Interfaces in Dye-Sensitized Solar Cells Studied with Photoelectron Spectroscopy at Elevated Pressures

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Abstract

With an increasing demand for renewable energy sources, research efforts on different solar cell technologies are increasing rapidly. The dye-sensitized solar cell (DSC) is one such technology, taking advantage of light absorption in dye molecules. The liquid based DSC contains several interesting and important interfaces, crucial for the understanding and development of the solar cell performance. Examples of such interfaces include dye-semiconductor, electrode-electrolyte and solute-solvent interfaces. Ultimately, complete interfaces with all these components included are of particular interest. One major challenge is to understand the key functions of these systems at an atomic level and one way to achieve this is to use an element specific and surface sensitive tool, such as photoelectron spectroscopy (PES). This thesis describes the use and development of PES for studying interfaces in the DSC.

The materials part of the thesis focuses on interfaces in DSCs studied with PES and the methodology development parts focus on methods to use PES for investigations of solvated heterogeneous interfaces of interest for photoelectrochemical systems such as the DSC. More specifically, beginning with standard vacuum techniques, dye molecules bound to a semiconductor surface have been studied in terms of energy level alignment, surface coverage and binding configuration. To increase the understanding of solvation phenomena present in the liquid DSC, liquid jet experiments have been performed in close combination with theoretical quantum calculations. As a step towards an in-situ method to measure a complete, functioning (in operando) solar cell, methodology development and measurements performed with higher sample pressures are described using new high pressure X-ray photoelectron spectroscopy techniques (HPXPS).

Keywords: Dye-sensitized solar cells, interfaces, solvation, photoelectron spectroscopy, HPXPS, HP-HAXPES, liquid jet

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To Arvid and Rickard
This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Geometrical and energetical structural changes in organic dyes for dye-sensitized solar cells probed with photoelectron spectroscopy and DFT
Susanna K. Eriksson, Ida Josefsson, Hanna Ellis, Anna Amat, Mariachiara Pastore, Johan Öscarsson, Rebecka Lindblad, Erik M. J. Johansson, Gerrit Boschloo, Simona Fantacci, Anders Hagfeldt, Michael Odelius and Håkan Rensmo
In manuscript

II Linker unit modification of triphenylamine-based organic dyes for efficient cobalt mediated dye-sensitized solar cells
Hanna Ellis, Susanna K. Eriksson, Sandra M Feldt, Erik Gabrielsson, Peter W. Lohse, Rebecka Lindblad, Licheng Sun, Håkan Rensmo, Gerrit Boschloo and Anders Hagfeldt
The Journal of Physical Chemistry C 117, 21029-21036, 2013

III Solvent dependence of the electronic structure of $I^-_{}$ and $I^-_3$
Susanna K. Eriksson, Ida Josefsson, Niklas Ottosson, Gunnar Öhrwall, Olle Björnholm, Hans Siegbahn, Anders Hagfeldt, Michael Odelius and Håkan Rensmo
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IV Collective hydrogen-bond dynamics dictates the electronic structure of aqueous $I^-_3$
Ida Josefsson, Susanna K. Eriksson, Niklas Ottosson, Gunnar Öhrwall, Hans Siegbahn, Anders Hagfeldt, Håkan Rensmo, Olle Björnholm and Michael Odelius
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V A versatile photoelectron spectrometer for pressures up to 30 mbar
Review of Scientific Instruments 85, 075119, 2014
VI  In-situ probing of H$_2$O effects on a Ru-complex adsorbed on TiO$_2$
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VII  A novel HPXPS experimental method for characterization of the
interface between a solid electrode and electrolyte demonstrated
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**Enhancement of p-type dye-sensitized solar cell performance by supramolecular assembly of electron donor and acceptor**

*Haining Tian, Johan Oscarsson, Erik Gabrielson, Susanna K. Eriksson, Rebecka Lindblad, Bo Xu, Yan Hao, Gerrit Boschloo, Erik M. J. Johansson, James M. Gardner, Anders Hagfeldt, Håkan Rensmo and Licheng Sun*

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**Dye-sensitized solar cells employing a SnO$_2$-TiO$_2$ core-shell structure made by atomic layer deposition**

*Martin Karlsson, Jogi Indrek, Susanna K. Eriksson, Håkan Rensmo, Mats Boman, Gerrit Boschloo and Anders Hagfeldt*

Chimia **67**, 142-148, 2013

**Energy level shifts in spiro-OMeTAD molecular thin films when adding Li-TFSI**

*Rebecka Schölin, Martin Karlsson, Susanna K. Eriksson, Hans Siegbahn, Erik M. J. Johansson and Håkan Rensmo*


**Phenoxazine dyes for dye-sensitized solar cells: relationship between molecular structure and electron lifetime**

*Karl Martin Karlsson, Xiao Jiang, Susanna K. Eriksson, Erik Gabrielson, Håkan Rensmo, Anders Hagfeldt, Licheng Sun*


**The protonation state of small carboxylic acids at the water surface from photoelectron spectroscopy**

*Niklas Ottosson, Erik Wernersson, Johan Soderstrom, Wandared Pokapanich, Susanna Kaufmann, Svante Svensson, Ingmar Persson, Gunnar Öhrwall and Olle Björneholm*

