Vacuum Ultraviolet Spectroscopy of Sub- and Supercritical Water

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The lowest-lying electronic state of light and heavy water has been studied via vacuum ultraviolet absorption spectroscopy over the temperature range 25-400 °C, beyond the critical temperature, where water becomes a highly compressible fluid. Results demonstrate a gradual red shift of the entire absorption band with increasing temperature and preservation of the band shape. These data confirm trends predicted by both recent experimental and computational work,1-5 indicating preservation of the water Franck-Condon envelope over the entire temperature range examined. Above the critical point, the absorption band red shifts slightly with decreasing pressure, possibly due to minor changes in the local clustering environment.

Results lay the groundwork for future studies of aqueous solute spectroscopy in the deep ultraviolet spectral region. The new experimental techniques developed to conduct these measurements are discussed, and can see application to any experiment with inherently large light absorption.