Numerical simulation of HDO IR and Raman spectra in aqueous salt solutions

Jun-Ho Choi[a,b], Minhaeng Cho[a,b]

[a]*Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science, Korea University, Seoul 02841, Korea*
[b]*Department of Chemistry, Korea University, Seoul 02841, Korea*

The OD stretch vibration of HDO as an IR probe has been used to investigate water H-bonding structure and dynamics in aqueous solutions containing various solute molecules. Although vibrational spectroscopic measurements such as IR absorption and Raman scattering provide critical information on water structure in solutions, interpretation on corresponding vibrational spectrum is not straightforward sometimes due to featureless band shape and difficulty in peak assignment of a given vibrational mode. Quantum mechanical (QM) calculation has been widely used for vibrational analysis and numerical simulation of vibrational spectrum for a target system. When an IR probe molecule is dissolved in liquid water, the configuration of water molecules around it is constantly changed causing fluctuating vibrational properties of solvatochromic frequency and transition dipole moment of a given mode. Therefore, this solvent induced inhomogeneous broadening factor needs to be considered carefully to describe fully band shape of a vibrational spectrum in solution system.

We recently developed a systematic theoretical way to calculate time-varying vibrational properties and numerically simulate HOD vibrational spectrum in aqueous salt solutions. Combining molecular dynamics (MD) simulation with the vibrational solvatochromism model [1], we already were able to successfully describe linear and nonlinear vibrational spectra of amide I mode and a variety of IR probes, that is, -CN, -SCN, -N_3, CO (MbCO) stretch modes. [1-3] Here, OD vibrational spectra in pure liquid water and salt solutions were numerically simulated estimating transition dipole moment as well as transition frequency in time and directly compared to experimentally measured vibrational spectra. [4,5]

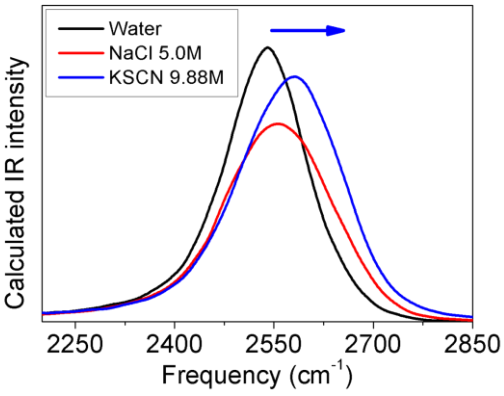

Fig. 1 HOD IR simulation in salt solutions.

Keywords: MD simulation; vibrational spectrum; QM calculation; solvatochromism

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