Physical Chemistry Chemical Physics **13**, 12261-12267, 2011
Comments on my own contribution

This thesis is based on a close teamwork between people with different expertise. In general I was responsible for all photoelectron spectroscopy results, while the theoretical calculations and device characterization were performed by others. In Paper I, I was responsible for the experimental part and had the main responsibility for the writing of the manuscript. In Paper II, I performed the PES measurements, wrote parts of the manuscript and participated in discussions. In Paper III and IV, I was responsible for the experimental work and wrote parts of the manuscripts (I was the main responsible for Paper III). In Paper V, I performed most of the measurements, did the data analysis, and had the overall responsibility for writing the paper. In Paper VI, I planned and performed the experiments and wrote most of the manuscript. In Paper VII, I took part in the experimental work and wrote parts of the manuscript.
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1. Introduction

1.1 Energy in the world

The energy consumption is increasing in the world resulting in environmental issues, such as increased emission of CO$_2$. The demand for renewable energy sources is thereby increasing rapidly. Examples of renewable energy sources include solar, hydro, wind and geothermal power technologies.

Currently, only a smaller fraction of the energy comes from renewable sources. To give some numbers one can look at the electricity production. In 2012, worldwide, around 75% of the total electricity production came from fossil fuels and only about 19% came from renewables [1]. In Sweden the electricity production is a bit different compared to the rest of the world as slightly more than 40% of the electricity comes from hydro power and about the same amount from nuclear power, hence the CO$_2$ emission is very low. In addition, both the contributions from wind and solar power are increasing. 7% of the electricity comes from wind power while solar power only stands for 0.03% (38.8 GWh) of the total production. The total installation of new solar power capabilities was 19 MW last year (2013) [2].

Another huge energy consumption problem, not accounted for above, is the transport sector where almost all of the energy used comes from fossil fuels that are combusted in engines producing enormous amounts of CO$_2$. The interest in electrical cars with limited emission of CO$_2$ is therefore increasing and such a development will also increase the need for sources producing electrical energy.

The energy from the sun is a unique source for renewable energy production. The solar irradiation that strikes the Earth each year is $1.7 \times 10^5$ TW and 600 TW is assumed to be accessible. In comparison, the current world wide energy consumption is estimated to be around 15 TW. Therefore, systems using solar irradiation as a source for energy production have a great potential. Using the solar irradiation for direct electricity production rely on the conversion of photons to voltage and current and the devices for generating electrical power from solar radiation is often referred to as photovoltaics.

1.2 Photovoltaics

With an increasing demand for electricity sources as such and renewable electricity sources in particular, the research and development of solar cell technologies have increased enormously during the past decades. Several different technologies are available with the characteristics that the photons in the
solar spectrum are, by using different materials, converted to voltage and current (electricity). A semiconductor solar cell is based on pn-junctions where the materials are doped in different ways to create a field to induce charge separation upon absorption of photons. Semiconductors, such as silicon are commonly used and commercially most of the solar cells available are based on silicon. Silicon gives quite efficient (25%) solar cells but is expensive to produce. Thin film solar cells such as CIGS and CdTe are also rather common where different thin film absorbers are deposited on top of each other.

In the last years a lot of effort has been put into creating new and alternative materials, which can be used in photovoltaics. New materials include organic semiconductors and dye molecules. Technologies based on these materials have in common that the materials and production costs are potentially lower compared to conventional photovoltaics. Here molecules instead of semiconductor crystals are responsible for the light absorption. One such upcoming technology is the dye-sensitized solar cell (DSC), which had a breakthrough in 1991 [3, 4]. The DSC will be described in more detail in Chapter 2 and is a main focus in the present thesis.

1.3 Aim of the thesis

Detailed molecular understanding of the working components in the solar cell is of great importance to be able to improve the conversion efficiency of the device. Such understanding can be obtained in different ways, usually by materials development and investigation of different material combinations. To better understand the reasons for these changes in behavior at an atomic level, an element specific and chemically sensitive tool is needed. Here photoelectron spectroscopy (PES) has been used as one such tool.

The liquid based dye-sensitized solar cell contains several important and interesting interfaces. The interactions at these interfaces are essential for the working mechanism. Within the scope of this thesis several of these interfaces (described later) have been studied using PES. Due to the difference in character of the interfaces different methodologies had to be implemented. The over-all objective was to investigate the interactions between the working components at ambient conditions with the over-all vision to measure PES on a working solar cell (in operando) to acquire knowledge in order to obtain structure function relationships at an atomic level. An aim with the current presentation is to show how this target can be achieved by experimental setup development. The work is by nature interdisciplinary and another aim with the thesis is to reach a broad community, specifically including those interested in experimental methods for understanding the physical chemistry of wet interfaces.
2. Dye-sensitized solar cells

