

Abstract Submitted  
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**Vacuum Ultraviolet Absorption of Supercritical Water** DAVID BARTELS, IRENEUSZ JANIK, Notre Dame University, TIMOTHY MARIN, Benedictine University — The first continuum  $\tilde{X} \rightarrow \tilde{A}$  peak in the gas phase absorption spectrum of H<sub>2</sub>O (maximum at 7.4 eV), is ascribed to promotion of a nonbonding valence electron to a dissociative excited state which is an admixture of antibonding sigma and 3s Rydberg orbitals. Due to the large spatial extent of this orbital the  $\tilde{X} \rightarrow \tilde{A}$  transition is strongly perturbed by the local environment. In liquid water, this peak is notably broadened and shifted to the blue, with an absorption maximum of 8.3 eV at room temperature. An obvious question is how this transition changes as a function of the water density in the supercritical regime as the system transitions from liquid to gas. As density decreases, most water molecules will be located at an interface between large clusters and voids. We will describe an experiment to measure the VUV absorption of the  $\tilde{X} \rightarrow \tilde{A}$  transition in supercritical water (T>374 °C, P>220 bar) where the density can be tuned continuously. Experimentally this requires over six orders of magnitude detector dynamic range in the vacuum UV and a short path (ca. 1 micron) high temperature/pressure cell with sapphire windows. This has not been accomplished in any previous experiment. Results will be discussed in the light of recent ab initio calculations of the spectrum in large and small clusters.

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