

The FT-IR Study of Hofmeister Anion Effect on the Aqueous Solution

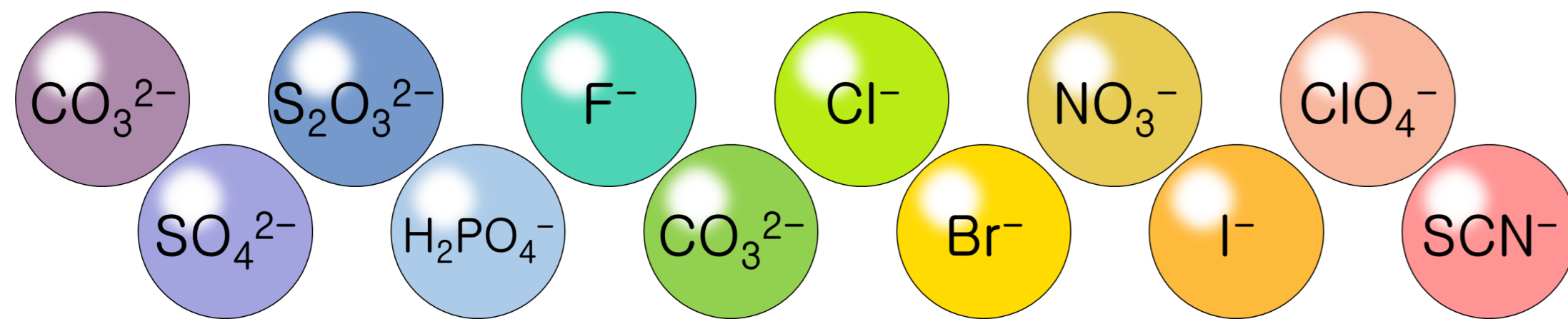
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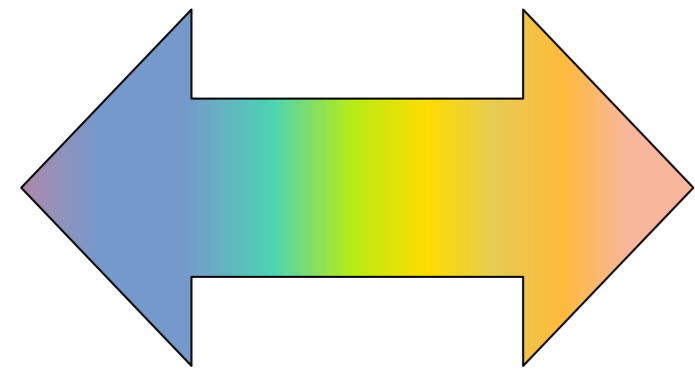
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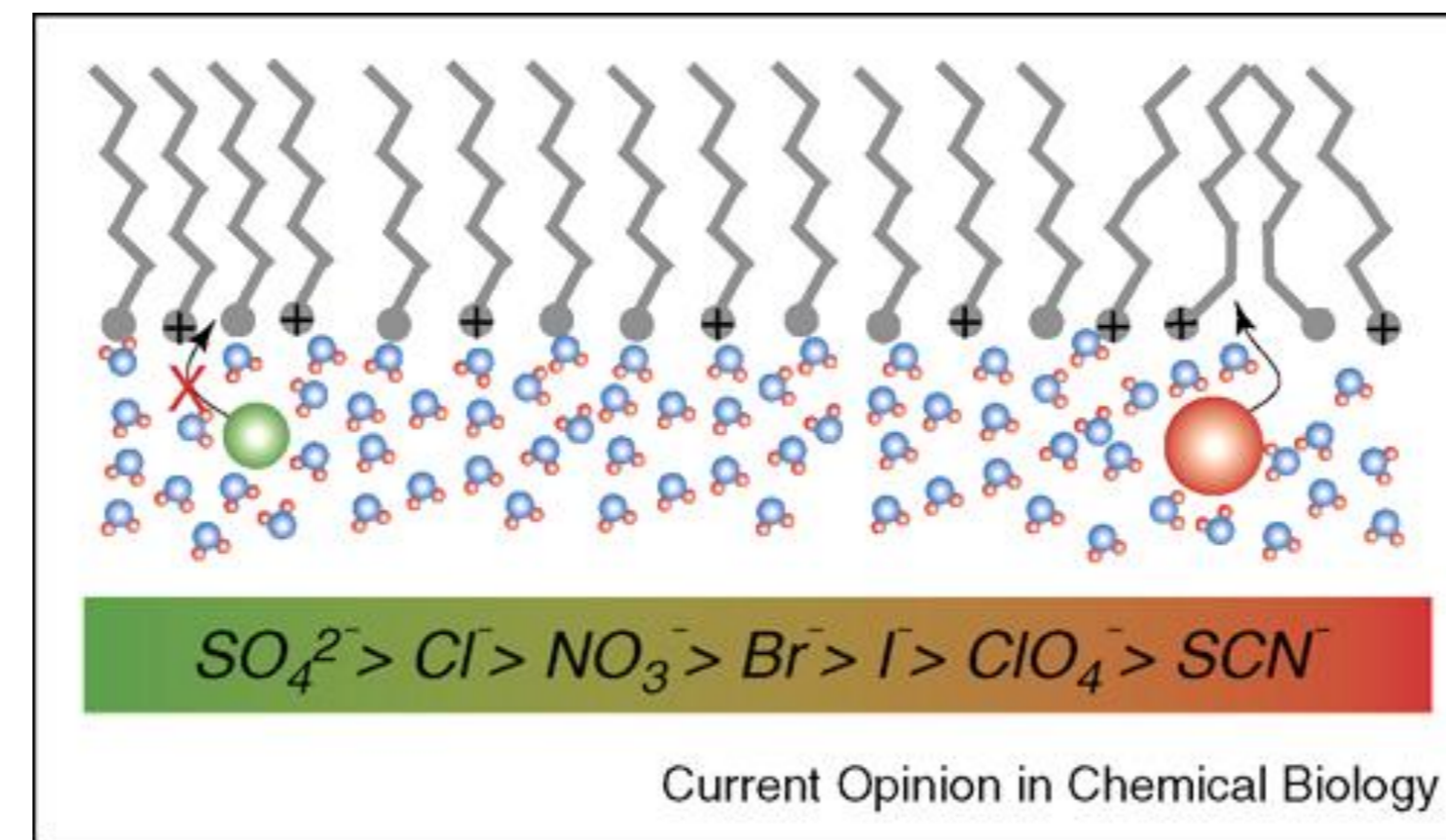
❖ Specific Ion Effect on the Water