The dye-sensitized solar cell (DSC) is very simple in its layout. It consists of a working electrode, which is a piece of conductive glass coated with a mesoporous semiconductor (usually TiO$_2$) with a monolayer of dye molecules adsorbed on top. The reason for using a mesoporous film is the higher surface area enabling higher dye loading and therefore more absorption of sunlight is possible. The counter electrode consists of conductive glass coated with either platinum or a carbon based catalyst. Between the electrodes is an electrolyte (or solid hole conductor). The first reported results, with higher efficiencies, of a DSC were published by Grätzel and O’Regan in 1991 [3] with a power conversion efficiency of 7% using an iodide/triiodide electrolyte system. Since then the reported efficiencies of liquid DCSs have increased and are now exceeding 13% [5, 6] using cobalt based electrolyte systems. Similar systems using perovskite materials as light absorber have been very successful during recent years with power conversion efficiencies exceeding 17% [7, 8]. In this thesis the focus will be on the conventional liquid-based DSC.

2.1 Materials and working principle

In Figure 2.1, a schematic picture of a DSC is shown. The numbers in the figure are marked in parenthesis in the following text. Upon illumination an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in the dye molecule (1). The energy required to perform this excitation should be in the visible light region. After excitation the electron is injected into the semiconductor and thus the dye is oxidized (2). The electron can then diffuse through the semiconductor and perform electrical work in an external circuit. The dye molecule is regenerated by a redox couple in the electrolyte (3) with the original standard redox couple being I$^-$/I$_3^-$ but for the last few years usually a cobalt based redox couple is used [9]. The electron in the outer circuit will then transfer back to the redox couple via the counter electrode and the cycle is completed.

The kinetics are of great importance for the function of the electrochemical solar cell. The injection of the electron from the excited dye into the semiconductor must be faster than the de-excitation of the excited state. The regeneration of the dye should also be fast to prevent the recombination process. There are three main electron transfer reactions that should be avoided: dye relaxation to the ground state (4), recombination of the injected electron...
Figure 2.1. Schematic picture of a dye-sensitized solar cell with an electron’s path upon illumination marked with solid arrows. The undesired back reactions are indicated with dashed arrows. 1. Excitation of an electron from HOMO to LUMO. 2. Injection of an electron into the TiO$_2$, 100 fs-100 ps. 3. Dye regeneration by the electrolyte, $\mu$s. 4. Dye relaxation, ns. 5. Recombination of electrons from the TiO$_2$ to the oxidized dye, $\mu$s-ms. 6. Recombination of electrons from the TiO$_2$ to the oxidized redox couple, $\mu$s.

with the oxidized dye molecule (5) and recombination of the injected electron with the electrolyte (6). These reactions are marked in Figure 2.1 (with time scales indicated in the caption) for the different processes [4, 10, 11].

The driving force for injection is set by the energy difference between the LUMO level of the dye and the conduction band edge of the semiconductor. For regeneration the driving force is limited by the difference between the redox potential of the redox couple and the HOMO level of the dye. The maximum photovoltage that can be generated by the cell is determined by the difference between the redox potential of the redox couple and the quasi-Fermi level of the electrons in the semiconductor. Losses due to resistance in the cell will decrease this number. How the potential can be tuned in the dye design will be discussed more in the Results chapter. The maximum photocurrent is limited by the light harvesting efficiency, the injection efficiency and the regeneration efficiency, as seen in Equation 3.11. One factor influencing these parameters is the surface coverage of dye molecules on the surface but also complete monolayers of dye molecules are important to prevent current losses. The electronic structure of the dye also plays a crucial role [12] and since the system is sensitive to changes in the kinetics the energy level alignment will be important.
2.2 Interfaces in dye-sensitized solar cells

The complexity of the DSC partly stems from the large variety of interactions between the different components. Below, the mutual interaction region is referred to as interfaces and their different nature in terms of e.g. solid, molecular or liquid give them different characters. The geometrical and energetic matching of these interfaces is vital for the function of the solar cell. A detailed understanding is therefore needed to resolve problems concerning function and also improvements of the performance. Means to obtain improved understanding of these interfaces at an atomic level has been an important target for the present thesis. The different schematically drawn interfaces in Figure 2.2 are studied in different papers in this thesis using photoelectron spectroscopy (PES).

Starting from the working electrode there is an interface between the conductive glass and the semiconductor where a good electronic connection is important. One well studied interface is between the dye molecules and the semiconductor electrode, i.e. a molecule-electrode interface (A) with interesting parameters such as energy matching, geometrical configuration and surface coverage. Another interface that is more difficult to study is the interface containing electrode, dye and solvent components, i.e. the electrode-electrolyte interface (B). Here geometrical changes as well as energy matching are of great importance. The electrolyte contains a solvent and at least two different salts, i.e. the solvent-solute interface (C). A final interface is between the electrolyte and the counter electrode. A good catalyst and electronic connection between the electrolyte and counter electrode is needed for a good charge transport to the oxidized dye molecules to improve regeneration.
2.2.1 Molecular-electrode interfaces

The energy matching between the dye molecules and the semiconductor sets the limit for the performance of the solar cell. If the difference between the energy levels of the excited dye and the conduction band of the semiconductor is too small no injection of electrons will occur. If the difference on the other hand is very large there will be unnecessary energy losses. The interface between the semiconductor and the dye molecules is well suited to be studied with PES since much information can be obtained by performing measurements in vacuum and standard instrumental setups can be used. In some cases a solid hole conductor is used instead of the liquid electrolyte. In such solar cell systems the interface between the hole conductor and the dye molecules can be studied in the same manner [13]. Topics that have been studied previously are e.g. surface coverage, energy matching, effect of co-adsorber or the effect of water in the dye solution [14–21]. Paper I and Paper II are about energy matching, surface coverage and binding geometry of series of dye molecules with changes in different parts of the molecules.

