

6 Appendix

6.1 I_3^- Complex Formation and its Photodissociation in Aqueous Solution

In this section the first test measurements studying the formation and the photodissociation/recombination of the I_3^- complex in aqueous solution (see Outlook, 5.2.2), will be presented.

One important issue was to identifying the new species, i.e. the photo-fragments I_2^- and I in solution, by their electron binding energies. Even from this *static* point of view electron binding energy differences for the various species, I^- (e.g. in aqueous NaI), I_2 and I_3^- (in equilibrium solution), I_2^- and I (after photodissociation) would be of fundamental interest. To begin with, photoemission spectra of bare water (bottom), 1 m aqueous NaI (center), and 0.4 m I_2 in 1 m NaI aqueous solution (top) are presented in Fig. 6.1. All spectra are obtained for 100 eV photon energy. Triiodide and molecular iodine are observed to give rise to additional emission peaks, labeled (1,1'), (2,2'), and 3 in the top panel, according to equation 5.1.

Fig. 6.2 depicts photoemission spectra from solutions of I_2 in 1 m NaI aqueous solution as function of the I_2 concentration. Concentrations range from 0.1 to 0.6 m I_2 . This concentration dependence was hoped to be useful in assigning the new peaks, as by the law of mass, the equilibrium of equation 5.1 shifts to the right. Yet, assuming that equation 5.1 is the only reaction relevant, no consistent conclusion as to the peak assignment could be drawn. Probably further reactions (equilibria) need to be accounted for. At this point the features (1,1'), (2,2') near 56 eV binding energy are tentatively assigned to $I^-(4d)$ emission from I_3^- . The small peak at 22.3 eV binding energy (labeled 3) may arise from I_2 emission. Additionally puzzling is the fact that the peaks labeled (1,1') do not exhibit the characteristic intensity ratio of the iodide structure, whereas features (2,2') do. Future experiments

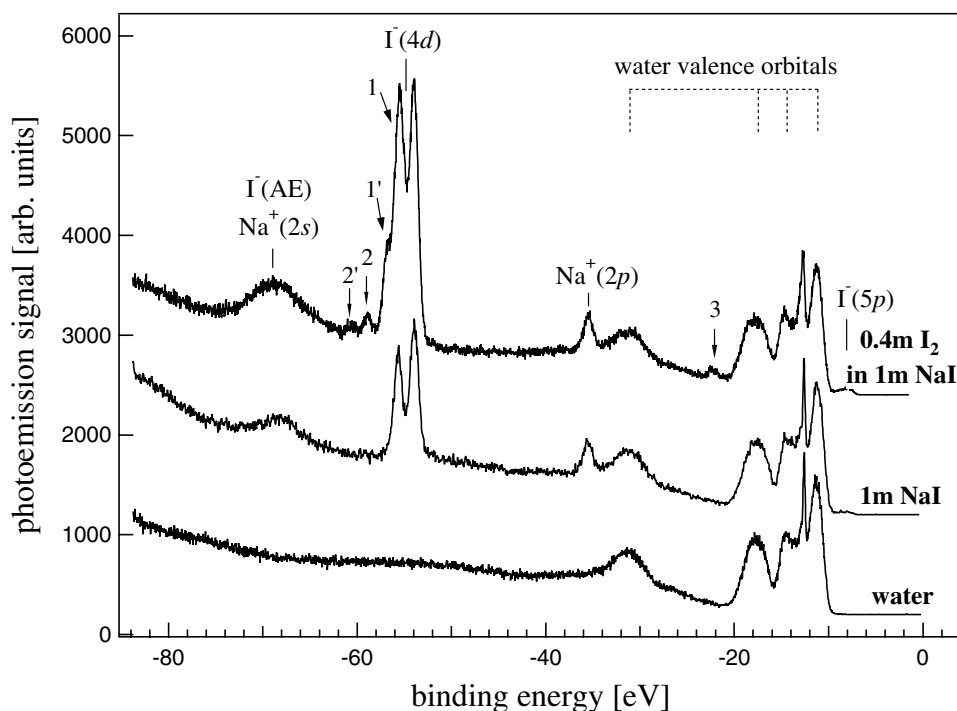


Figure 6.1: Photoemission spectra of pure water (bottom), 1 m aqueous NaI (center) and 0.4 m I_2 @ 1 m NaI aqueous solution (top) obtained for 100 eV. New features, labeled 1, 1', 2, 2', and 3, appear for the solution containing aqueous I^- , I_2 , and the I_3^- complex (top spectrum; see equation 5.1). Probably, feature 3 arises from I_2 emission. The precise assignment of the former features is unclear, however, they are proposed to originate from $I^-(4d)$ emission, likely from the complex.

will unravel these issues.

