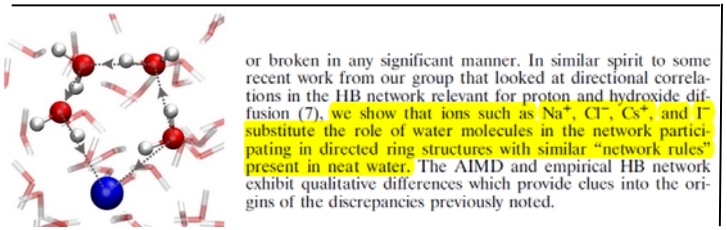


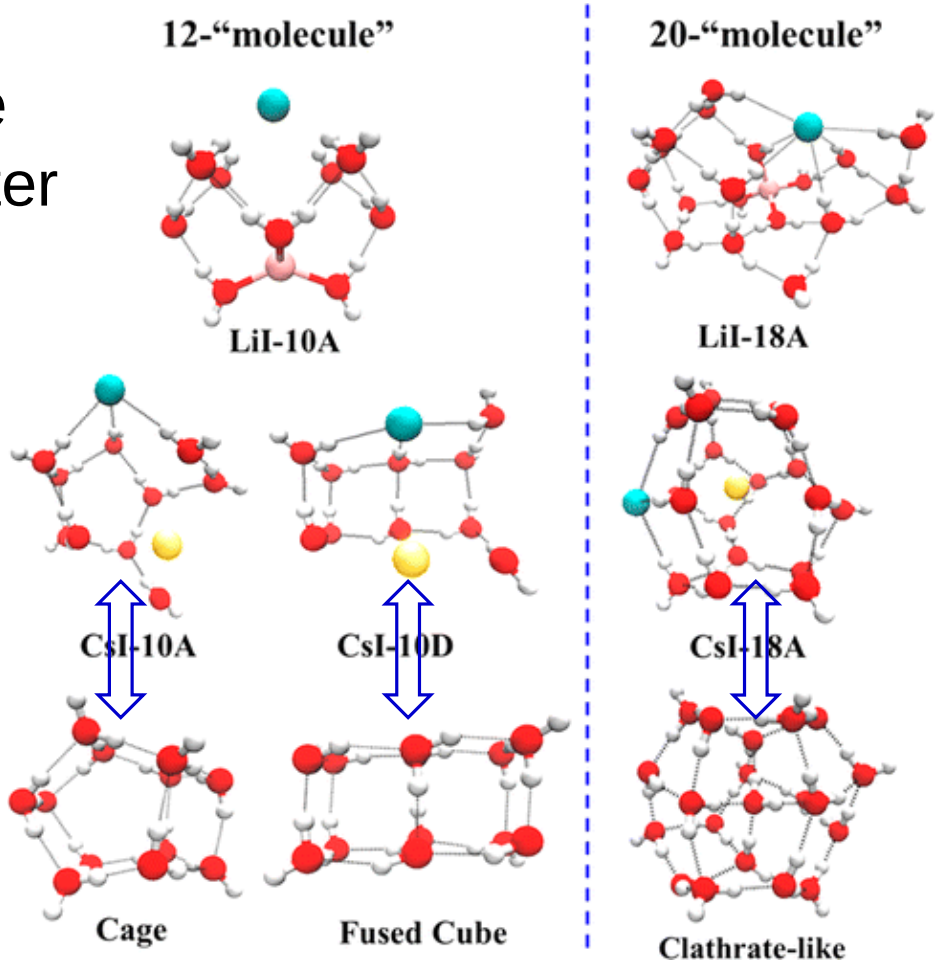
Fig. The global minimum structures for salt-water clusters $LiI(H_2O)_{1\text{-}6}$ and $CsI(H_2O)_{1\text{-}6}$.

