

List of Figures

2.1	The water molecule. Dipole moment and symmetry of the water molecule . .	7
2.2	Molecular orbital energy level diagram of H ₂ O	8
2.3	Illustration of the H-bonding in liquid water	9
2.4	Cartoon of the two-dimensional ionic solvation of a NaCl crystal in water . .	12
2.5	Schematic depicting the difference of anion and cation solvation	13
2.6	Simplified presentation of the photoionization process of a solvated cation by a Born-Haber cycle	14
3.1	Molecular beam time-of-flight spectra	19
3.2	Schematic of the liquid jet decay into droplets	21
3.3	Illustration of photoelectron spectroscopy	22
3.4	Mean free path of electrons in solids as a function of their kinetic energy . .	24
3.5	Angular distribution of photoelectrons for specific values of the anisotropy parameter β	25
3.6	The layout of a wiggler/undulator	29
3.7	Schematic of the water-jet apparatus at BESSY II	31
3.8	Ice filaments from NaI aqueous solution growing at the LN ₂ cold trap (photo- graph)	32
3.9	View inside the interaction chamber (photograph)	33
3.10	Schematic detailing the directions of the water jet, the synchrotron light and the photoelectron detection	33
3.11	Schematic of the two water reservoirs	35
3.12	Injection system and nozzle support	36
3.13	The path of the electrons inside the hemispherical electron analyzer and schematic of the electronics	37
3.14	Photon flux values of undulator U125/1 for 0.2 A ring current	39

3.15	Schematic of the MBI-Beamline at BESSY II at the U125/1 undulator	40
3.16	Principle of the MBI spherical grating monochromator at BESSY II (U125) .	41
4.1	Photoemission spectrum of pure water obtained after photoexcitation of the water jet using 100 eV photon energy	43
4.2	Photoemission spectra of liquid water jet sampled for maximum liquid signal, of gas phase water, and the difference spectrum, obtained for 60 eV photon energy	45
4.3	Gas-phase subtraction from the measured (gas and liquid) photoemission spectrum	46
4.4	Gas-phase subtracted, photoemission spectra for 60, 80 and 100 eV	47
4.5	Representative Gaussian peak fitting shown for a photoemission spectrum of pure liquid water	48
4.6	High-resolution photoemission spectra of gas-phase H ₂ O	52
4.7	Comparison of electron binding energies of water orbitals in liquid, gas-phase, and ice	55
4.8	Measured <i>differential</i> partial photoionization cross sections, $d\sigma_i/d\Omega$, of water orbitals for liquid H ₂ O and D ₂ O, obtained for 60, 80, 100 eV photon energies	57
4.9	Relative partial cross section σ_i of the four water valence orbitals for three photon energies, 60, 80, 100 eV	61
4.10	Photoemission spectra from 10 bilayers hexagonal ice grown on Pt(111) and liquid water obtained for 75 eV and 80 eV, respectively	62
4.11	Photoemission spectra of liquid H ₂ O and D ₂ O measured for 100 eV photon energy	64
4.12	Absorption cross section of liquid water vs. incident photon energy	65
4.13	Electron scattering loss processes in liquid water	66
4.14	Electron scattering loss processes in liquid water	67
4.15	The loss function, $\text{Im}(-1/\epsilon)$, of liquid water	68
4.16	Photoemission spectra of pure liquid water and of 1 m NaI aqueous solution obtained for 100 eV photon energy	72
4.17	Photoemission spectra of aqueous XCl (X = Li, Na, K, Cs) solutions obtained for 100 eV	74
4.18	Evidence for cesium Auger emission in CsI aqueous solution	75

4.19 Photoemission spectra of aqueous XBr ($X = \text{Na}, \text{K}, \text{Cs}$) solutions obtained for 100 eV	76
4.20 Photoemission spectra of aqueous XI ($X = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) solutions obtained for 100 eV	77
4.21 Evidence for iodide Auger emission in NaI aqueous solution	77
4.22 Photoemission spectra of aqueous-sodium halides solutions NaX ($X = \text{Cl}, \text{I}, \text{Br}$) obtained for 100 eV	78
4.23 Photoemission threshold energies for halide ions solvated in water	79
4.24 Photoemission spectra of 2 m NaI and 2 m CaI_2 aqueous solutions obtained for 100 eV	80
4.25 Photoemission spectra of 3 m NaCl and 3 m MgCl_2 aqueous solutions obtained for 100 eV	81
4.26 Photoemission spectra of 2 m NaBr and 3 m MgBr_2 aqueous solutions obtained for 100 eV	81
4.27 Photoemission spectra of 1 m NaI and 0.75 m Na_2CO_3 aqueous solutions . . .	82
4.28 Photoemission spectra of 1 m NaI and 0.6 m $\text{Na}_4[\text{Fe}(\text{CN})_6]$ aqueous solutions obtained for 100 eV	83
4.29 Photoemission spectra of 3 m KI, 1 m $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 m $\text{K}_4[\text{Fe}(\text{CN})_6]$ aqueous solutions obtained for 100 eV	84
4.30 Gauss fits to $\text{I}^-(4d)$ and $\text{Na}^+(2p)$ emission features	85
4.31 Comparison of electron binding energies for a given solvated cation $E_{aq}(X^+)$, with the respective gas-phase binding energy, $E_g(X^+)$	87
4.32 Comparison of electron binding energy for a given solvated anion $E_{aq}(Y^-)$ with the respective gas-phase binding energy $E_g(Y^-)$	89
4.33 Photoemission spectra of Cs and Cs halides in the gas phase obtained for 100 eV photon energy	91
4.34 Photoemission spectra of atomic Cs, gas-phase CsI, and aqueous solution CsI obtained for 100 eV photon energy	93
4.35 Photoemission spectra of gas-phase CsI, NaI, and aqueous solution NaI obtained for 100 eV photon energy	94
4.36 Partial relative cross section for aqueous $\text{I}^-(4d)$, gas-phase NaI, I_2 , I and I^+ .	96
4.37 Angular-distribution asymmetry parameter of the $\text{I}(4d)$ subshell in CH_3I . .	97
4.38 Schematic depicting the polarization effects for ion solvation relevant for the photoemission process	102