The photodissociation experiment mentioned was a *single-try run* at the very end of the most recent beamtime, and at this point the experimental data are characterized by poor statistics. Fig. 6.3 presents two photoemission spectra from 0.89 m I_2 in 0.89 m NaI aqueous solution, the lower spectrum obtained for synchrotron excitation only, and the top one for synchronized laser excitation. The bottom trace in the Fig. 6.3 displays the ratio between the difference and the sum of the two upper spectra. Due to the considerable noise level the differences of the photoemission spectra are difficult to be quantified. Future experiments, using an improved setup, will head for better statistics.

The spectra shown in Fig. 6.3 were obtained for BESSY multi bunch (see section 3.1.4). The laser wavelength of the Ti:Sapphire laser was set to 380 nm (ca. 300 mW output power), which corresponds to one of the absorption maxima of triiodide (see Fig. 5.4), and the laser pulse width was 200 fs. The laser repetition rate was 83 MHz. Details on the synchronization

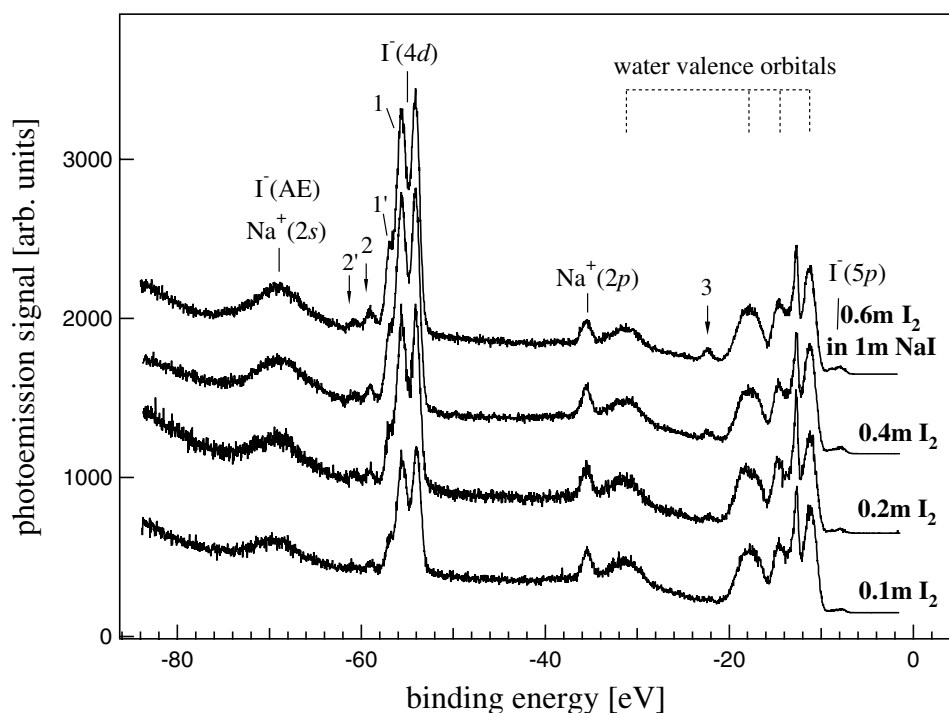


Figure 6.2: Photoemission spectra of I_2 aqueous solution in 1 m NaI aqueous solution as a function of the I_2 concentration (as indicated), obtained for 100 eV. In this way the ratio of products over educts (see equation 5.1) is varied; i.e. from bottom to top the complex concentration increases on the expense of aqueous I^- and I_2 . The features arising from the complex are marked by arrows (compare Fig. 6.1).

