Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Solvated electrons at the water/air interface: Surface versus bulk signal in low kinetic energy photoelectron spectroscopy

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Supporting material

Gaussian Fit of individual one-color spectra

Here, we present the individual one-color spectra together with Gaussian fits for solution A and B and compare them with corresponding spectra of a 0.2 mM NaI solution (Figures S1 to S3. The fitparameters are summarized in Table S1 and Table S2. In Figure S1 we show the one-color photoelectron spectra of a 0.2 mM NaI solution for 4.65 eV photon energy and 5.2 eV photon energy.

The 4.65 eV spectrum is well reproduced by contributions from 2-photon photodetachment of iodide and by 3-photon ionization of the $1b^1$ band of water. The spin-orbit splitting of the two iodide ionization potentials was kept fix to 0.95 eV. The binding energy of the water $1b^1$ band was set to the value given in Ref.[1] The photoelectron bands for iodide appear at kinetic energies that compare well with expected values based on the published binding energies.[2] We also used

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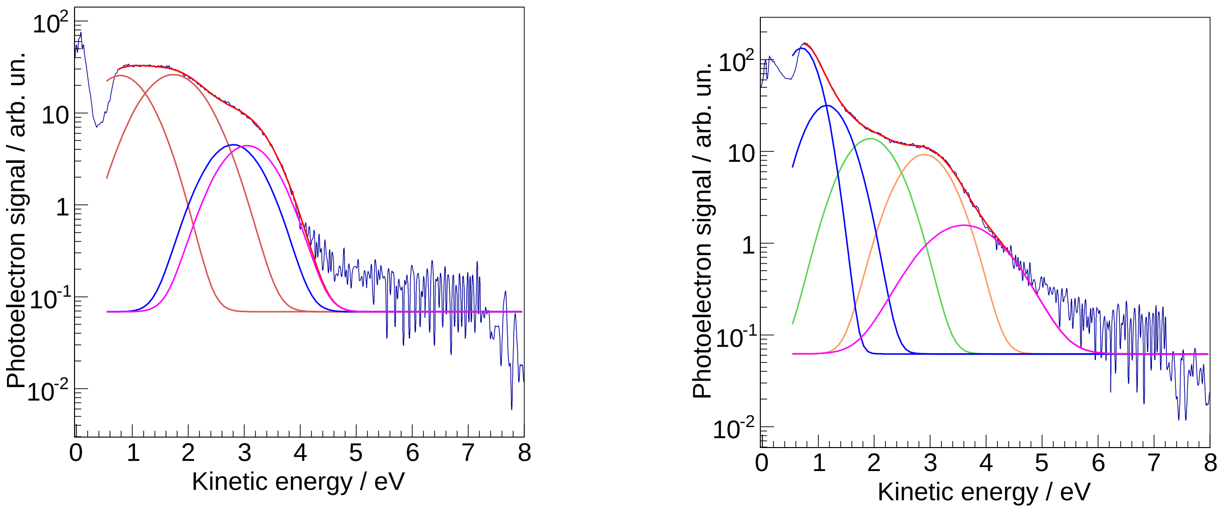

Figure S1: One-color spectra of a 0.2 mM NaI solution. Left: 4.65 eV photon energy, right: 5.2 eV photon energy. Contributions are from 2-photon photodetachment of iodide (brown), multiphoton ionization of water (blue), chloride photodetachment (blue), e^-_{solv} (green, orange) and a species with binding energy of 1.6 eV (magenta).

a photoelectron band centered at 3.05 eV which corresponds to a transient species with binding energy of 1.6 eV.

