

Ab initio studies of ionization potentials of hydrated hydroxide and hydronium

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Solvated hydroxide (OH^-) and hydronium (H_3O^+) are important solutions of water defects. In a recent state-of-the-art photoelectron spectroscopy (PES) experiment¹, the ionization potentials of these water defects have been measured. Theoretically, we show that the photoelectron spectroscopy can be accurately computed based on a GW quasi-particle excitation theory^{2,3}, in which the molecular solvation structures are generated by ab initio molecular dynamics (AIMD). The resulting OH^- and H_3O^+ ionization potential distributions are centered at ~ 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 can be associated with the $1b_1$ -like ($1b_2$ -like) states of the OH^- (H_3O^+) molecular excitations. These excitations are further strongly distorted by the surrounding water molecules, mainly in the first solvation shell, in which the OH^- and H_3O^+ excitations are clearly localized on the stable solvation complexes for the respective ions. Electron excitations are more delocalized during proton transfer which changes the excitation energies and distributions for both hydrated ions. As a result, the ionization potentials of the hydrated ions are broadened and shift into the main features of the bulk water PES spectrum.

- [1] W. Chen, X. Wu, and R. Car, Phys. Rev. Lett. **105**, 017802 (2010).
- [2] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **86**, 134203 (2012).
- [3] B. Winter, M. Faubel, I. Hertel, C. Pettenkofer, S. Bradforth, B. Jagoda-Cwiklik, L. Cwiklik, and P. Jungwirth, J. Am. Chem. Soc. **128**, 3864 (2006).