and on the laser/liquid jet setup are presented in section 6.2. It is noteworthy to emphasize two experimental details concerning the spatial overlap of laser and synchrotron light at the interaction spot. Despite tight focussing of the laser, which is necessary in order to obtain as many as possible excited molecules within the jet interaction region, the jet experiment does not suffer from mismatch of focal sizes of synchrotron (see Fig. 6.4) and laser radiation. Given the small dimension of the jet and the narrow detection angle, photoelectrons are only detected from a region being hit by both laser and synchrotron light. Hence, background emission due to focal mismatch is of no concern at all. The other aspect is of more practical relevance; it concerns the laser alignment. Specifically, introducing the laser beam collinear to the synchrotron beam, but in opposite direction (see Fig. 6.4), allows for a precise control of the overlap of both beams over about 2 m. This is done by three (transparent) fluorescence plates, which can be introduced at different positions into the beam path.

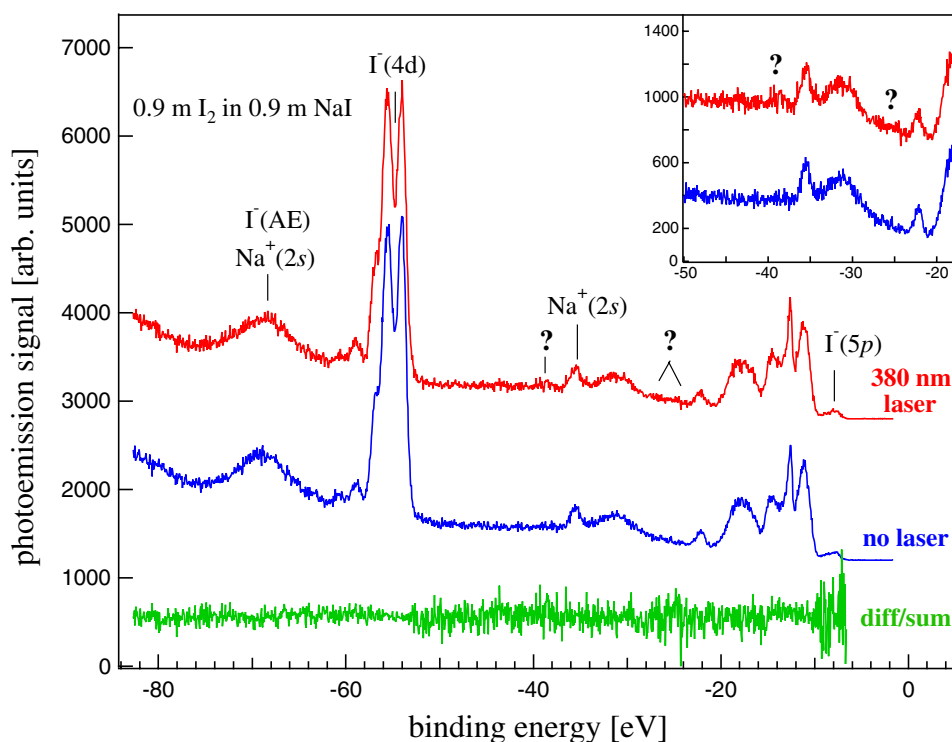


Figure 6.3: Photoemission spectra of laser-excited (top) and non-excited (center) I_3^- complex aqueous solution ($0.9\text{ m } I_2$ @ 0.9 m NaI ; compare Fig. 6.1 and equation 5.1). The bottom curve is the difference spectrum. Marked (?) spectral changes are weak and need to be confirmed by future experiments. Laser excitation was at 380 nm and the synchrotron photon energy was 100 eV .

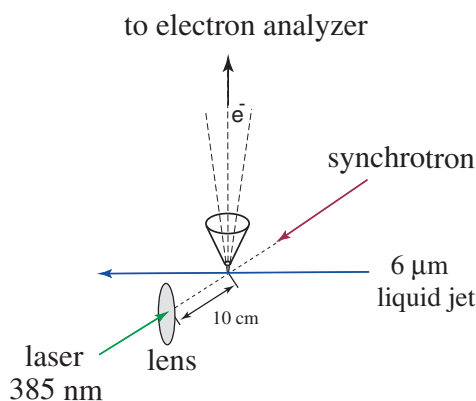


Figure 6.4: Schematic of the time-correlated laser and synchrotron pulse experimental setup used for studying the dissociation of the aqueous I_3^- complex. The laser and synchrotron beams are collinear but of opposite propagation direction. A $20\text{ }\mu\text{m}$ laser focus at the liquid jet was achieved by a lens of 10 cm focal length positioned outside the vacuum chamber. The synchronization (500 MHz synchrotron pulse and 83 MHz laser pulse repetition rate, respectively) is described in section 6.2.