Surface tension ↑
Harder to make cavity
Solubility of proteins ↓
Salting out (aggregate)
Protein denaturation ↓
Protein stability ↑



Surface tension ↓
Easier to make cavity
Solubility of proteins ↑
Salting in (solubilize)
Protein denaturation ↑
Protein stability ↓



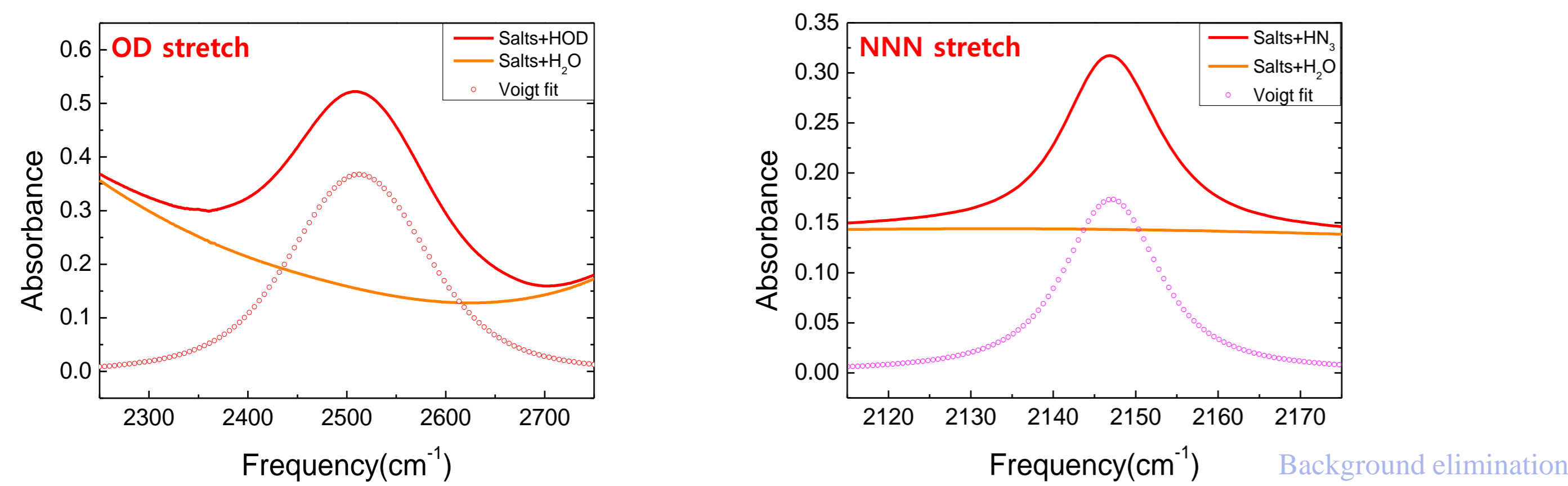
Y. Zhang et al. *Curr. Opin. Chem. Biol.* 2006, 10, 658-663

❖ OD and HN₃ as IR Probe

The OD stretch band is well-known probe of local H-bond strengths & molecules environment in systems containing water. The OD spectrum of HOD in water is very broad due to a wide range of H-bond strengths & different numbers of H-bonds. Species with stronger and more hydrogen bonds