Salt-water and water clusters

- LiI largely changes the overall structures of water clusters
- $CsI(H_2O)_n$ resemble the overall structures of water clusters

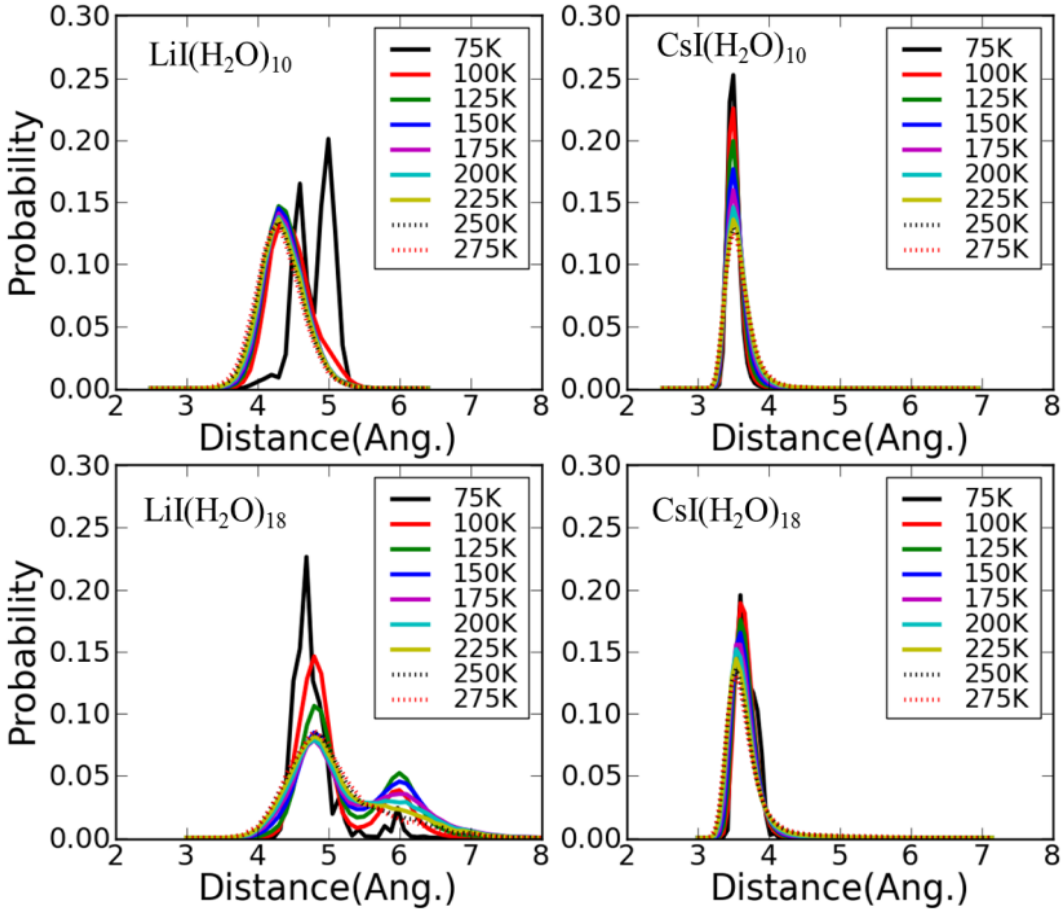


or broken in any significant manner. In similar spirit to some recent work from our group that looked at directional correlations in the HB network relevant for proton and hydroxide diffusion (7), we show that ions such as Na^+, Cl^-, Cs^+, and I^- substitute the role of water molecules in the network participating in directed ring structures with similar "network rules" present in neat water. The AIMD and empirical HB network exhibit qualitative differences which provide clues into the origins of the discrepancies previously noted.



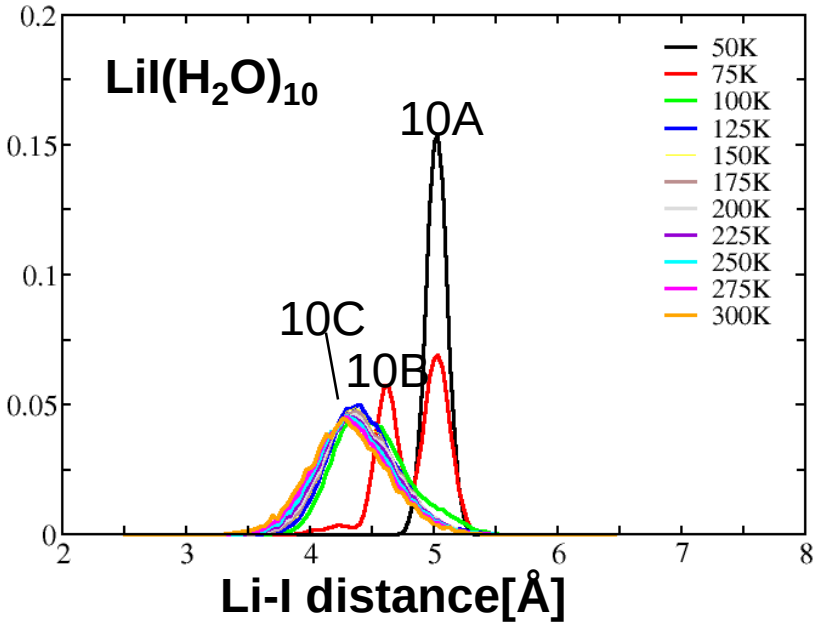
Ding Y., Hassanali A. A., Parrinello M., ***PNAS****, 111, 3310 (2014)*

