

## Supporting Information

### Quantitative electronic structure and work-function changes of liquid water induced by solute

Bruno Credidio<sup>1,2</sup>, Michele Pugini<sup>1</sup>, Sebastian Malerz<sup>1</sup>, Florian Trinter<sup>1,3</sup>, Uwe Hergenahn<sup>1</sup>,  
Iain Wilkinson,<sup>4</sup> Stephan Thürmer<sup>5\*</sup>, and Bernd Winter<sup>1\*</sup>

<sup>1</sup> *Molecular Physics Department, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

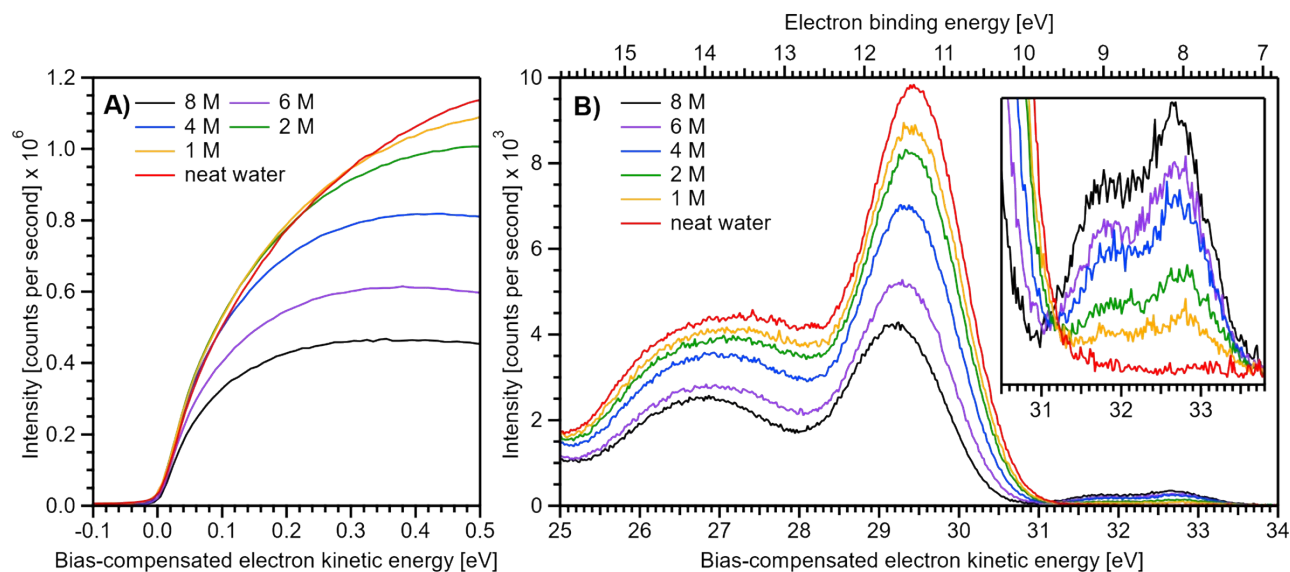
<sup>2</sup> *Institute for Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*

<sup>3</sup> *Institut für Kernphysik, Goethe-Universität, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany*