4.39	Photoemission spectra of $\text{I}^-(\text{H}_2\text{O})_n$ clusters	104
4.40	Photoemission spectra of NaI aqueous solution obtained for different salt concentrations	107
4.41	Photoemission spectra of NaI aqueous solution obtained for different salt concentrations	108
4.42	Increase of the $\text{I}^-(4d)$ and $\text{Na}^+(2p)$ photoemission signal as a function of the NaI concentration	109
4.43	Decrease of the $2a_1$ photoemission signal as a function of NaI concentration .	110
4.44	Experimental $\text{I}^-(4d_{5/2})$ electron binding energies as a function of the NaI concentration	111
4.45	Photoemission spectra of pure water, 1 m NaI, and 0.02 m But_4NI aqueous solutions	114
4.46	Photoemission spectra of But_4NI aqueous solution obtained for different salt concentrations	116
4.47	Increase of the $\text{I}^-(4d)$ photoemission signal and decrease of the $2a_1$ photoemission signal as a function of the But_4NI concentration	117
4.48	Comparison of the relative $\text{I}^-(4d)$ emission intensity obtained for But_4NI and NaI aqueous solutions as a function of the respective salt concentrations . . .	120
4.49	Full-range photoemission spectra, including the cutoff region, from aqueous But_4NI obtained for different concentrations	121
4.50	Schematic energy level diagram illustrating the origin of the observed (rigid) spectral energy shifts for the But_4NI solution	123
4.51	Experimental $\text{I}^-(4d)$ and $1b_1$ (liquid) relative peak shifts observed for But_4NI aqueous solutions of different concentrations	124
4.52	Photoemission spectra of Prop_4NI aqueous solutions obtained for different salt concentrations	126
4.53	$\text{I}^-(4d)$ signal increase as a function of the Prop_4NI concentration	127
4.54	Photoemission spectra of 1 m NaBr, 0.02 m But_4NI @ 1 m NaBr and 0.02 m But_4NI aqueous solutions	128
4.55	Photoemission spectra of 1 m KBr, 0.02 m But_4NI @ 1 m KBr and 0.02 m But_4NI aqueous solutions	129
4.56	Photoemission spectra of 1 m CsBr, 0.02 m But_4NI @ 1 m CsBr and 0.02 m But_4NI aqueous solutions	130

4.57	Photoemission spectra of 1 m NaBr, 0.14 m Prop ₄ NI @ 1 m NaBr and 0.14 m Prop ₄ NI aqueous solutions	131
4.58	Cartoon depicting the exchange of the I ⁻ anions with Br ⁻ anions in the bulk solution	132
5.1	Cartoon of the processes relevant in CTTS state excitation for an aqueous anion together with the corresponding energy levels	138
5.2	Schematic for the detachment experiment	139
5.3	Transient absorption scan at 700 nm following 308 nm photolysis of triiodide in ethanol solution	141
5.4	Absorption and emission spectra of triiodide in ethanol	142
5.5	Jablonski diagram of the photophysics of triiodide	142
6.1	Photoemission spectra of pure water, 1 m aqueous NaI and 0.4 m I ₂ @ 1 m NaI aqueous solution obtained for 100 eV	145
6.2	Photoemission spectra of I ₂ aqueous solution in 1 m NaI aqueous solution as a function of the I ₂ concentration obtained for 100 eV	146
6.3	Photoemission spectra of laser-excited and non-excited I ₃ ⁻ complex aqueous solution	147
6.4	Schematic showing the time structure using time-correlated laser and synchrotron pulses	147
6.5	Phase-locked loop (PLL) scheme of the laser-to-synchrotron pulse synchronization	148
6.6	Time structure using time-correlated laser and synchrotron pulses	149