

Vibrational spectral diffusion in aqueous systems

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We present a first principles theoretical study of vibrational spectral diffusion in aqueous solutions under normal and supercritical solutions. The present calculations are based on ab initio molecular dynamics [1] for trajectory generation and a time series analysis using the wavelet method [2] for calculations of time dependent vibrational frequencies. Population correlation function method [3] is also employed in order to extract time scales of various dynamical processes in these solutions. The dynamics of vibrational spectral diffusion is investigated by means of frequency time correlation and spectral hole dynamics calculations. Results are obtained for a variety of aqueous systems containing ionic and molecular solutes at varying concentrations and also under varying thermodynamic conditions. At room temperature, generally the dynamics is found to have a short time component that is attributed to dynamics intact hydrogen bonds and a slower longer time component that arises from breaking dynamics of hydrogen bonds and local structural relaxation [4]. The slow escape dynamics of solvent molecules can also influence the long-time dynamics depending on the concentration of the solutions. The overall dynamical scenario can be different for supercritical solutions or for water molecules at interfaces [5]. Correlations of vibrational frequency changes with simple chemical reactions such as proton transfer processes in aqueous systems are also investigated.

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