

# Cooperative Hydrogen Bonding in Ionic Hydration

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**Summary:** We illustrated spectral patterns of many-body interactions that can be elucidated using a single near-infrared absorption band.

**Introduction:** In concentrated ionic solutions the ratio of the total number of water molecules to ions becomes sufficiently small to generate a different solvating environment. Depletion of bulk water causes overlap between the hydration shells of anions and cations, which places the water molecule under simultaneous influence of both ions. Under these influences the cooperative effect arises which causes modifications in water-chlorine hydrogen bonds. Cooperativity principle utilizes only single OH bond to explain the dynamics of many-body interaction between anion-cation and several surrounding water molecules.

**Methods:** Near-infrared spectra of pure water and alkali-halide ion solutions are taken over wide concentration range, from 10 mM to 5000 mM, using FT-NIR spectrometer (MPA, Bruker) fitted with 1mm quartz cuvette in spectral range between 800-2500 nm with spectral resolution of 2 nm. All spectra were normalized using standard normal variate transform after which averaged spectrum of pure water was subtracted from the spectra of solutions.

**Results and Discussion:** Figure 1 shows the near infrared spectra of ionic solutions from which the spectrum of pure water was subtracted [1]. We observe the main positive band around 1420 nm that describes the details of cooperative hydrogen bonding and its spectral signatures.

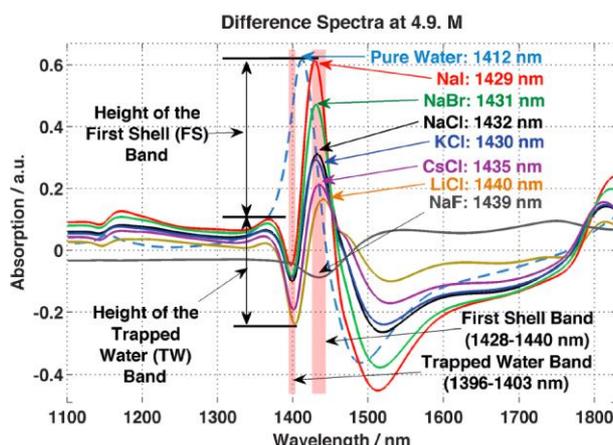


Figure 1. Near infrared spectra can describe cooperative hydrogen bonding. Dotted line is the spectrum of pure water at 70°C from which the spectrum at room temperature was subtracted and designates thermally induced quasi-free OH bonds of water. For comparison, this spectrum was scaled down, to illustrate the spectral description of water-water hydrogen bonds. In ionic solutions this band is red-shifted in response to more stable water-ion hydrogen bonds.

Nearly all solutions follow this trend except for the solution of CsCl, which deviates from trends dependent on charge density. We investigated the possible reasons for this unexpected arrangements and in a recent study on hydration of alkali-halide salts [2] it has been revealed that K, Rb and Cs possess hydration shells that differ from smaller ions, namely Li and Na. Their hydration shells were

described with non-linear hydrogen bonds that enabled waters in the first shell to form cage-like structures.

This finding suggests a different structure of the first hydration shell for CsCl ions and the origin for apparently stronger hydrogen bonds between water and chlorine. The explanation is that additional water-water hydrogen bonds are built around cesium ion that contribute to stronger cooperative effect between Cs and Cl. Therefore, even apparent exceptions from trends in charge density can be explained by cooperativity principle.

This finding is valuable since it enables us to infer a complex many-body type of interaction from the observation of a single near infrared band of a single OH bond that was previously found to be the one pointing towards the anion [1].

The main negative band around 1490 nm is probably related to anti-cooperative effect and belongs to the OH bond of water belonging to the first shell of ions, and that is pointing away from anion and towards outer shell water molecules.

The weaker negative band around 1400 nm was previously found [1] to correspond well to the law of matching affinities and is believed to describe the water molecules that are trapped in the local field of both ions.

**References:**

1. Kojić D., Tsenkova R., Tomobe K., Yasuoka K., Yasui M., ChemPhysChem 15, 2014, 4077-4086.
2. Ke H. van der Linde C. Lisy J.M., J. Phys. Chem. A 2015, 119 (10), 2037-2051.