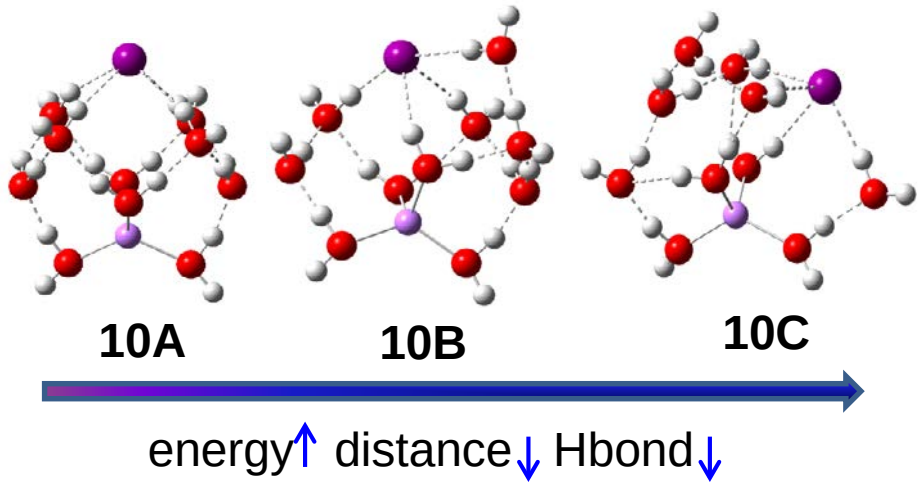
Cation-anion distance distribution



Note: These data come from ITS simulations.

