

6.3 Publications

The following aspects of the present work were published or submitted for publication. Also included is part of my work on organic thin films during my activities devoted to setting up the MBI-BESSY beamline.

Full valence band photoemission from liquid water using EUV synchrotron radiation (*J. Phys. Chem.*, submitted Feb. 2003)

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Abstract. The valence band photoelectron spectra of liquid H₂O, and of liquid D₂O, are studied in the photon range between 60 and 120 eV. The experiments were performed using a 6 μm diameter liquid jet free-vacuum surface, installed at the MBI undulator beamline of the synchrotron radiation facility BESSY. In liquid water photoemission the four valence molecular orbitals are broadened, and the centerlines of the corresponding peak structures are shifted to lower binding energies up to 1.4 eV. Due to a lack of fine structures in the liquid spectra, we discuss the liquid photoelectron spectra in terms of peak shifts, peak half widths, and relative peak amplitudes, only. The global, overall shift of all spectral features is attributed primarily to the electronic polarization of the solvent molecules around an ionized water molecule. Gas-liquid binding energy shifts, as well as peak broadening, differ for the four valence electron peaks, which can be attributed to changes of the H₂O molecular orbital character induced by the hydrogen bonding (H-bonding) in liquid water. Weak but distinctly structured emission features at, apparently, constant binding energies, superimposed on a broad background, arise from photoelectron energy losses in the liquid phase with the loss channels corresponding to the optical absorption of liquid water. The effect is most clearly observable for 18 eV energy losses of 2a₁ photoelectrons. Relative photoionization *partial*

cross section of the molecular orbitals of liquid water have been measured for 60, 80, and 100 eV photon energy. The main difference as compared to gaseous water is the relative intensity decrease of the $1b_2$ orbital and an apparent signal decrease of the $3a_1$ orbital, both as a result of molecular orbital changes due to H-bonding. The former can be interpreted in terms of the variation of the respective anisotropy parameter β_{1b_2} , while the latter is associated with considerable peak broadening due to energy level splitting.

Photoemission from aqueous salt solutions using EUV synchrotron radiation

(J. Phys. Chem., submitted June 2003)

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Abstract. The valence band photoemission of aqueous alkali-metal solutions is studied for photon energies from 90 to 110 eV. The experiments were performed at the MBI undulator beamline of the synchrotron radiation facility BESSY. A $6\ \mu\text{m}$ diameter liquid microjet provides a free vacuum surface, allowing water molecules to evaporate without collisions, and hence enables the direct detection of photoelectrons originating from the liquid. Here, we focus on the investigation of aqueous solutions of alkali iodide salts, specifically on the determination of the electron binding energies of solvated ions. The effect of different counter ions, MI ($M = \text{Li, Na, K, Cs}$), and concentrations is systematically investigated. Electron binding energies of solvated ions are found to differ considerably from those in the gas phase. The observed shifts are, to a first approximation, explained surprisingly well by a simple Born solvation model. However, contrary to intuition they do not depend on the salt ion concentration.

Surface segregation in aqueous solutions probed by photoemission using VUV synchrotron radiation (*to be submitted*)

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Abstract. Full-range valence-band photoemission spectra of tetrabutylammoniumiodide (But₄NI) in aqueous solution were measured for photon energies up to 120 eV at the electron synchrotron facility BESSY, Berlin. The sample was a 6 μm diameter liquid jet. For this small size water molecules evaporate without collisions, and consequently kinetic energies of electrons originating from the aqueous solution can be directly measured. Due to the inherent surface sensitivity of photoelectron spectroscopy, for sufficiently low kinetic energies, surface segregation can be readily investigated. Enrichment of the But₄NI salt at the *water* surface is confirmed by a ca. 80 time increase of the I⁻(4d) signal as compared to a NaI aqueous solution where ions are rather uniformly dispersed in the bulk. The completed segregation layer, which corresponds to a *single* surface monolayer of salt anion and cation pairs, can be identified by a discontinuity of both the absolute increase of the iodide signal and the water signal depletion as a function of the salt concentration. Our measurements also confirm that the salt concentration drops abruptly just below this solute monolayer. The effects are not as pronounced for the shorter, less hydrophobic tetrapropylammoniumiodide (Prop₄NI). For both salt solutions analysis of the uniform spectral shifts of the photoemission spectra, as a function of the concentration, is largely attributed to work function changes, $\Delta\Phi_{\text{dipole}}$, associated with the molecular dipole in the segregation layer. Dehydration effects of near-surface ions have not been observed. The systematic study of $\Delta\Phi_{\text{dipole}}$ provides invaluable information on the details of the orientation of the ions (pairs) within the segregation layer. For comparison, we have also measured photoemission spectra of But₄NI dissolved in aqueous XBr solutions, X = Na, K, Cs, as this reveals some details of the processes governing surface segregation. The data will be discussed in the light of But₄NI versus But₄NBr solutions, the latter being known to be less surface-active.

Radiation induced degradation and surface charging of organic thin films in ultraviolet photoemission spectroscopy (*Thin Solid Films* **391** (2001) 81-87)

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Abstract. The effect of vacuum ultraviolet radiation on the valence electronic structure of the electroluminescent organic materials p-sexiphenyl (6P) and tris-(8-hydroxy quinoline) aluminum (Alq₃) was investigated by ultraviolet photoemission spectroscopy (UPS). The intense radiation of an undulator at the storage ring BESSY II (Berlin) caused a loss of conjugation in 6P, evidenced by a decrease in intensity of delocalized π -orbitals in the UPS spectra. Depending on the degree of film degradation surface charging was observed for both materials. It is shown that by illuminating the sample with laser light that can be absorbed by the organic/metal substrate system the surface charging could be compensated. Thus, the generation of free charge carriers by optical means appears to be a useful substitute for the use of an electron flood-gun in photoemission experiments, whenever sensitive samples could suffer from irradiation with electrons.

Photoemission from azobenzene alkanethiol self-assembled monolayers*(J. Phys. Chem., in press)*R. Weber¹, B. Winter¹, I. V. Hertel¹, B. Stiller², S. Schrader², L. Brehmer², N. Koch³¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A,
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Abstract. Photoelectron spectra were measured for films of self-assembled azobenzene-terminated alkanethiol monolayers on gold using synchrotron radiation. The azobenzene was substituted either by a CF₃ or a CH₃ group in the para position. Due to the orientational order of the molecules within the films, as indicated by the pronounced angle dependence of the photoemission spectra, it is possible to identify laser-induced optical switching of the molecules using combined laser and synchrotron pulses. Molecular switching, i.e. photoisomerization, is recognized by relative intensity changes of the photoemission peaks and also by spectral shifts to higher binding energies. The latter result from a change of the molecular dipole moment associated with the trans-cis laser-induced photoisomerization of the azobenzene-CF₃ group.