

Vibrational spectral diffusion and chemical dynamics in aqueous solutions

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We present a first principles theoretical study of vibrational spectral diffusion and chemical dynamics 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 water 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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Electrical resistivity of a Precambrian native iron sample at high-pressures up to 9.0 GPa

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The origin of native iron in nature has been a subject of much speculation and various theories have been suggested ranging from meteoritic impact to chemical reaction between magma and carbonaceous sediments. In India presence of native iron has been observed by Abbott *et al.* [1] by using scanning electron microscopy, and magnetic susceptibility measurements on the pre 1.6 Ga sediments of the Chaibasa shales. Subsequent detailed studies on the same samples by using Mössbauer and X-ray photoelectron spectroscopy [2, 3] not only confirmed the presence of native iron Fe⁰, but also the presence of residual stress in the sample. In this study we report the room-temperature electrical resistivity measurements on the native iron sample by using opposed anvil cell technique and solid – pressure transmitting medium. The uncertainties and calibration of pressure of the system have been discussed elsewhere [4]. The relative electrical resistance (R (P)/R (1 bar)) of iron decreases continuously with the increase of pressure from room pressure to 6.5 to 7.5 GPa, where the relative resistance increases discontinuously from 0.90 to 1.6 indicating the well-known pressure-induced bcc-hcp structural phase transition of iron. But the transition occurs at 13 GPa for pure iron. We suggest the pressure difference of 5 to 6 GPa could be due to the permanent densification of the native iron sample due to the Precambrian impact.

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