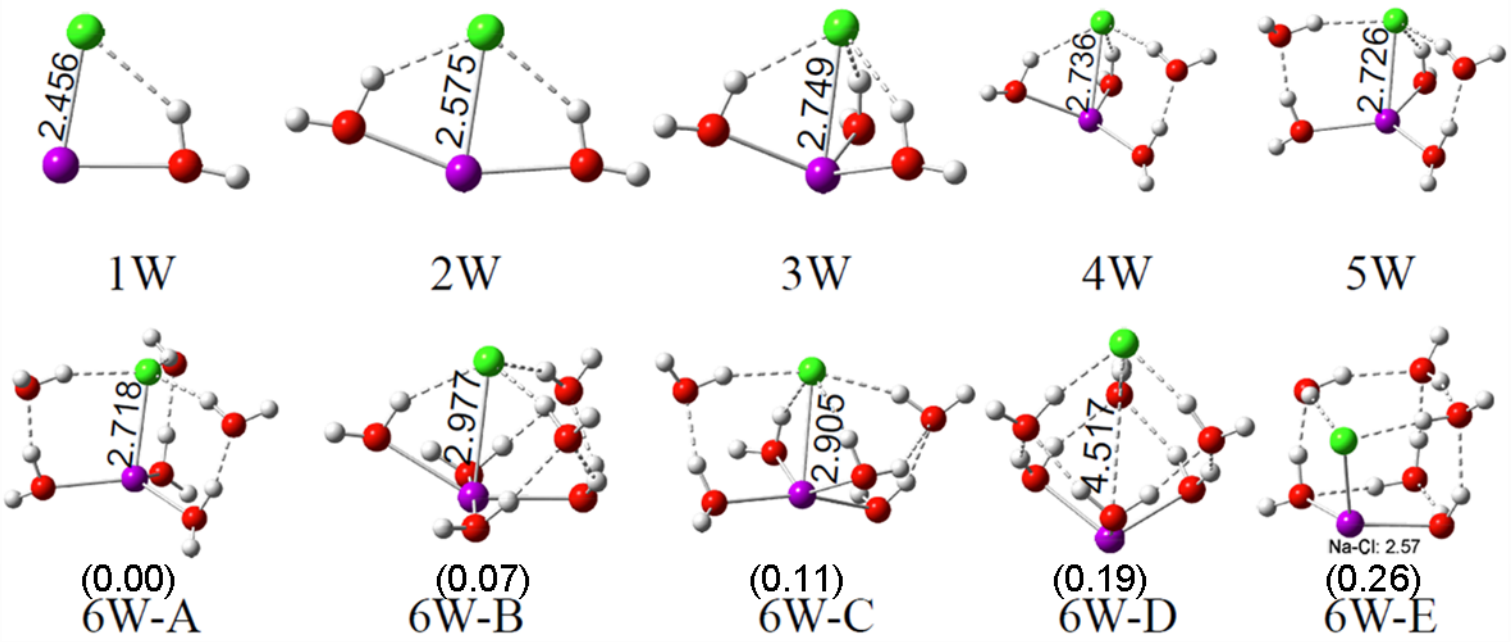
Cation-anion distance distribution





Structure	P.E. (kcal/mol)	Coordination No. Li^+	Coordination No. I^-	No. of HB	Distance (Å)	Temperature (K)
10A	-301.8	4	4	5	5.0	50
10B	-297.6	4	4	3	4.6	75
10C	-281.9	4	4	2	4.3	100

Structures of $NaCl(H_2O)_{1\text{-}6}$



Na-Cl is NOT separated by water.

How Many Waters Are Necessary To Dissolve a Rock Salt Molecule?

Pavel Jungwirth

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

Received: August 24, 1999; In Final Form: October 19, 1999

6 waters are enough !

It is textbook knowledge that in order to dissolve rock salt in liquid water at ambient conditions at least nine water molecules per salt molecule are needed. An obvious but until now unsolved question arises: How many water molecules are necessary to solvate a single sodium chloride molecule? In other words, what is the smallest water cluster in which a solvent separated Na^+/Cl^- ion pair becomes stabilized? The answer, based on accurate quantum chemical calculations, is that simple extrapolation from the liquid is quantitatively wrong and that the *hexamer* represents the smallest water species that dissolves the NaCl molecule.

Solvation of Sodium Chloride: An Effective Fragment Study of $NaCl(H_2O)_n$

Christian P. Petersen and Mark S. Gordon*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

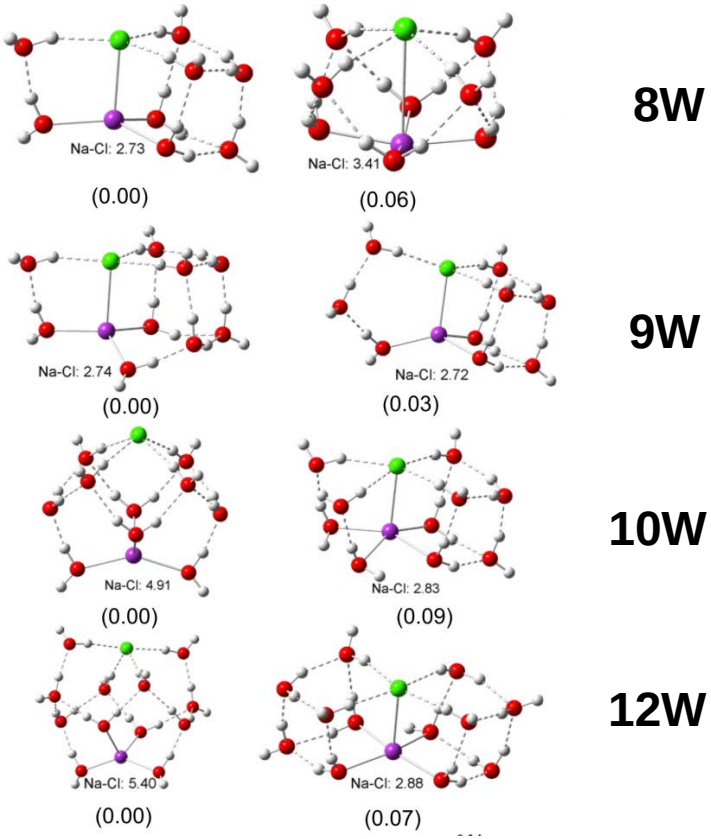
Received: December 29, 1998; In Final Form: March 3, 1999

Analysis of the structures in Figure 3 and the incremental binding energies in Table 3 clearly suggest that NaCl in the presence of 10 water molecules is far from fully solvated. NaCl-$(H_2O)_{10}$ is a contact ion pair, not a separated ion pair, and it is likely that many more water molecules are needed to attain the latter state. A simple calculation reveals that NaCl + 10 water molecules comprises a very concentrated (~6 M) solution. A dilute solution would require 2−3 orders of magnitude more waters. Such calculations are certainly feasible with the efficient

10 waters are NOT enough !

