The study of salt effect on water network in THz region: KSCN vs NaCl

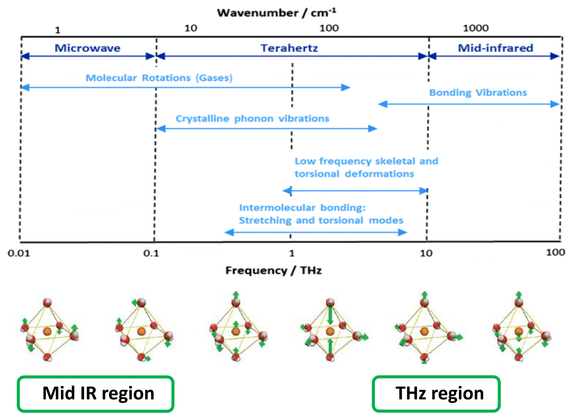
Euihyun Lee and Minhaeng Cho

Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Korea University, Seoul 02841, Republic of Korea
Department of Chemistry, Korea University, Seoul 02841, Republic of Korea

Abstract

The THz spectroscopy is sensitive technique that can investigate their collective motions. THz spectroscopy is corresponding to intermolecular interaction while general Mid-IR is related with intramolecular vibration. So this technique can provide different aspects to us. And classical MD simulation revealed separated contribution for total absorption what is dominated contribution. Using two systems, KSCN and NaCl solution within solubility limit, we investigated relative intensities of each species, they showed not only clear concentration dependence but also the effect of cross correlation term which occupies significant amount between ions at high concentration.

What can we show in THz region ?



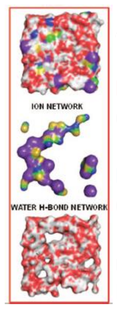
Vibrational mode of molecule

Structural collective motion (bending & stretching mode of OH bond..etc)

To obtain a deeper understanding of the interaction of the network-coupled motions with the ions → Have to probing collective motions on picosecond time scales (THz)

Sensitive to changes in the hydrogen bond network & allows to detect low-E vibrational modes(50-350cm^{-1}) , very sensitive to **the structure of the solvated solutes**

Simulation Details

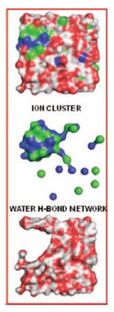


AMBER program package

KSCN aqueous solution : **0.96 m, 3.89 m, 7.3 m, 11.92 m, 21.88 m**
(for each case, 17, 70, 132, 215, and 395 KSCN with 1000 TIP3P water)

NaCl aqueous solution : **1.02 m, 2.08 m, 3.19 m, 4.36 m, 5.59 m**
(for each case, 18, 38, 58, 79, and 101 NaCl with 1000 TIP3P water)

non-bonding interaction cutoff=10 Å, periodic boundary condition
Long-range electrostatic interaction : PME method



The steepest descent method + conjugate gradient method Minimization
2ns NPT ensemble simulation (p=1 atm, T=298 K, dt=1 fs)
2ns constant volume and temperature simulation (298 K)

MD : NVE condition for 3ns, SHAKE algorithm, dt=2fs, cutoff=10 Å
saved every 20fs for velocities (~800 cm^{-1}) · · · for KSCN
MD : NVE condition for 5ns, SHAKE algorithm, dt=2fs, cutoff=10 Å
saved every 20fs for velocities (~800 cm^{-1}) · · · for NaCl

