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Study of super-critical water through the Widom line using infrared spectroscopy

Infrared spectroscopy is an important tool to probe inter-molecular and
intra-molecular motions as it is sensitive to the details of inter-molecular interactions. In the present study, we use this tool to explore structure and dynamics of super-critical water (SCW) across the Widom line (i.e. by varying density at a constant temperature
just above the gas-liquid critical temperature of the phase diagram) to interpret the transient density fluctuations. Although such studies have been reported for liquid nitrogen, no such study has been carried out for water.
The important feature of this work is a combined molecular dynamics simulation with electronic structure calculation (ES/MD) approach. We use the discrete variable representation (DVR) scheme to construct the spectroscopic maps for transition frequencies and transition dipoles and obtain the infrared spectrum of the O-H stretch across the Widom line.

We find several new results. Below we summarize the main results of this work.
i) The line shapes show sharp changes as we cross the Widom line by varying the density while keeping temperature fixed slightly above the critical temperature of water. A crossover from the Lorentzian–like to a Gaussian-like line shape is observed as the Widom line is approached.

ii) The line broadening at critical density exhibits a divergent-like density dependence of the IR line width across the Widom line. This is in agreement with earlier studies on nitrogen. In supercritical water, the increase in frequency fluctuations on approaching the Widom line is found to be the origin of the anomalous rise in the lineshape. This effectively explains the role of density heterogeneity/inhomogeneity on vibrational spectra of supercritical water.
iii) In liquid water at ambient conditions, orientational correlation time is of the order of ps. In SCW, the time scale is found to be shorter. Because of high temperature, the dynamics is expected to be ultrafast.

The present study effectively demonstrates the strength of linear spectroscopic methods (like IR line width measurement) to capture important aspects of critical phenomena. This is the first theoretical infrared spectroscopic study of super-critical water (using ES/MD approach) across the Widom line.

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