2.2.2 Solute-solvent interfaces

Inside the electrolyte several ions are present in a solvent. The traditionally used redox couple is as mentioned iodide/triiodide or more recently a cobalt complex based system. The kinetics of these redox couples are quite well studied in an electrochemical manner [9, 10, 22–24]. In this thesis focus has been on the iodide/triiodide system and the solvation of the ions in different organic solvents and water as presented in Paper III and IV. Solvation of these ions in different solvents will lead to different geometries and energy levels and is important for the energy matching in the solar cell.

2.2.3 Electrode-electrolyte interfaces

The most difficult interface to study with photoelectron spectroscopy techniques is the electrode-electrolyte interface. Since PES usually demands vacuum the presence of a liquid in contact with the solid electrode has not been possible. In recent years high pressure XPS has emerged as a new available technique [25]. Attempts were made already in the 1970’s but no systems have been generally available [26–28]. The solvation of the dye molecules and perhaps also of the semiconductor interface can affect the energy level alignment of the solar cell system and the understanding of the structure and size of this solvation can help in the development of new materials. In this thesis, Paper V describes a new laboratory based setup for performing studies on liquid (gas)-solid interfaces. In Paper VI, HPXPS is used to study the influence of water on hydrophobic ruthenium based dye molecules.
3. Methods

In this chapter the main methodologies will be described. The focus will be on photoelectron spectroscopy (PES) since this has been the main method employed and developed within the thesis. After the description of PES some general solar cell characterization methods will follow and the chapter ends with an introduction to the theoretical calculation methods used for interpreting PES data.

3.1 Photoelectron spectroscopy

In the following sections a brief introduction to photoelectron spectroscopy will be presented. The general concepts are described in various textbooks [29, 30].

3.1.1 Basic principle

Photoelectron spectroscopy is a surface sensitive and atomic specific analysis technique. The working mechanism is based on Einstein’s photoelectric effect, that states that matter will emit electrons when irradiated with light of an appropriate wavelength, see Equation 3.1 [31]. The energy of the emitted electron \( E_{KE} \) is equal to the difference between the photon energy \( h\nu \) and the electron binding energy \( E_{BE} \). In Equation 3.2 the photoemission process can be followed in terms of energy. The total energy is the initial state energy, \( E_i \), (energy in a system with N electrons) plus the photon energy. This is equal to the final state energy, \( E_f \), (energy in a system with N-1 electrons including electronic relaxation effects) plus the kinetic energy \( E_{KE} \) of the photoelectron. When Equation 3.1 and 3.2 are combined, it follows in Equation 3.3 that the binding energy is the difference between the final state energy and the initial state energy.

\[
E_{KE} = h\nu - E_{BE} \quad (3.1)
\]
\[
E_i + h\nu = E_f + E_{KE} \quad (3.2)
\]
\[
E_{BE} = E_f - E_i \quad (3.3)
\]
Usually PES is divided in core and valence level spectroscopy where core levels refer to atomic levels with atomic orbital character, typically at higher binding energies. Valence levels are of more molecular orbital character and located at lower binding energies. In Figure 3.1 the basic principles for core level and valence level photoemission are shown. In the valence band the Fermi level of a metal or the HOMO level of a molecule are located.

![Intensity Graph](image)

**Figure 3.1.** The basic principle of core and valence level excitations. Left: An example of a core level spectrum is the Ti2p spectrum, where the Ti2p\(_{3/2}\) and Ti2p\(_{1/2}\) are clearly visible. Right: An example of a valence band of a sensitized TiO\(_2\)-film. The dye used in this case is D35. In the outermost part at low binding energy the HOMO and HOMO-1 peaks for the dye are visible.

### 3.1.2 Relaxation processes

When an electron is removed from a core level in the photoionization process a core hole is created. This hole is unstable and the system will eventually decay to a more favorable energetic state. These decay processes can either be an Auger decay when an autoionization process occurs or an X-ray emission process where a photon is emitted.
The internal nuclear geometry is always assumed to be unaffected by the ionization process and only electronic relaxations are considered. There are several degrees of approximations used when discussing relaxation effects from photoionization. One approximation is Koopmans’ theorem, where one assumes that there are no further electronic relaxations that contribute to the final state energy. The Koopmans energy is the negative Hartree-Fock energy (see Theoretical calculations). This approximation with frozen orbitals is crude but works as an estimation.