Theoretical Method

$$I(\omega)=\frac{1}{\omega^2}\int_{-\infty}^{\infty}dt\langle\dot{\mathbf{M}}(t)\cdot\dot{\mathbf{M}}(0)\rangle e^{i\omega t} \qquad \dot{\mathbf{M}}(t)=\frac{d}{dt}\sum_{i=1}^{N}q_i\mathbf{r}_i(t)=\sum_{i=1}^{N}q_i\mathbf{v}_i(t)$$

$$\Rightarrow \alpha(\omega)n(\omega)=\frac{4\pi\omega}{3\hbar cV}\tanh\left(\frac{\beta\hbar\omega}{2}\right)I(\omega)$$

$$\dot{\boldsymbol{M}}_{tot}(t)=\dot{\boldsymbol{M}}_{ion}(t)+\dot{\boldsymbol{M}}_{water}(t)$$

$$C(t)=\langle\dot{\boldsymbol{M}}_{tot}(0)\dot{\boldsymbol{M}}_{tot}(t)\rangle=\langle[\dot{\boldsymbol{M}}_{ion}(0)+\dot{\boldsymbol{M}}_{water}(0)]\cdot[\dot{\boldsymbol{M}}_{ion}(t)+\dot{\boldsymbol{M}}_{water}(t)]\rangle$$

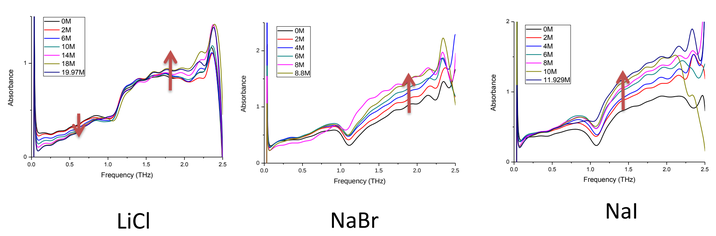
$$=\langle\dot{\boldsymbol{M}}_{ion}(0)\dot{\boldsymbol{M}}_{ion}(t)\rangle+\langle\dot{\boldsymbol{M}}_{ion}(0)\dot{\boldsymbol{M}}_{water}(t)\rangle+\langle\dot{\boldsymbol{M}}_{water}(0)\dot{\boldsymbol{M}}_{ion}(t)\rangle+\langle\dot{\boldsymbol{M}}_{water}(0)\dot{\boldsymbol{M}}_{water}(t)\rangle$$

Ion contribution **Water contribution**

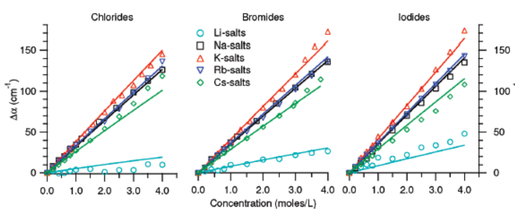
To avoid periodic box problem for ionic system,

We used velocity trajectories instead of coordinates

Experimental examples (ref.)

