479. Title:Hydroxide hydrogen bonding: Probing the solvation structure through ultrafast time domain Raman spectroscopy
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Abstract:The mechanism of charge transport in aqueous media is critical in molecular, materials, and life sciences. The structure of the solvated hydroxide ion has been an area of some controversy. Polarization-resolved ultrafast time domain polarizability relaxation is used here to resolve the terahertz frequency Raman spectrum of hydroxide solutions. The measurements reveal the totally symmetric hydrogen-bond stretching (HO-&mellip;HOH) mode of the solvated hydroxide, permitting an experimental measurement of the bond force constant. The observed polarized Raman spectra are compared with those obtained from DFT calculations performed on HO-(H2O)n clusters. Good agreement between the observed frequency and the polarization dependence is found for the n = 3 or 4 clusters, particularly for those in which the solvating water molecules adopt a planar structure. The frequency of the symmetric stretch increases with concentration, consistent with an effect of ionic strength on either the H-bond or the structure of the cluster.