Another model that is valid for higher excitation energies (X-rays) is the sudden approximation that states that the core ionization process is instantaneous (when using X-rays) and the core levels will not have time to adjust to a new potential. The total PES spectrum can be expressed as a sum of relaxed eigenstates with features known as shake-ups and shake-offs included. These states are found at higher binding energies (compared to the main line), created when the emitted electron interacts with valence electrons. The frozen wavefunction is expressed as a sum of possible relaxed final states, hence, it is called the sudden approximation.

3.1.3 Chemical shift

All electrons originating from a specific atomic orbital have a rather defined binding energy, however, depending on the chemical state of the atom there can be differences in the electronic binding energy, known as chemical shifts. The chemical shift, originating from two atoms of the same kind but with different chemical environments, is due to both final and initial state effects [32]. Initial state effects are often referred to as factors influencing the energy before ionization such as binding configurations etc. Final state effects are those arising from the photoionization process itself such as those giving rise to the observed spin-orbit split. The difference in electronegativity is sometimes used as a crude measure for chemical shifts. If the difference is large (e.g. C-F compared to C-C), the C1s peak associated with fluorine will have a higher binding energy due to screening of the C1s electrons. One way to better estimate the chemical shift is to use the Z+1 approximation to illustrate the final state effects. Upon photoionization one electron is removed from the system, which in this approximation is equivalent to adding a proton (Z+1) which will relax the electronic structure.

3.1.4 Peak intensity

The intensity of a peak in a PES spectrum is limited by the probability overlap between the wavefunctions of the initial state and the final state. This is described by Fermi’s Golden rule (see Equation 3.4) where \( P \) is the transition
probability, $\Psi_f$ and $\Psi_i$ are the wavefunctions for the final state and the initial state, respectively. $\rho$ is the density of final states and $H'$ is the Hamiltonian.

$$P \propto \frac{2\pi}{\hbar} |<\Psi_f|H'|\Psi_i>|^2 \rho$$

(3.4)

The intensity of a peak in a PES spectrum can be estimated theoretically using Equation 3.5, where $\sigma$ is the cross section, $\rho$ is the density of the element, $\lambda$ is the IMFP (inelastic mean free path) and $\Theta$ is the angle between the sample and the detector. The cross section is specific for each orbital and also depends on the photon energy and is usually decreasing with increased photon energy. The IMFP is a measure of how far an electron can travel in a solid before losing energy [33]. It is also dependent on the photon energy. If normal emission and a flat surface is assumed the angle contribution of the intensity can be neglected.

$$I \propto I_0 \sigma \rho e^{-\frac{d}{\lambda \sin\Theta}}$$

(3.5)

3.1.5 Resolution

The instrumental resolution of a hemispherical analyzer is set by Equation 3.6 where $\Delta E$ is the resolution, $s$ is the entrance slit width, $E_p$ is the pass energy and $r$ is the radius of the analyzer. The pass energy is the mean energy that the electrons are accelerated (or retarded) to when they enter the analyzer through the entrance slit. The best resolution is obtained by using a small slit and a small pass energy. However, the trade off is the intensity. The intensity is increased with higher pass energy and larger entrance slit since more electrons will reach the analyzer [34]. There are also broadening contributions to the spectral lines from the photon source, lifetime broadening depending on the sample and a small contribution depending on the temperature (vibrational broadening). The line shape is usually said to be a Voigt shape with a Lorentzian part (lifetime broadening) and a Gaussian part (other contributions including instrumental broadening) [35]. The total resolution can be estimated by Equation 3.7. The lifetime broadening is typically 310 meV for Ag3d and 175 meV for I4d [36]. In Figure 3.2 an example of the resolution for a system containing a VG Scienta R4000 analyzer with a MX650 X-ray source (AlK$\alpha$) used in room temperature with different pass energies and entrance slits is shown.

$$\Delta E = \frac{sE_p}{2r}$$

(3.6)

$$\Delta E_{Voigt} = ((\Delta E_{Gauss})^{3/2} + (\Delta E_{Lifetime})^{3/2})^{3/2}$$

(3.7)
Figure 3.2. The theoretical resolution in room temperature for a VG Scienta R4000 analyzer with a MX650 X-ray source (AlKα) for different entrance slits and pass energies.

3.1.6 X-ray sources

For PES measurements two different X-ray sources are generally used: in-house systems and synchrotron radiation based facilities. In all X-ray sources, monochromators are included to select the wavelength. AlKα radiation is often used in in-house laboratories and have an energy of 1486.7 eV. The AlKα X-rays are produced using an electron gun. The working principle of an electron gun X-ray source starts with a filament where a high current is applied. Electrons are then emitted and accelerated in one or two steps onto a rotating or static anode. The anode is usually made from aluminum and therefore emits AlKα radiation. The rotating anode allows for higher flux/intensity but is more expensive. A sufficient cooling system is important since the anode gets hot when irradiated with electrons. The intensity and flux of an in-house setup are generally lower compared to synchrotrons.