6.2 Time-Synchronized Laser and Synchrotron Pulses for Two-Color Two-Photon Photoemission (2C-2PPE)

This paragraph briefly describes the main technical features of the synchronization of laser pulses, from a 83 MHz oscillator, to the synchrotron light pulses for BESSY multi-bunch (MB) operation (500 MHz). Time-correlated laser and synchrotron pulses were used to studying laser-excited organic molecular thin films by photoemission, which was the initial focus of my work at MBI. Related results are summarized in section 6.3. I have applied the identical synchronization scheme at a later point for investigating the laser-dissociation of aqueous triiodide (see section 6.1).

Laser-based pump-probe techniques have been widely applied to study various aspects of the ultrafast dynamics of valence electrons in metals and adsorbate systems [143, 144, 145, 146, 147, 148, 149, 150]. Comparable dynamical studies involving inner-shell electrons, however, are scarce since ultrashort photon pulses in the XUV and X-ray range are far more

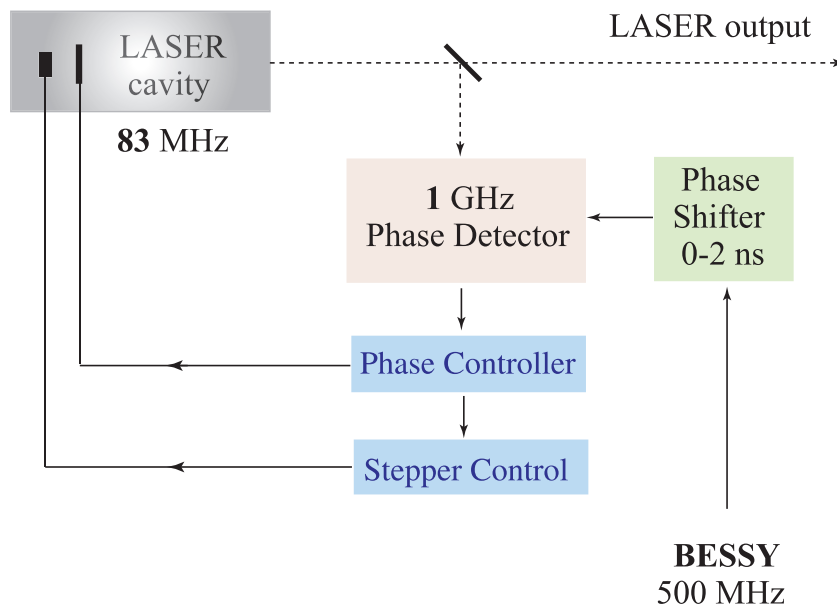


Figure 6.5: Phase-locked loop (PLL) scheme of the laser-to-synchrotron pulse synchronization. Mixing at 1 GHz matches the 12th electronic harmonic of the laser repetition rate with the 2nd harmonic of the synchrotron master frequency. Recently a 500 MHz detector has been installed for MB operation.