absorb on the red-side (low-frequency region) or the spectrum while those with weaker and fewer absorb on blue-side (high-frequency region).

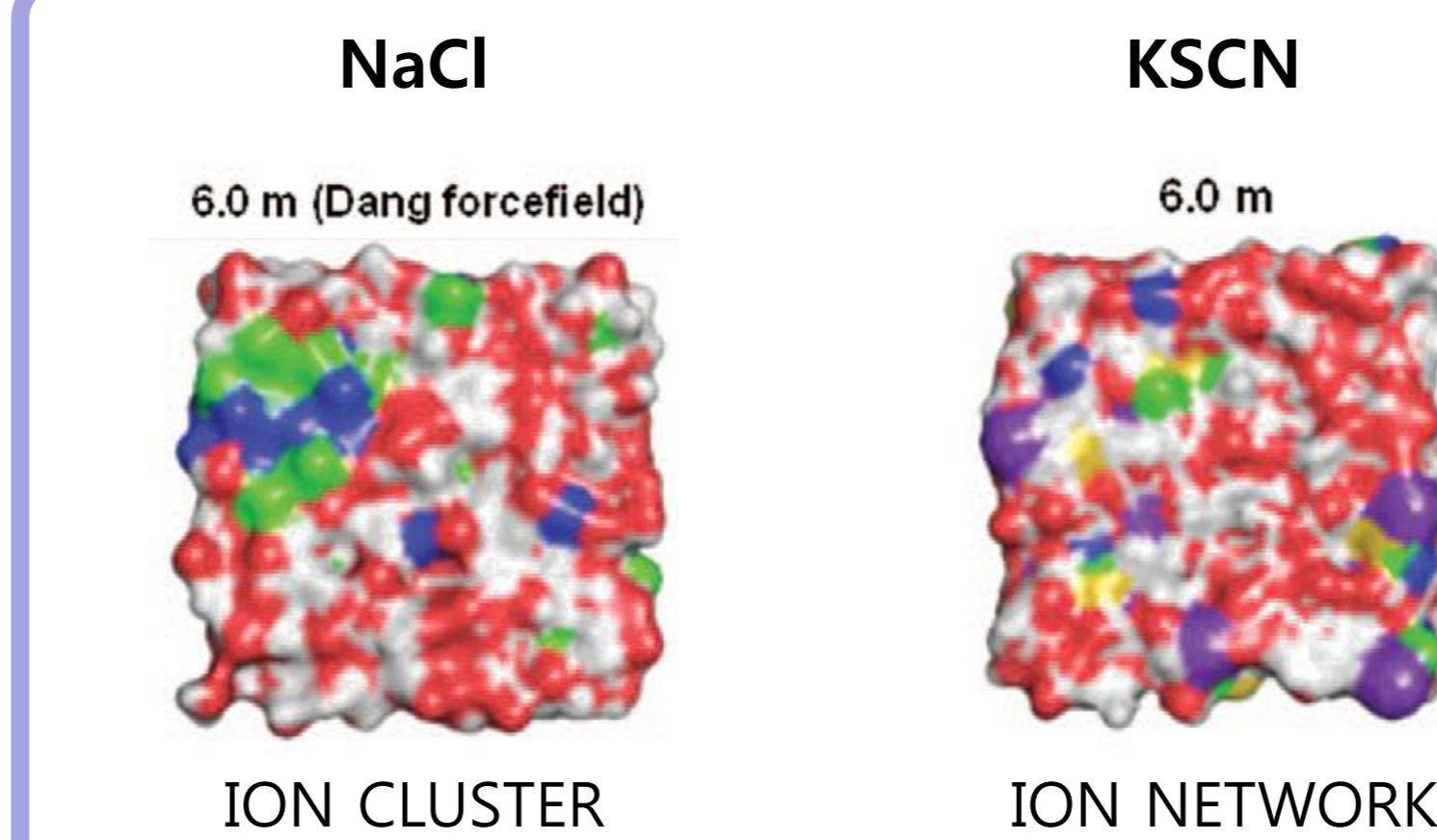
HN₃ has a unique sense of hydration, not only in systems containing others H-bonding groups like amide and alcohols, but also in nanometer-sized water-pool of reverse micelle. Its stretching frequency shows no remarkable dependency on solvent polarity. But is highly correlated to the numbers & orientation of H-bond donors. Therefore, HN₃ provides a promising model system to probe whether the addition of a third molecules component (here anions) will affect NNN-H₂O H-bonding interaction.