A synchrotron is another kind of facility where X-ray radiation can be produced. It consists of a ring with straight elements and bent sections with magnets. Electrons are accelerated close to the speed of light in the straight elements of the ring and the electron path is bent by strong magnets (bending magnets) and the electrons will then emit electromagnetic radiation such as X-rays. To improve the intensity, amplifying devices known as wigglers and undulators can be inserted. The radiation from synchrotrons have various photon energies and measurements can be performed from the UV-range and up to more than 10 keV. The advantages of synchrotrons compared to in-house sources are improved intensity, better brilliance, the possibility to tune the energy of the light and high polarization of the light. During the work in this thesis, experiments have been performed at three different synchrotrons; MAX IV in Lund, BESSY II in Berlin and Advanced Light Source (ALS) in Berkeley.
3.1.7 Hemispherical analyzers

A hemispherical analyzer consists of two parallel half spheres with a distance in between. The electrons that are emitted from the sample reach the analyzer via a system of lenses and are accelerated close to a certain energy known as the pass energy and thereafter enter the hemisphere through an entrance slit. Depending on their kinetic energy, the path the electrons will take in the hemisphere will be different and they will hit the detector at different positions [37]. The detectors used in this work consist of a MCP (micro-channel plate) and a camera where the electrons are detected and counted. There are typically two different types of modes for the analyzer, fixed mode and swept mode (notations from Scienta). In fixed mode, each energy is just detected in one spot of the detector. In swept mode on the other hand, the energies are scanned with fixed lens settings over all positions of the detector leading to a more reliable spectrum since all energies have been in all spots of the detector, decreasing the effect of irregularities on the detector. The counts are integrated to obtain a spectrum. A schematic picture of an Scienta R4000 analyzer and also a schematic layout of the two hemispheres are displayed in Figure 3.3. All PES results presented in this thesis are collected with hemispherical analyzers. Some general information about design of hemispherical analyzers is found in refs. [34, 37–41].

![Figure 3.3. Schematic drawings of an R4000 analyzer with the electron path visible (left) between the two hemispheres. The electron is entering the analyzer through the lens system and then goes into the hemisphere via an entrance slit. After travelling in the hemisphere, it hits the detector at a certain position depending on its energy. Figure courtesy to VG Scienta.](image)
3.1.8 Energy calibration issues

When it comes to energy matching a stringent and reliable energy calibration method is crucial. Depending on the kind of sample different approaches can be used. For solid and metallic materials usually the Fermi level is measured and the binding energy scale is defined as having the Fermi level at 0 eV. In semiconductors and molecular materials this Fermi level calibration is usually not possible in a direct way. One way to overcome this is to connect the sample to a known and well defined material, such as Au, and then use that for calibration. For liquid samples one can choose to use theoretical literature data for the valence bands of the corresponding gas lines [42]. However, it has been seen that this method can cause problems due to accumulative charging of the surface of the liquid jet [43]. Recently, it has been shown that using the HOMO peak for the liquid in the valence band is a more reliable method for internal energy calibration, if the same solvent is used.

For a sample measured at high pressure one has to decide a method amongst these to make an internal calibration. The work function of a surface will change with pressure leading to relative binding energy shifts of the gas line if the solid surface is used as reference [44]. In Figure 3.4 it can be seen that energy calibration performed on a semiconductor solid substrate (530 eV) will lead to a large shift in the O1s line from the gas phase water (the peak found at higher binding energy) depending on pressure.

![Figure 3.4](image)

*Figure 3.4. O1s spectra recorded at different pressures of water on a substrate of sensitized TiO$_2$. The green spectrum is recorded using the in-house HiPP-2 system and measured with AlK$_\alpha$ radiation with 2 mbar water atmosphere. The other spectra are measured with 4000 eV at the ALS (Advanced Light Source). All spectra are recorded using the same kind of analyzer. The intensities for the 4000 eV spectra are normalized vs. one sweep while the 2 mbar spectrum is adjusted to fit in the figure. The shift of the gaseous O1s spectra is due to changes of the work function of the surface when the pressure is increased. All spectra are energy calibrated vs. the substrate.*
3.1.9 X-ray absorption spectroscopy - XAS

Normal PES only probes occupied states (unless inverse-PES is used). A method to probe unoccupied levels is X-ray absorption spectroscopy (XAS). In this work near edge X-ray absorption spectroscopy (NEXAFS) has been used. During the absorption process an electron from a core level is excited to an unoccupied valence state by using a photon energy close to the absorption edge. The core hole created has a short lifetime and will either be filled through an Auger process (emitting secondary electrons) or an emission process (emitting photons). The detection is performed by detecting either the number of secondary electrons (electron yield mode) or the photons (fluorescence yield mode). In this work electron detection has been used. The intensity is proportional to the number of core holes created and hence proportional to the emitted electrons. The spectrum is created by sweeping the photon energy over the edge of interest. The transition observed in XAS will always occur from one state to another obeying the dipole rule ($l=\pm1$) on the same atom making it element specific. Photon energy calibration can be performed by measuring a substrate line with both first and second order light. The difference observed in kinetic energy will determine the incident photon energy.

3.1.10 High pressure XPS

Normally PES requires vacuum or even UHV to work properly due to electron collisions (elastic and inelastic scattering) with a media lead to energy losses of the electrons and problems to reach the analyzer; hence no photoelectrons will be detected. This effect is highly dependent both on the media and the kinetic energy of the electrons and will be discussed in more detail later. To study liquids or gases using PES techniques, these problems have to be overcome. The efforts on non-vacuum based XPS techniques were initiated in Uppsala by Siegbahn in the 1970’s where laboratory based systems for gases and liquids were developed [28, 38, 45, 46] and later also by others [47, 48].