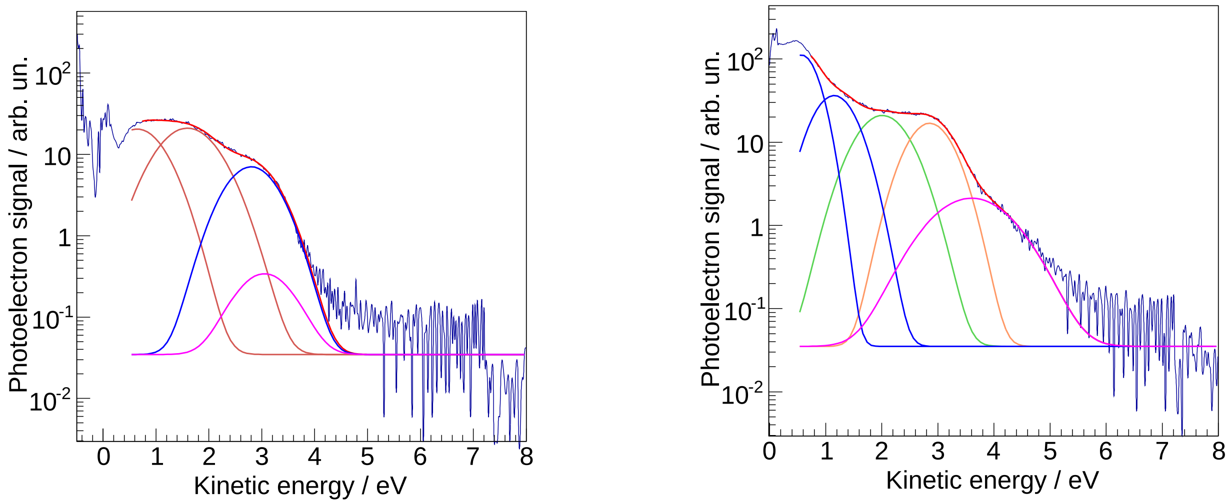

Figure S2: One-color spectra of a 0.2 mM TBAI solution. Left: 4.65 eV photon energy, right: 5.2 eV photon energy. Contributions are from 2-photon photodetachment of iodide (brown), multiphoton ionization of water (blue), chloride photodetachment (blue), e^-_{solv} (green, orange) and a species with binding energy of 1.6 eV (magenta).

Comparable fit results were obtained for the other 2 solutions that contain TBAI. There is one important difference: The iodide photoelectron bands are systematically shifted towards smaller kinetic energies, i. e. higher binding energies. Within errorbars, the results for solution A and B are comparable and differ from the value for the 0.2 mM NaI solution by about 200 meV.

The photoelectron spectra for the 5.2 eV pulse are fit with 5 Gaussians to account for signal due