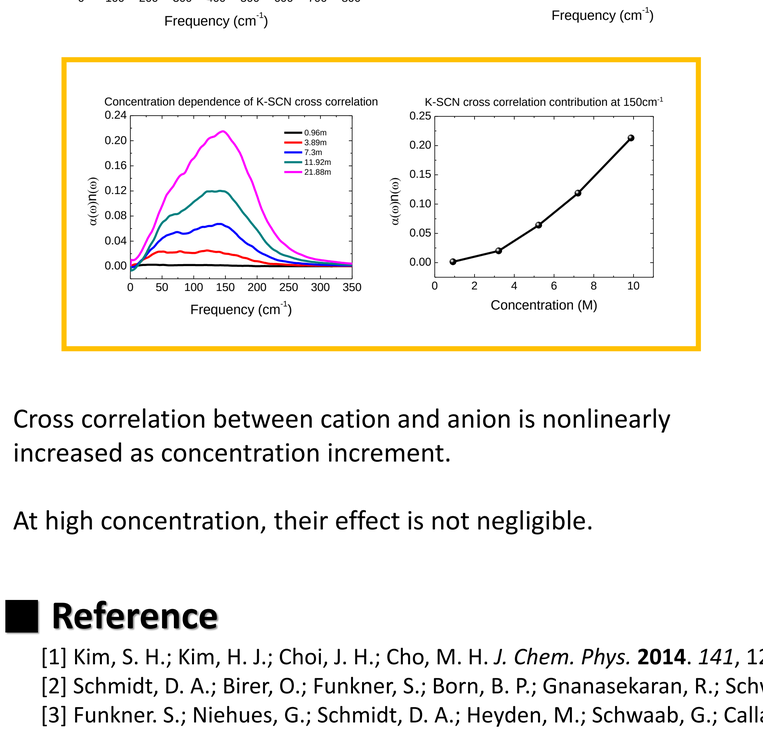


LiCl NaBr NaI



▶ THz excess for monovalent ions

What is the main effect on Ion absorption for KSCN

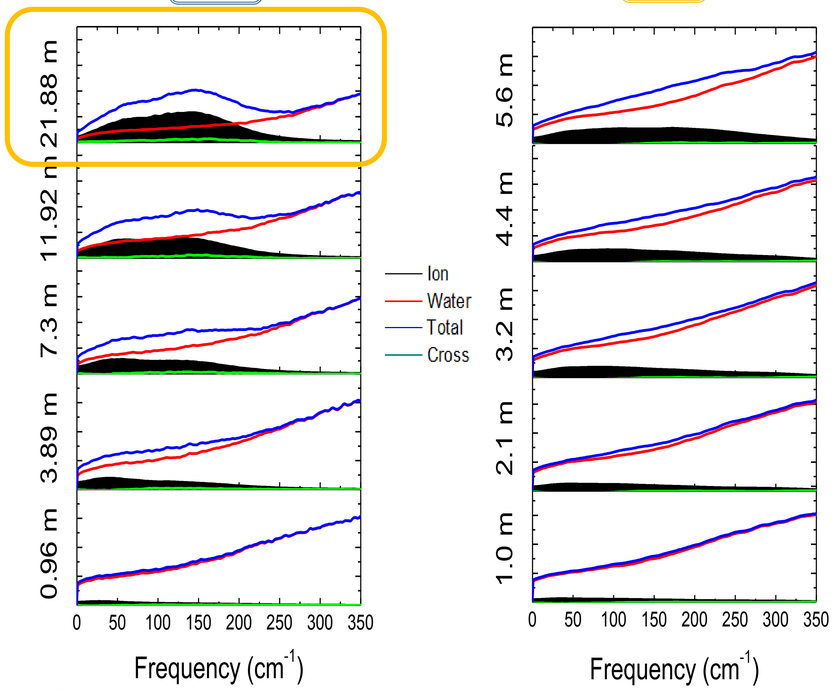


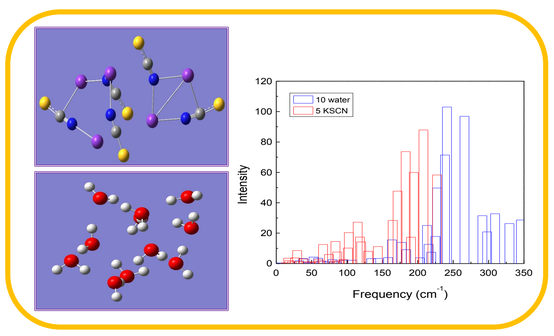
Cross correlation between cation and anion is nonlinearly increased as concentration increment.

At high concentration, their effect is not negligible.