These early systems were equipped with differential pumping stages to maintain a sufficient vacuum in the analyzer but allowing higher pressures in the analysis chamber. Another method introduced later is to use a liquid jet setup where a pressure of $10^{-5}$ mbar is sufficient in the analysis chamber and by that, photoelectrons from a solvent-solute interfaces can be detected [43, 49]. The analysis chamber and analyzer is separated by a small skimmer to prevent the vapor from entering the lens system and analyzer.

Nowadays several HPXPS systems are available at different synchrotrons worldwide [50–55]. Also newer laboratory based systems have emerged during the last years [56–59].

The electron analyzer always has to be kept under vacuum conditions to work properly. To achieve this, a small entrance aperture into the lens system
can be used decreasing the gas flow but this will also decrease the intensity. The longer the distance the photoelectrons have to travel in high pressure the higher the scattering losses. Another method is to introduce differential pumping stages between the analysis chamber and the analyzer to rapidly decrease the pressure before the electrons reach the analyzer. This can be further improved by using differentially pumped electrostatic lens systems where the electrons are re-focused in each pumping stage [50, 60]. As with the analyzer, the X-ray source has to kept in vacuum. To allow for X-rays to irradiate the sample, different kinds of X-ray windows or differentially pumped systems are used.

When electrons are emitted from a material under high pressure conditions elastic and inelastic scattering will occur as the electrons hit the surrounding gas. The intensity of the PES spectra will therefore decrease rapidly with increased pressure. The attenuation is dependent both on the nature of the gas and kinetic energy of the photoelectrons. The attenuation at different pressures is described by Equation 3.8 [60] where $I_p$ and $I_0$ are the intensities at pressure $p$ and in vacuum, respectively. The electron scattering cross section ($\sigma$) is tabulated in various references [61, 62]. The distance the electron has to travel in the gas ($z$) can be estimated to be in the order of the distance between the sample and the first aperture since the pressure is decreasing very fast just behind the first aperture when entering the differential pumping stage zone [50]. When comparing spectral intensities of different elements measured in high pressure it is preferable to change photon energy so the photoelectrons will have equal kinetic energy. Otherwise the change in electronic cross section has to be accounted for.

\[
\frac{I_p}{I_0} = e^{-\frac{\sigma p}{\pi T}}
\]

One way to decrease the problems with inelastic scattering of electrons when measuring in gas or liquid environments is to increase the kinetic energy of the photoelectrons. This can be done by increasing the photon energy. HAXPES (hard X-ray photoelectron spectroscopy), makes use of higher photon energies at synchrotrons. Since the kinetic energy of the photoelectrons will be higher more electrons will reach the detector. Another advantage with higher energies is the larger penetration depth due to higher IMFP in the actual material investigated, making it possible to probe the actual interface even with a liquid film on a solid sample.
3.2 Experimental PES setups

In this section the experimental setups used for PES measurements in this thesis will be described.

3.2.1 BL I411: Vacuum

Most of the experimental work in this thesis has been performed at the soft X-ray beamline I411 at the synchrotron facility MAX IV in Lund [63]. The photon energy range is 50-1500 eV. The analyzer is a Scienta R4000WAL hemisphere. The beamline is for multi purposes and users can handle solid, liquid and gaseous samples with rather small modifications of the setup.

Figure 3.5. Pictures from the undulator beamline I411 at the synchrotron MAX IV in Lund. Left: The beamline and the end station. To the left is the storage ring. The beamline has a monochromator and a number of mirrors to adjust the beam to the desired wavelength and focus. Right: The measurement setup with manipulator, load lock, preparation chamber and measurement chamber. The spectrometer is not visible in the picture since it is hidden behind the chambers.

The standard PES measurements are performed on solid samples, where a high vacuum can be kept in the analysis chamber and spectrometer. A picture of the end station when used for solid solar cell samples are shown in Figure 3.5. The system consists of a load lock chamber with a transfer rod attached were the samples are inserted from air. The rod is used to transfer the samples into a preparation chamber. The analysis chamber and the preparation chamber are separated with a valve and when the pressure is sufficiently low in the preparation chamber a manipulator is used to transfer the sample to measurement position. The angle between the analyzer and the sample is 30° and the X-rays are hitting the sample at 60° to optimize intensity and surface sensitivity. There are turbo pumps situated on all chambers to assure a good pressure. Usually the samples are measured in the $10^{-8}$ mbar regime. The vacuum system was used for collecting data for Paper I and II.
3.2.2 BL I411: Liquid jet

The experimental setup for liquid samples at beamline I411 is based on a differential pumped micro liquid jet. An HPLC (high pressure liquid chromatography) pump is used to pressurise the liquid up to typically 5-20 bar. The liquid is pushed through a stainless steel tube and is entering the analysis chamber through a 15 \( \mu \text{m} \) glass nozzle. The radiation hits the liquid beam in its laminar region and the spectrometer is parted from the analysis chamber by a 0.5 mm copper skimmer to prevent liquid or gas from entering the analyzer. The pumped liquid is frozen in a liquid nitrogen cold trap. Usually the spectrometer is mounted in the magic angle (54.7\(^\circ\)) to the polarization direction of the X-rays to prevent changes in intensity ratios due to angle dependence of the photoelectrons interactions. The pressure in the analysis chamber is usually in the \( 10^{-5} \) mbar range. The solutions are filtered before use and stored in blue cap bottles with the possibility to switch between different samples. The setup and some applications are described in the following papers [43, 64–70]. The setup was used for obtaining data presented in Paper III and IV.