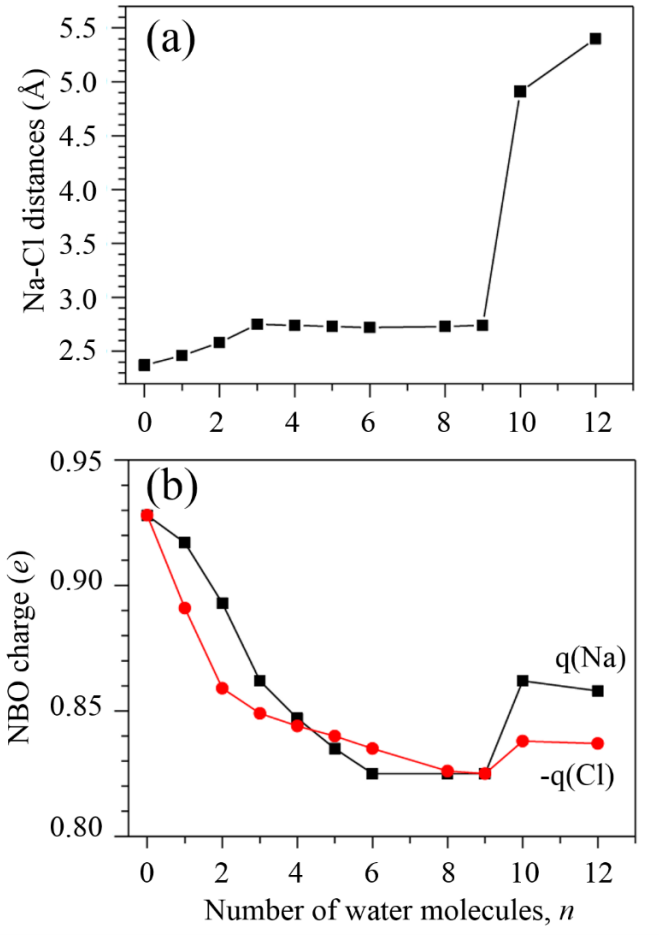
Transition from CIP to SSIP

Structures

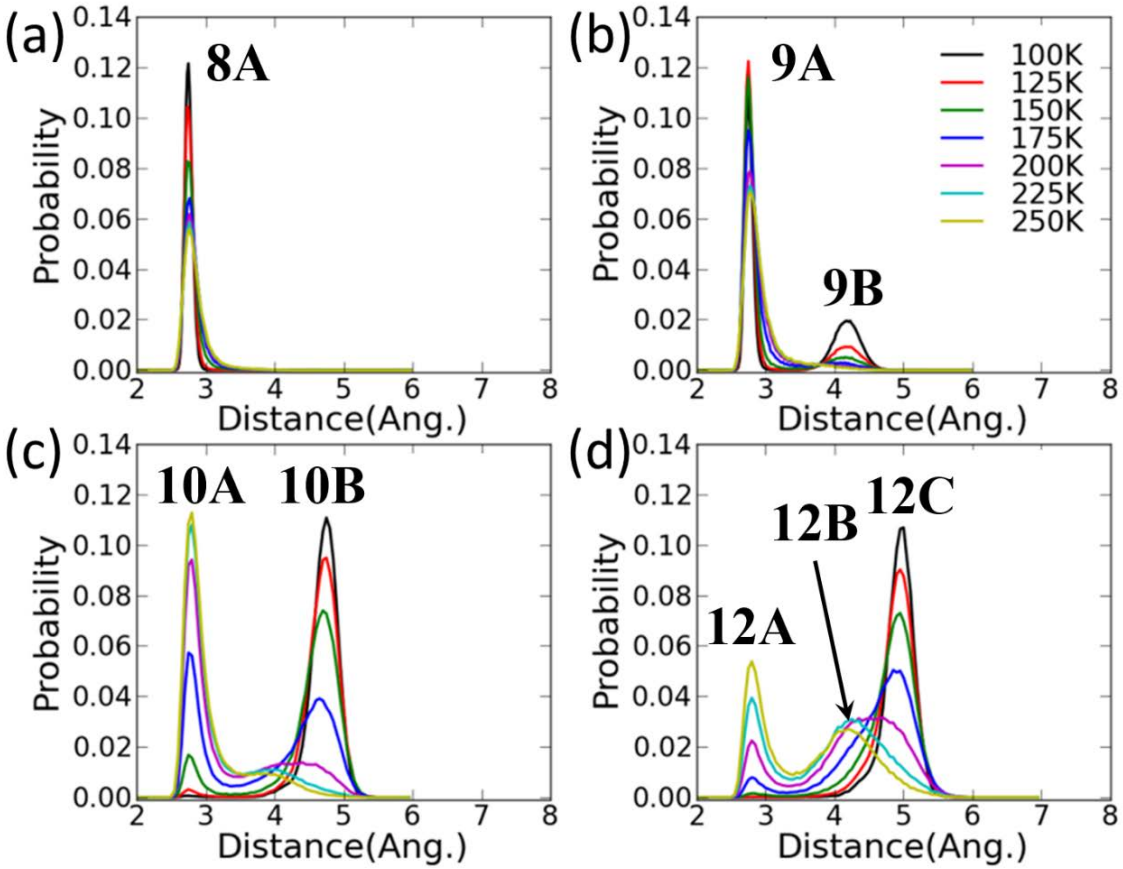


(Relative energy in eV)

Distances and charges

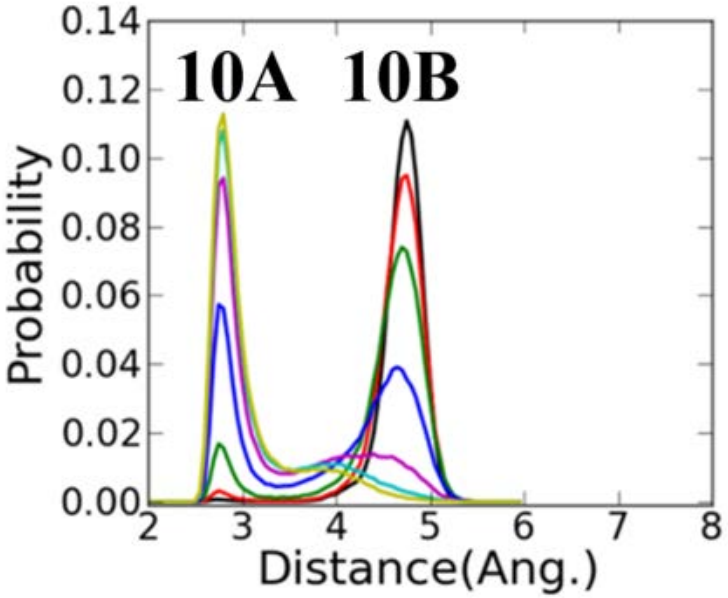


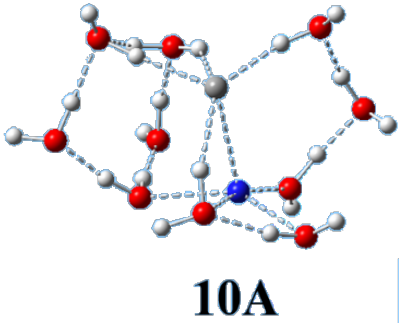
Transition from CIP to SSIP: temperature effect



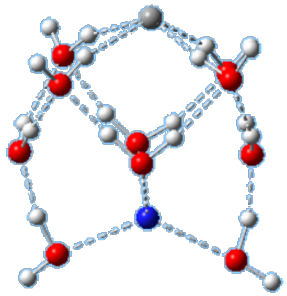
Note: These data come from ITS simulations.

