

Spatial decomposition and assignment of vibrational spectra: Dipolar coupling and correlated particle motion in aqueous Li⁺

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Terahertz (THz) spectroscopy has been demonstrated to be able to detect even small solute-induced changes of the hydrogen bond dynamics in aqueous solutions [1, 2]. The THz spectra reveal long-ranged dynamical correlations around solutes that can be approached theoretically by analyzing vibrational spectra in a spatially-resolved manner. Recently, it has been shown on the basis of *ab initio* MD simulations that intra- and intermolecular vibrational modes of liquid water are modulated by the solvation shells in a qualitatively different manner [3]. In order to probe these effects, novel spatial decomposition methods have been introduced that allow for deep insights into the mechanisms of this frequency-dependent dynamics and the resulting distance-dependent dipolar responses of the solvating water molecules [3, 4].

Here, several spatial decomposition schemes for infrared spectra are used to reveal the distinct distance- and frequency-dependent contributions of the solvation shells to the spectral response in aqueous solutions of Li⁺, based on extensive *ab initio* MD simulations. The solvent's response to the presence of the solute is systematically disentangled and reveals important structure-spectra relationships in the THz spectral window, highlighting differences between dipolar response and correlations in particle motion [5].

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