

Abstract Submitted
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X-ray absorption of liquid water studied by advanced *ab initio* methods¹ ZHAORU SUN, JIANPING WANG, Temple University, WEI KANG, Peking University, ROBERTO CAR, Princeton University, XIFAN WU, Temple University — Oxygen K-edge X-ray absorption spectra (XAS) provide a sensitive local probe of the H-bond structure of liquid water. Based on the static COHSEX approach, we computed the XAS spectra of liquid water from molecular structures generated by *ab initio* molecular dynamics (AIMD) simulations using a van der Waals (vdW) inclusive hybrid functional (PBE0) that gives ambient water structure in quantitative agreement with experiment [JCP 141, 084502 (2014)]. We find that good agreement between experimental and theoretical XAS requires both improved molecular modeling and excitation treatment. In our simulation the over-structured H-bond network resulting from GGA-AIMD is systematically reduced as the directional H-bond strength is lowered by the mitigated self-interaction error in PBE0 and the increased population of interstitial water molecules promoted by vdW interactions. The better H-bond structure in turn gives improved XAS spectra. Moreover, we find that the orbitals obtained from the self-consistent diagonalization of the self-energy are crucial in obtaining spectra that compare well with experiment.

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