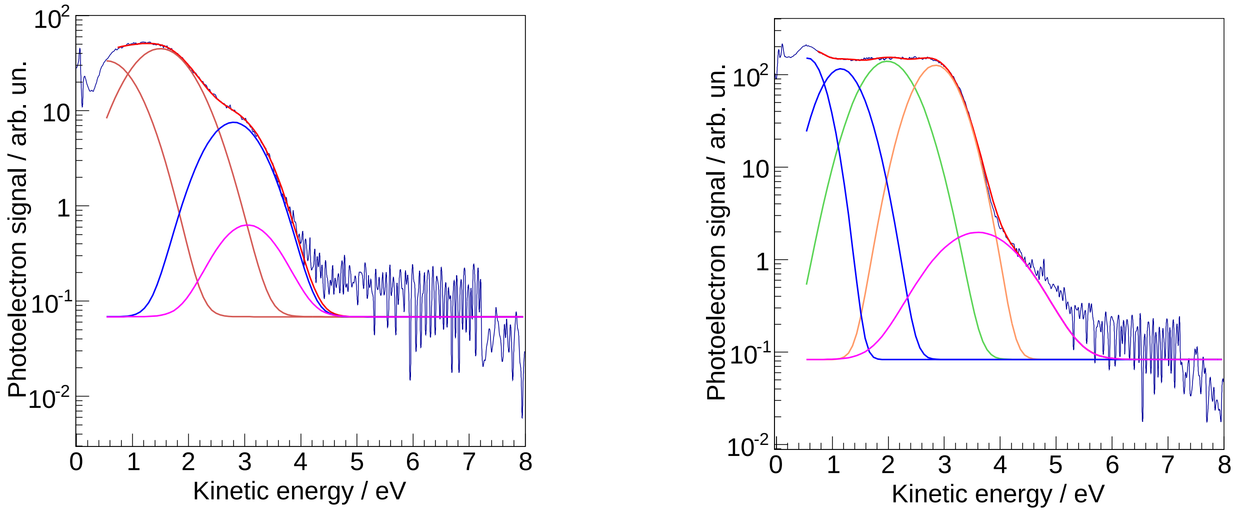

Figure S3: One-color spectra of a 0.2 mM NaI+1.8 mM TBAI solution. Left: 4.65 eV photon energy, right: 5.2 eV photon energy. Contributions are from 2-photon photodetachment of iodide (brown), multiphoton ionization of water (blue), chloride photodetachment (blue), e^-_{solv} (green, orange) and a species with binding energy of 1.6 eV (magenta).

to water 2-photon ionization, Cl^- 2-photon photodetachment, "hot" and "cold" e^-_{solv} as well as a feature with binding energy of 1.6 eV. The agreement between fit and data is very good. Positions of the individual contributions for the 5.2 eV pulses compare well for the different solutions. Slight changes occur for the photoelectron contributions of water 2-photon ionization and chloride 2-photon photodetachment between the 0.2 mM NaI solution and solution A and B. This might be due to different Cl^- distributions close to the surface in the presence of TBAI.[3]

Table S1: Fit parameters of the 4.65 eV one-color spectra. Spin orbit splitting for the I5p level of 0.95 eV was used.

	(1)	(2)	(3)	(4)
assignment	I5p	I5p	H_2O 1b^1	
4.65 eV, 0.2 mM NaI				
A	5000±200	5800 ± 200	900 ± 100	900 ± 100
FWHM / eV	1.1	1.2	1.1	1.1
E_0 / eV	0.79 ± 0.02	1.74	2.79[1]	3.05
4.65 eV, 0.2 mM TBAI				
A	4000 ± 400	4700 ± 400	1300 ± 300	60 ± 200
FWHM / eV	1.1	1.2	1.1	1.1
E_0 / eV	0.65 ± 0.07	1.60	2.79[1]	3.05
4.65 eV, 0.2 mM TBAI+1.8 mM NaI				
A	6600 ± 600	9900 ± 500	1400 ± 300	100 ± 200
w / eV	1.1	1.2	1.1	1.1
E_0 / eV	0.55 ± 0.03	1.50	2.79[1]	3.05

Table S2: Fitparamters for the 5.2 eV one-color spectra. Spin orbit splitting for the I5p level of 0.95 eV was used.

	(1)	(2)	(3)	(4)	(5)
assignment	e^-_{solv} (cold)	e^-_{solv} (hot)	H_2O 1b^1 / Cl3p		
5.2 eV, 0.2 mM NaI					
A	2500 ± 300	1700 ± 400	4600 ± 700	4600 ± 600	400 ± 100
w / eV	1.0[4]	1.0 ± 0.2	0.80	0.61	1.55
E_0 / eV	1.9 ± 0.1	2.9 ± 0.1	1.15	0.71	3.6
5.2 eV, 0.2 mM TBAI					
A	3800 ± 400	2700 ± 500	5300 ± 500	12300 ± 1400	600 ± 100
w / eV	1.0[4]	0.87 ± 0.09	0.80	0.61	1.55
E_0 / eV	2.01 ± 0.09	2.86 ± 0.07	1.15	0.57 ± 0.04	3.6
5.2 eV, 0.2 mM TBAI+1.8 mM NaI					
A	25200 ± 800	20000 ± 1000	17000 ± 1000	17000 ± 2000	500 ± 100
w / eV	1.0[4]	0.85 ± 0.02	0.80	0.61	1.55
E_0 / eV	1.98 ± 0.03	2.85 ± 0.02	1.15	0.56 ± 0.04	3.6

References

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