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First-principles studies of photoelectron spectroscopy of solvated hydronium and hydroxide in water CHARLES SWARTZ, XIFAN WU, Temple University — Solvated hydronium ($H3O^+$) and hydroxide (OH^-) are important solutions of water defects. In a recent state-of-the-art photoelectron spectroscopy (PES) experiment, the binding energies of these water defects have been measured. Theoretically, we show that the photoelectron spectroscopy can be accurately computed based on GW quasi-particle theories, in which the molecular solvation structures are generated by ab initio molecular dynamics (AIMD). The resulting hydronium and hydroxide binding energies are 10 eV and 19 eV respectively, which are closely consistent with the recent PES experimental values of 9.2 eV and 20 eV. A close inspection reveals that the defect orbitals originate from the $1b_2$ ($1b_1$) state of $H3O^+$ (OH^-) molecules in the gas phase. These orbitals are further strongly distorted by the surrounding water molecules, in which the H3O+ and OH- defects states are clearly localized on the so-called Zundel and Eigen solvation structures respectively. Proton transfers are found to further broaden the PES spectrum, which is more prominent in $H3O^+$ than in OH^- solutions.

Charles Swartz
Temple University

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