Separated each contribution for Total absorption

KSCN NaCl





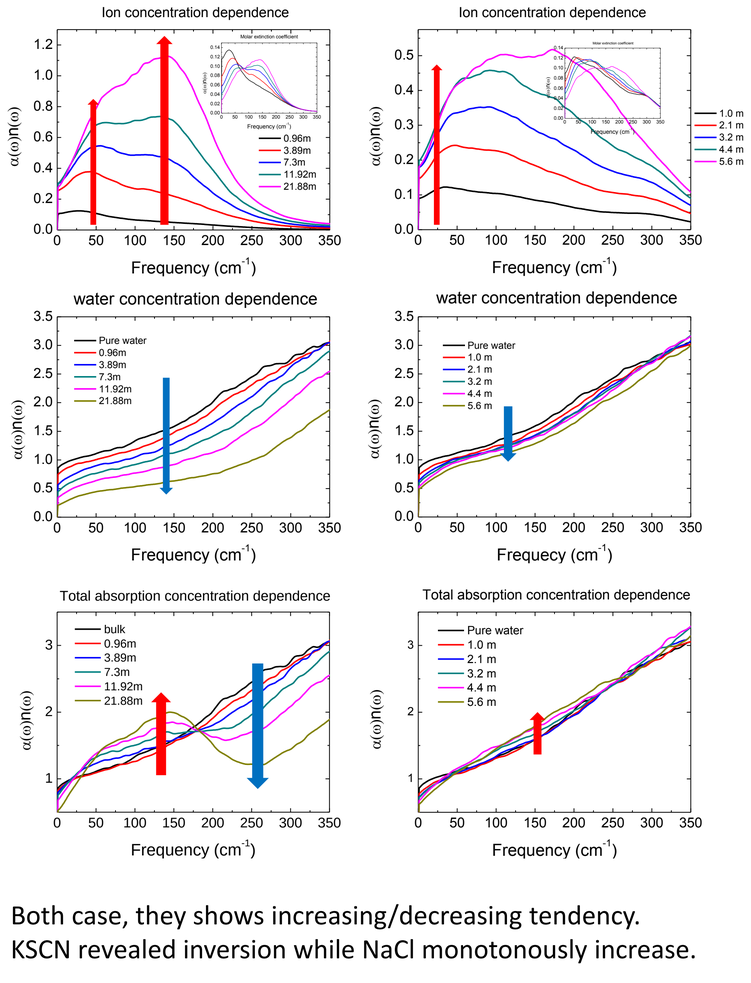
▶ QM calculation for small system

5 KSCN vs 10 Water

Similar result to simulation result at 200 cm^{-1}

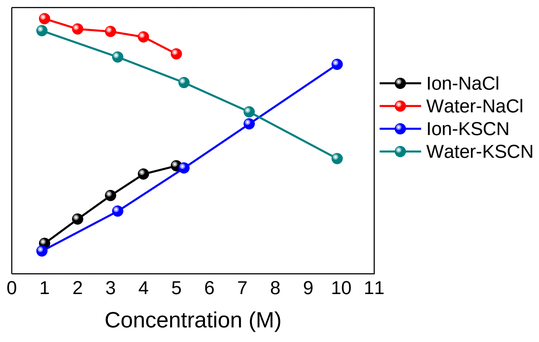
Concentration dependence of each contribution

KSCN NaCl



Both case, they shows increasing/decreasing tendency.
KSCN revealed inversion while NaCl monotonously increase.

Comparison at 100 cm^{-1}



In aspect of solubility limit, there are no significant difference.

Conclusion & Future work

For KSCN and NaCl solutions, we found clear increasing/decreasing tendency about ion and water contribution.

But due to solubility limit, NaCl doesn't show any significant change for total spectrum.

~5 M, there are no big difference between KSCN and NaCl contribution.

To analyze peak position change, we have to calculate INM (Instantaneous normal mode).

Reference

[1] Kim, S. H.; Kim, H. J.; Choi, J. H.; Cho, M. H. *J. Chem. Phys.* **2014**. *141*, 124510.
[2] Schmidt, D. A.; Birer, O.; Funkner, S.; Born, B. P.; Gnanasekaran, R.; Schwaab, G. W.; Leitner, D. M.; Havenith, M. *J. Am. Chem. Soc*. **2009**, *131*, 18512-18517.
[3] Funkner. S.; Niehues, G.; Schmidt, D. A.; Heyden, M.; Schwaab, G.; Callahan, K. M.; Tobias, D. J.; Havenith, M. *J. Am. Chem. Soc.* **2012**, *134*, 1030-1035.