❖ IR spectrum in Ion solution



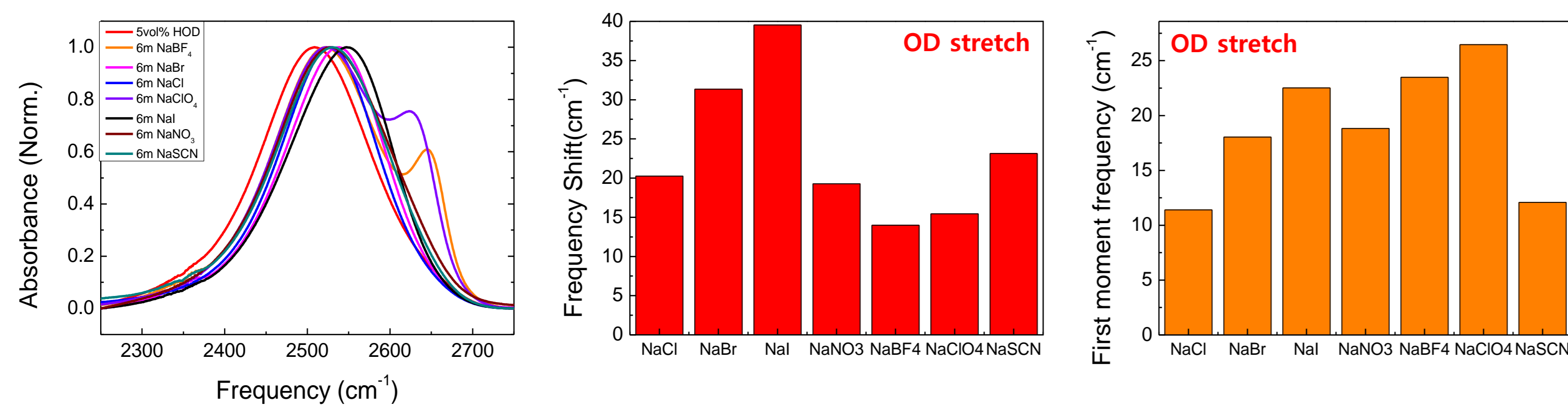
Background elimination

❖ MD simulation suggests Ion cluster or network

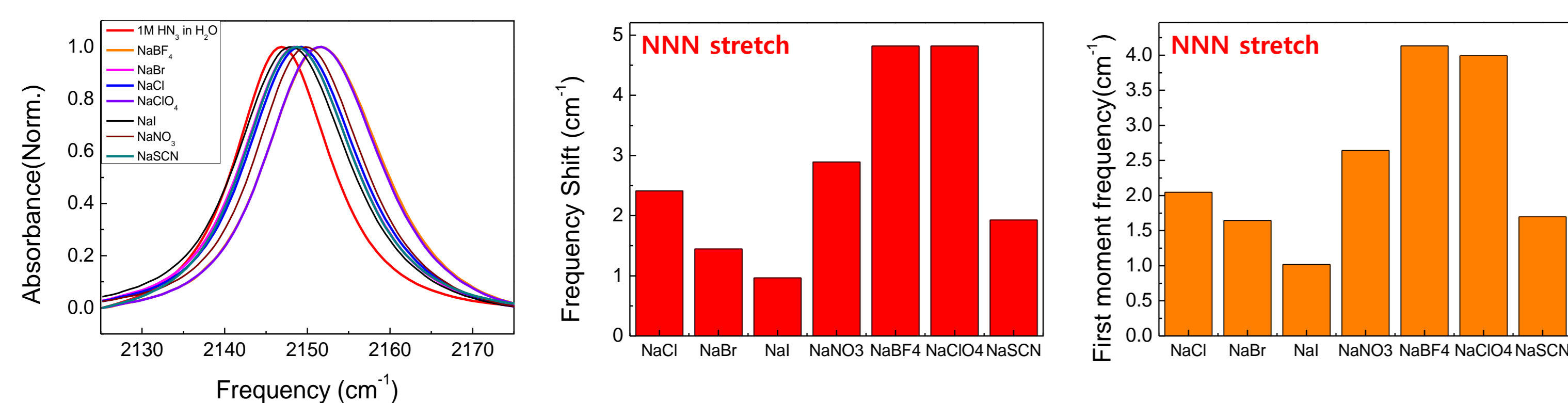


Cl⁻ ion tends to form large ion cluster structure, whereas SCN⁻ ions tends to form ion network structure in their solubility limit. This indicates that Cl⁻ ion is kosmotropic ion and SCN⁻ ion is chaotropic ion.