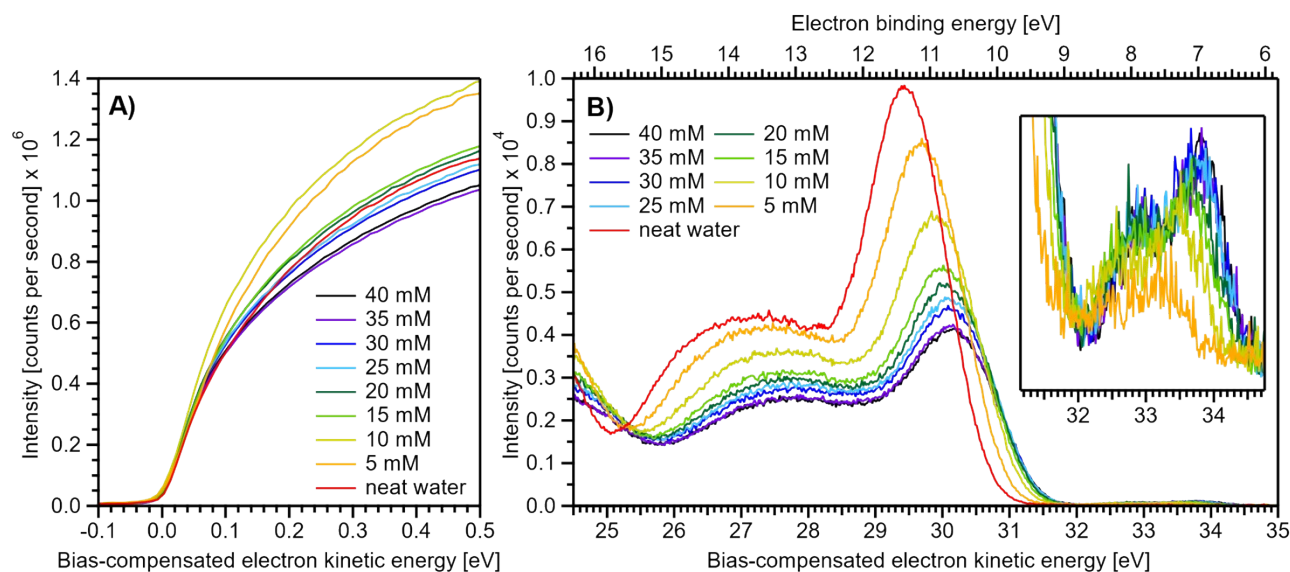
<sup>4</sup> *Department of Locally-Sensitive & Time-Resolved Spectroscopy, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

<sup>5</sup> *Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-Ku, Kyoto 606-8502, Japan*