Discussions on temperature effect





10A



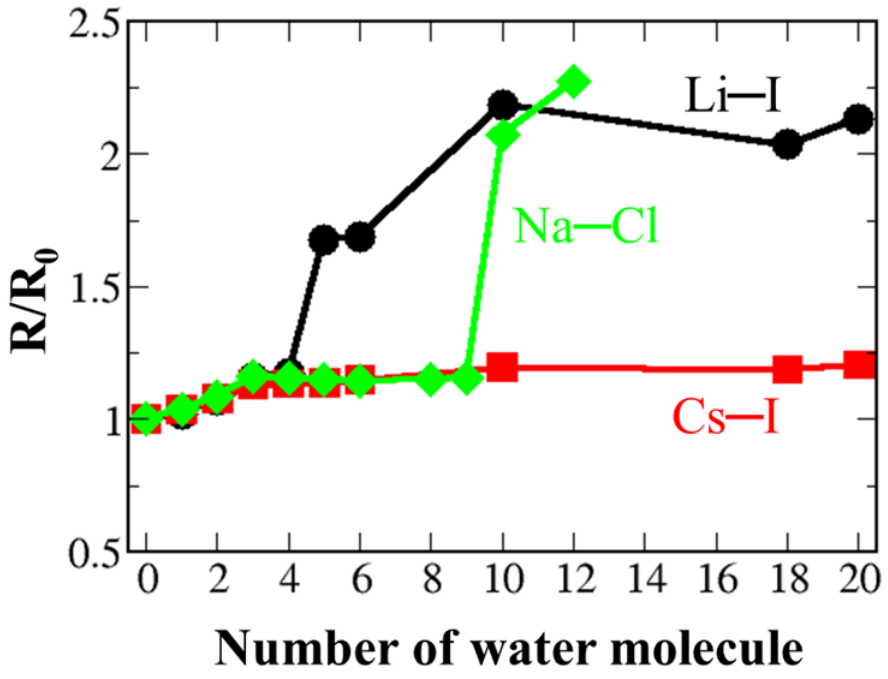
10B

G=H-TS

High temperature: entropy; CIP

Low temperature: enthalpy; SSIP

I. Effective dissolution



- **Ion pairing propensity**

  CsI(1:>20) > NaCl(1:9) > LiI(1:4)

- **Solvent/solute ratio in their saturated solutions at room temperature**

LiI: 12.5 M	4.5
NaCl: ~6.2 M	9
$NiCl_2$: ~5.3 M	11*

*Xia F.-F. et al, ***J. Phys. Chem. A***, *117, 8468 (2013)*

II. Law of matching water affinity

- Interactions of these ions with water
  - Li: strongly hydrated
  - Cs, I: weakly hydrated
  - Na, Cl: moderately hydrated

Li^+,Na^+// K^+,Rb^+,Cs^+

F^-// Cl^- ,Br^- ,I^-

- The overall structures of salt-water clusters are ***ion pair*** specific, indicating ion cooperativity
  - $CsI(H_2O)_n$ resemble the structures of $(H_2O)_{n+2}$
  - $LiI(H_2O)_n$ largely change the structures of $(H_2O)_{n+2}$
  - $NaCl(H_2O)_n$ tend to form cuboid when *n* is large enough

III. ITS(MM)-QM framework

- ITS(MM)-QM framework is validated in studying pure and salt-water clusters
- ITS part can be described by semi-empirical methods, such as AM1, PM3, SCC-DFTB etc.
- Improved framework can be used in other interesting systems such as
  - Chemical reactions in clusters and water/air interfaces
  - Atmospheric species like SO_4^{2-} and NO_3^-

Computational details

- **ITS simulations**
  - Software: Amber9
  - Water model: SPC/E
  - Ions parameter: ions08
  - Integrating step: 0.5 fs
  - Integrated tempering range: 50-350K
- **Quantum calculations**
  - Software: Gaussian 09 (Version A02)
  - Functionals used in optimization: LC-ωPBE, BLYP-M2; ωB97XD, B2PLYPD, M06-2X
  - Single point energy: MP2, CCSD, CCSD(T)
  - Basis sets: Li,Na,Cl,H,O:6-311++G(d,p);
    Cs,I:Lanl2DZdp ECP

Selected publications

1. Cheng-Wen Liu, Feng Wang, Lijiang Yang, Xin-Zheng Li, Wei-Jun Zheng, Yi Qin Gao: Stable Salt–Water Cluster Structures Reflect the Delicate Competition between Ion–Water and Water–Water Interactions. **J. Phys. Chem. B**, 118, 743–751 (2014)
2. Cheng-Wen Liu, Yi Qin Gao: Understanding the Microsolvation of Salts in Molecular Clusters. **Int. J. Quantum Chem.**, 115, 541–544 (2015) (Invited Perspective)
3. Cheng-Wen Liu, Gao-Lei Hou, Wei-Jun Zheng, Yi Qin Gao: Adsorption of Water Molecules on Sodium Chloride Trimer. **Theor. Chem. Acc.**, 133,1–10 (2014)
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