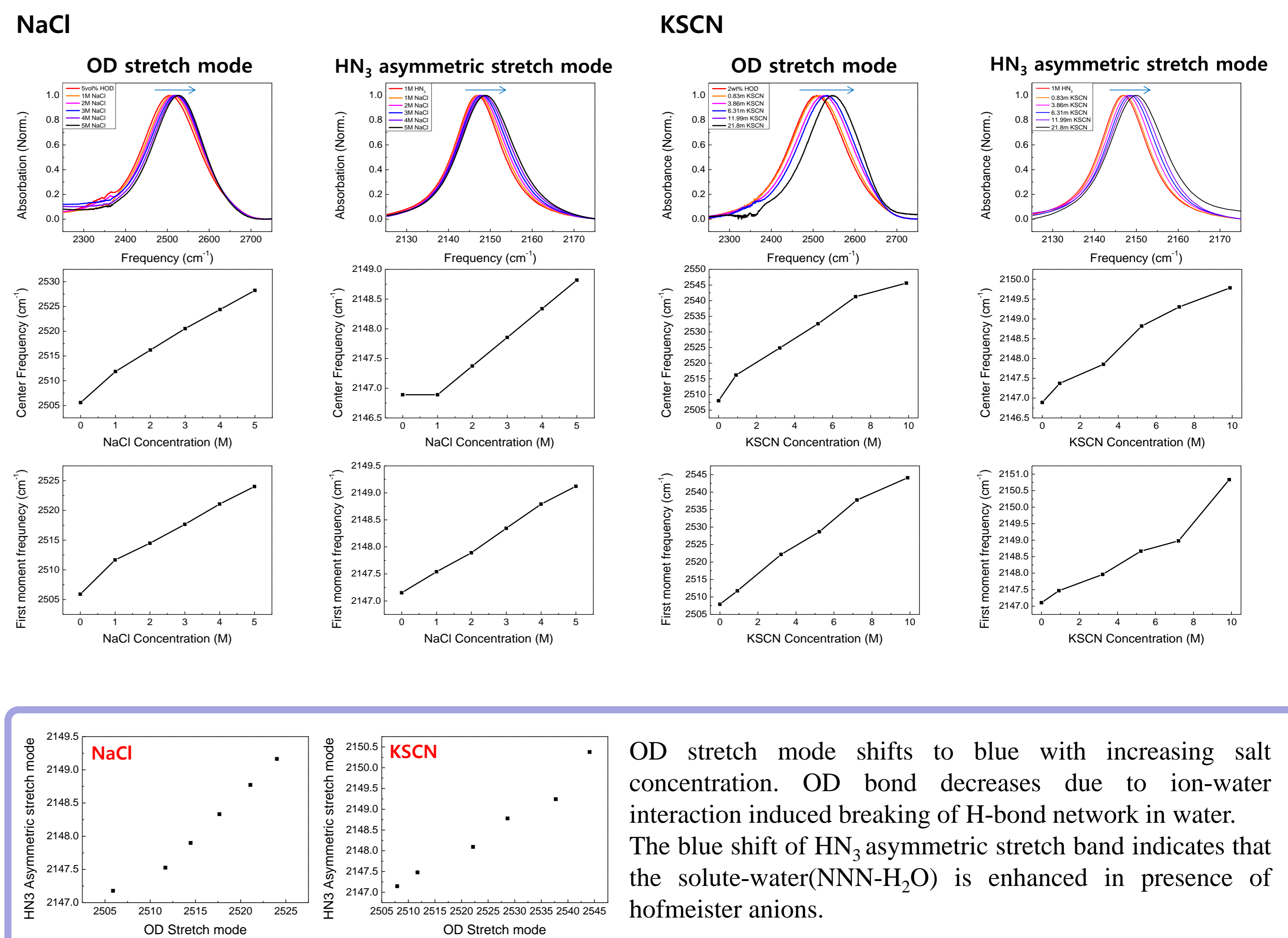
S. Kim et al. *J. Chem. Phys.* 2014, 141, 124510



The shoulder peak in 6m NaClO₄ and NaBF₄ originate from OD stretch interacting with anion.



