

Study the Spatial Range of Ion Effect using 1D and 2D

Vibrational Spectroscopy

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The range of ion effect on water in ionic solutions was studied theoretically using 1D and 2D vibrational spectroscopy. Evidence of ion effect beyond its hydration shell was addressed in infrared photodissociation spectra and low frequency vibration spectra.

Ions alter the three dimensional hydrogen bond network in water, change the orientations of the water molecules, and affect their dynamical properties. For decades, the correlation between the ion hydration and the solution dynamics has been a topic of great scientific interest. A fundamental question about the impact of ion pertains to the range of it on the molecular properties of the surrounding water molecules.

Most previous solution phase studies at room temperature suggest that ions, except those with high charge densities (such as Li^+ , Mg^{2+} and Al^{3+}), affect only the water molecules in their first solvation shells. Recent gas phase infrared photodissociation (IRPD) experiments on the large ion-water nano droplets, on the other hand, present the strong evidence that ion effect can go far beyond the solvation shells. Combining the enhance sampling technique and spectroscopically accurate polarizable model, we successfully simulate the IRPD signals of the large ion-water droplets. Further analysis using complex network analysis (CNA) technique indicates that the droplets at 133K have a more ordered water structure than that at 300K. Ion effect on its hydration shell can therefore be transferred to the droplet surface, which explains the discrepancy between the results of infrared photodissociation and the solution phase experiments at room temperature.

By investigating the low frequency vibration (GHZ~THz) spectra, we further demonstrate that ions can affect the delocalized collective motions of water, therefore their influence can go beyond the solvation shells. Our simulation shows that the dielectric relaxation spectrum of $MgSO_4$ exhibits a significant feature around 0.5 GHz, which is missing in the signals of pure water as well as NaCl solutions. Further coarse graining study using a gaussian field model clearly demonstrate that this is a delocalized ion effect on a collective water motion, rather than the ion par rotation as traditionally believed.

Further theoretical study of low frequency 2D (Raman-THz) vibrational spectra of ionic solution demonstrate that ion can not only affect the transition frequency and dipole of these collective water modes, but more interestingly affect the correlation between two different collective modes. These studies therefore open the new spectroscopic windows for understanding the spatial range of ion effect on the environments.