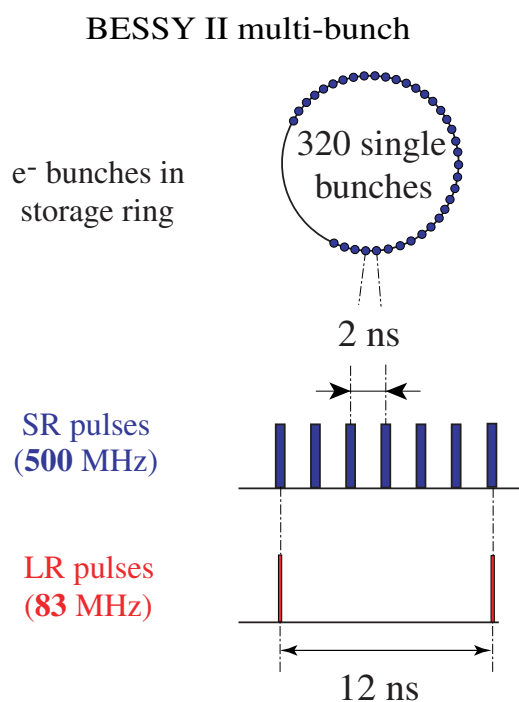


Figure 6.6: Time structure of synchrotron and laser pulses (for 500 MHz BESSY master oscillator and 83 MHz laser repetition rate). Laser and synchrotron widths are about 200 fs and 30 ps, respectively. For discussion of the incomplete ring filling (320 vs. 400) see section 3.1.4.

difficult to obtain. At such a high photon energy, particularly in combination with high-intensity laser pulses 2C-2PPE allows for instance, probing of core level binding energies in the presence of some laser-induced transient modification. An example would be the transient photon-induced isomerization and the resulting change of the dipole moment in large molecules (see section 6.3). More generally, with this new technique the change of a given core level energy may be followed in real time as the system undergoes a structural change (dynamical ESCA).

The synchronization of the two oscillators is performed by an analog phase-locked loop (PLL) scheme based on electronic high-harmonic mixing [151] (Fig. 6.5). Precise frequency and phase matching is achieved by controlling the laser cavity length in response to the PLL error signal which is proportional to the mismatch of the two signals. A small fraction of the laser beam is directed onto a fast photodiode which provides the input signal for the phase detector, the central element of the PLL. The required reference signal is directly obtained from the high precision BESSY RF 500 MHz oscillator.

For the present BESSY multi-bunch (500 MHz) mode a high-repetition rate (83.3 MHz) Ti:Sapphire laser (Coherent Mira 900) producing pulses of about 200 fs width at ca. 1.6 eV fundamental (tunable from 740 nm to 910 nm) and ca. 3.2 eV second harmonic was used. The output power was about 2 W for the fundamental when pumped by 10 W NdYAG

laser (Verdi). Phase and frequency mixing is performed at the sixth laser harmonic. In the current experiment every laser pulse is time-synchronized with a synchrotron pulse but there are five residual synchrotron pulses between two adjacent laser pulses, see Fig. 6.6. With the synchrotron pulse spacing being 2 ns (see section 3.1.4) and the laser interpulse spacing being 12 ns the available dynamical time window in pump-probe experiments was 2 ns. Future experiments will make use of a specially developed multi-channel detector [152]. The time delay between laser and synchrotron pulses can be electronically controlled as well as by optical time delay of the laser pulses. The synchronization accuracy is better than 5 ps.

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)

B. Winter¹, R. Weber¹, W. Widdra^{1,2}, I. V. Hertel¹, M. Dittmar³, M. Faubel³

¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

²Institut für Atomare Physik und Fachdidaktik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

³Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany

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)

R. Weber¹, B. Winter¹, W. Widdra^{1,2}, I. V. Hertel¹, M. Dittmar³, M. Faubel³

¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

²Institut für Atomare Physik und Fachdidaktik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

³Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany

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*)

R. Weber¹, B. Winter¹, W. Widdra^{1,2}, M. Faubel³

¹Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

²Institut für Atomare Physik und Fachdidaktik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

³Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany

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⁻(4*d*) 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)

N. Koch^{1,2}, D. Pop³, R. L. Weber³, N. Böwering³, B. Winter³, M. Wick³, G. Leising^{1,2}, I. V. Hertel³, W. Braun⁴

¹Institut für Nanostrukturierte Materialien und Photonik, Joanneum Research, A-8160 Weiz, Austria

²Institut für Festkörperphysik, TU-Graz, Petersgasse 16, A-8010 Graz, Austria

³Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12489 Berlin, Germany

⁴Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), D-12489 Berlin, Germany

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,
D-12489 Berlin, Germany²Universität Potsdam, Institut für Physik, Lehrstuhl Physik Kondensierter Materie, Am
Neuen Palais 10, D-14469 Potsdam, Germany³Institut für Physik, Physik von Makromolekülen, Humboldt-Universität zu Berlin,
D-12489 Berlin, Germany

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.