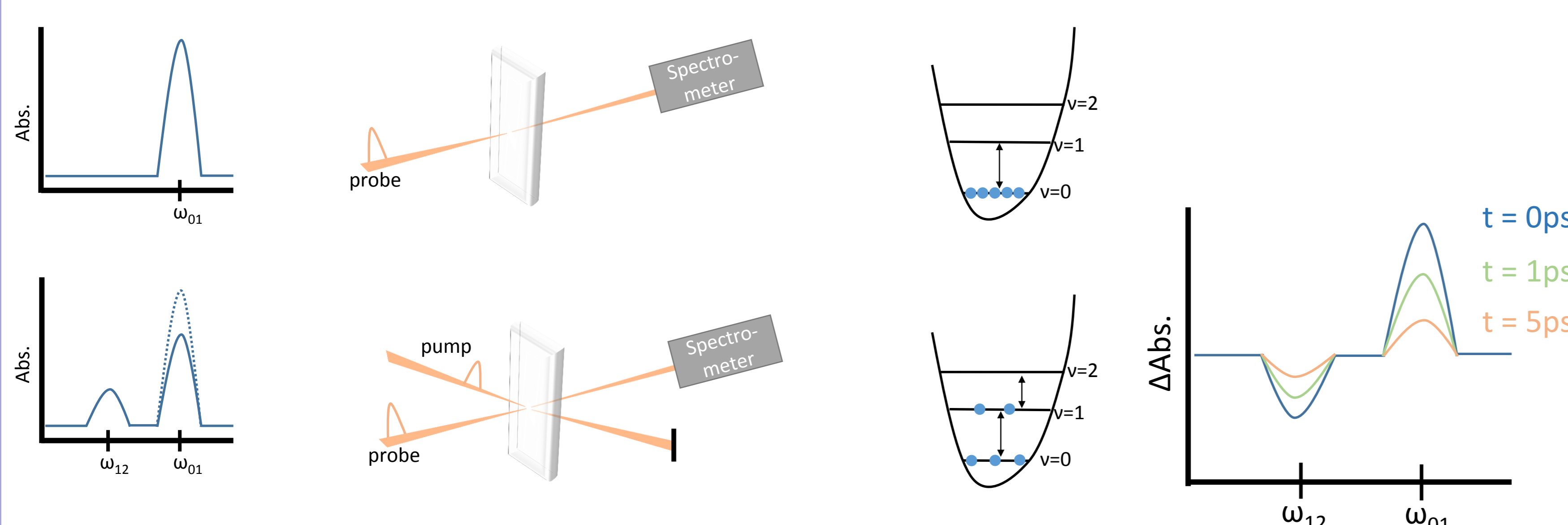
It is different to shift order. It is the degree of peak shift. The order of the Hofmeister ion series data for the shift is much happened. Trends are almost contrary.