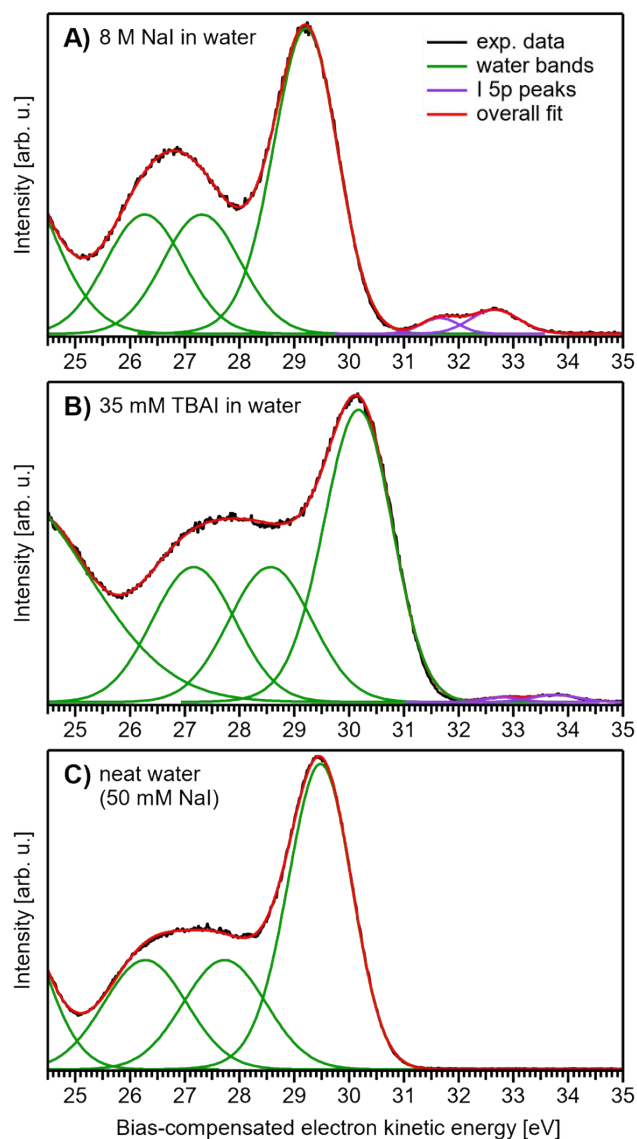
## Figures



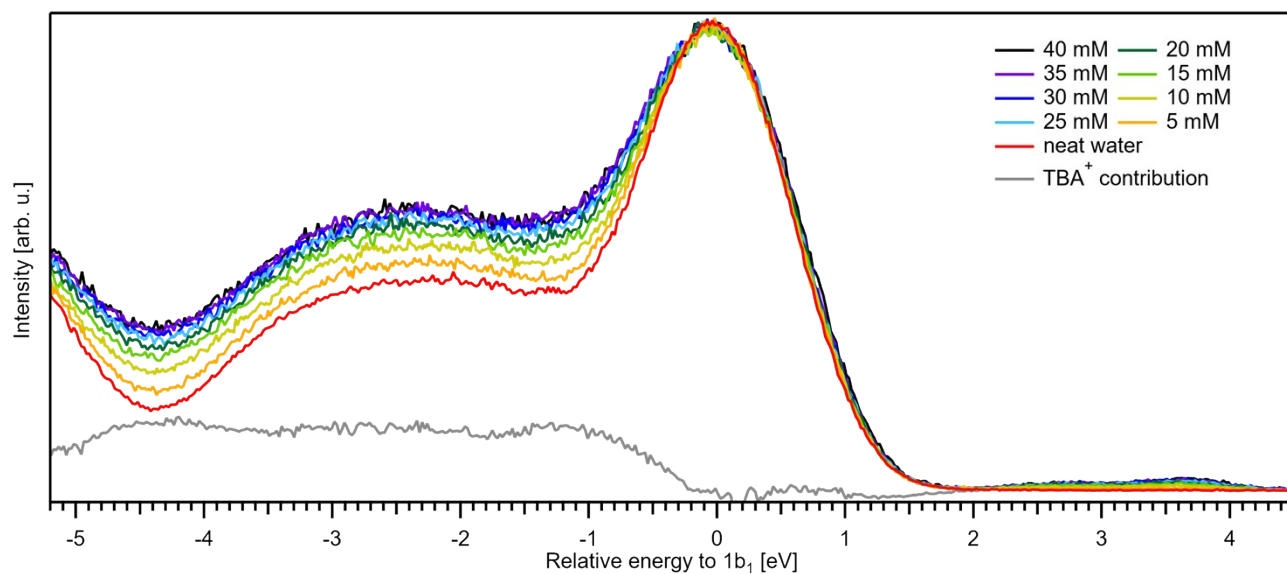
**Figure SI-1:** The same data for NaI<sub>(aq)</sub> as in Fig. 1, but here the intensity is shown as measured. The water signal decreases with higher NaI concentration.



**Figure SI-2:** The same data for TBAI<sub>(aq)</sub> as shown in Fig. 5, but here the intensity is shown as measured. Similar to NaI, the water signal decreases with higher TBAI concentration.



**Figure SI-3:** Exemplary fits to the spectra: **A)** 8 M NaI solution, **B)** 35 mM TBAI solution, and **C)** neat water (*i.e.*, with only 50 mM NaI added for charge compensation and to enable sample biasing); measured data in black, the overall fit in red, water-band features in green, and the I<sup>-</sup> 5p doublet peak in violet. See text for details.



**Figure SI-4:** The same data for TBAI<sub>(aq)</sub> as in Figs. 5B and SI-2B but aligned to the same 1b<sub>1</sub> peak position for better comparison of spectral changes with increasing concentration. The grey curve shows the difference between the 35-mM TBAI<sub>(aq)</sub> and neat water spectrum, which we assign to TBA<sup>+</sup>.