

ULTRAVIOLET ABSORPTION SPECTRA OF CHARGE TRANSFER TO SOLVENT TRANSITIONS FOR AQUEOUS HALIDE AND HYDROXIDE IONS IN SUBCRITICAL WATER

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The temperature dependence of the vacuum ultraviolet charge transfer to solvent (CTTS) absorption spectra of aqueous halide and hydroxide ions was measured up to 300 °C in subcritical water. With increasing temperature, absorption spectra are observed to broaden and redshift, much in agreement with previous measurements below 100 °C. We discuss these changes alongside classic cavity models of the solvated species, where a gradual increase in cavity size is observed as a function of temperature while the Gibbs energy of hydration is largely unaffected. The changes in solvation properties are considered in the context of recent studies of the ultraviolet spectroscopy of subcritical water and historic studies of the CTTS absorption.