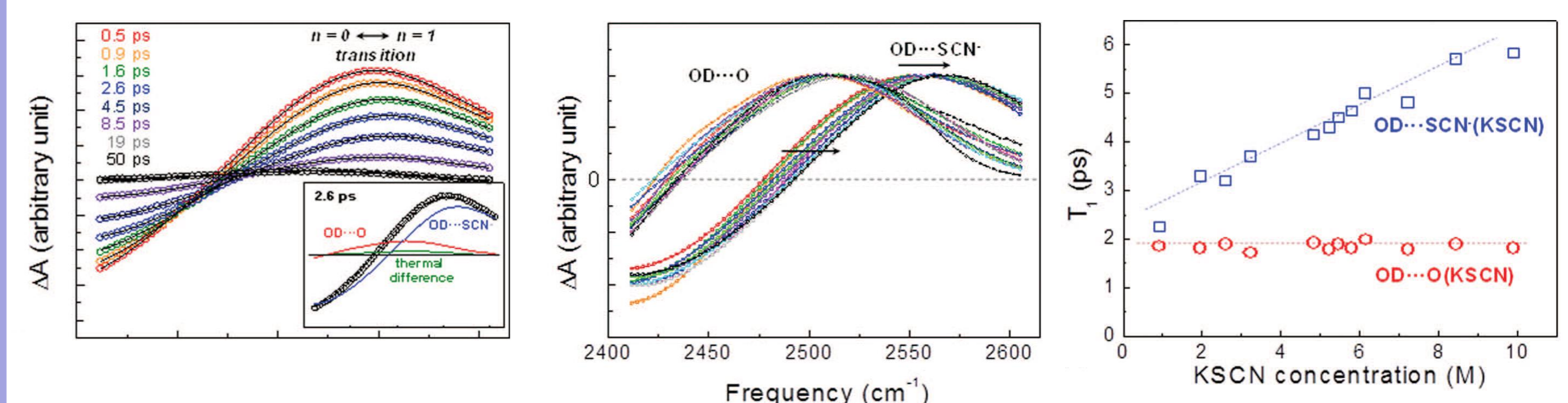
OD stretch mode shifts to blue with increasing salt concentration. OD bond decreases due to ion-water interaction induced breaking of H-bond network in water. The blue shift of HN₃ asymmetric stretch band indicates that the solute-water (NNN-H₂O) is enhanced in presence of hofmeister anions.

❖ Future work

IR pump-probe spectroscopy



Perspective



Specific ion effects on water H-bond structure and dynamics result from a balance between ion-water and ion-ion interaction. We will study vibrational lifetime of the HN₃ stretch band in aqueous solution of hofmeister anion using femtosecond IR pump-probe setup.

S. Kim et al. *J. Chem. Phys.* 2014, 141, 124510