3.2.3 Laboratory based HiPP-2 system

An upcoming family of spectrometers is those able to measure at high pressures on in-house systems meaning that high pressure spectra can be acquired without going to a synchrotron. One such system is presented in Paper V and will be briefly described here. Some applications where the system is used are described in Paper VI and VII.

The HiPP-2 system is developed and produced by VG Scienta and follows on the the HiPP-system [56]. It consists of an X-ray source (Scienta MX 650 HP), a stainless steel analysis chamber with a \( \mu \)-metal coating, a load lock chamber for easy sample transfer and an electron energy analyzer (Scienta R4000 HiPP-2) which is based on the conventional R4000 analyzer (see Figure 3.3). A schematic drawing of the system is displayed in Figure 3.6.

During high pressure operation all high voltage elements in the analyzer and the monochromator must be kept under high vacuum, while a gas pressure is present in the chambers. To achieve this, the X-ray source has been separated from the analysis chamber by a reinforced aluminum coated window, and two additional pumping stages have been introduced between the analysis chamber and the electron energy analyzer. The pumping stages are shown in Figure 3.7.
Figure 3.6. A schematic drawing of the HiPP-2 instrument where the different components are marked. The gas inlet valve can be connected either to a gas flask or a test tube containing a liquid.

Figure 3.7. A schematic drawing of the HiPP-2 system with the different pumping stages marked. Turbo pumps are attached at all different pumping stages. The exchangeable front cone (first aperture) is indicated to the left in the figure.

The chamber is filled with gas by back-filling the entire chamber through a needle valve. Two valves are used to better adjust the pressure. Either a gas flask or a test tube with a liquid can be attached to the system. The load lock chamber is also attached to a nitrogen source for venting purposes or measurements with N₂. When a liquid (here water) is used the liquid is freeze pumped three times using liquid nitrogen to remove dissolved gases that can cause bubbles in the system. A backing pump and two valves are attached to the test tube and when the liquid freezes all excess gas is pumped away. When the frozen liquid is melting more gas will be released and pumped away when the procedure is repeated.

The outermost front cone of the differential pumping setup protruding into the analysis chamber is exchangeable, which allows the size of the first aperture to be varied (0.3, 0.5 and 0.8 mm available) to optimize the setup for the
particular pressure range of interest. To investigate the optimum cone diameter in every pressure range, Ag3d$_{5/2}$ high-resolution spectra were acquired at pressures ranging from high vacuum up to several mbar using the different cones available. The distance from the sample to the front cone aperture was adjusted to one aperture diameter. The attenuation curves (signal intensity versus pressure) for the three different cones are presented in Figure 3.8.

![Figure 3.8](image)

*Figure 3.8.* Different intensities obtained at different pressures using the 0.3 mm, 0.5 mm and 0.8 mm front cone. For lower pressures (below 2 mbar) the larger 0.8 mm cone is preferable. For high pressures (above 4 mbar) the smallest 0.3 mm cone will give the highest intensities. The 0.5 mm cone is optimal for pressures between 2 and 4 mbar.

The spot size of the X-ray beam on the sample is larger than any of the available cone diameter sizes. Therefore, under high vacuum conditions, the cone size defines the field of view for the analyzer. As the pressure increases the signal intensity becomes increasingly affected by the electron losses in the gas phase. Therefore, the distance the electrons have to travel at high pressure will have a higher influence on the intensity for higher analysis pressures. As the pressure increases the loss in intensity is more rapid for the larger cones. It can be concluded that the 0.5 mm cone offers the best performance only within the 2 to 4 mbar pressure range, and the 0.8 mm cone for lower pressures and the 0.3 mm cone performs best for all pressures above 4 mbar.

To demonstrate the performance of the analyzer over a broad energy range, overview spectra of a clean silver sample in vacuum and 1 mbar N$_2$ are shown in Figure 3.9. The spectra show good statistics over the full kinetic energy range, including the MVV Auger transition of Ag at around 350 eV kinetic energy. The overview spectra were collected using the 0.8 mm front cone since the pressure used was below 2 mbar.

To test the limit of the system a Ag3d spectrum under 30 mbar N$_2$ atmosphere was acquired. At such high pressures the 0.3 mm front cone is necessary. The pressure limit is set both by the X-ray window and the transmission of electrons into the analyzer.
Figure 3.9. Overview Ag spectra recorded in vacuum and 1 mbar N₂ atmosphere. Small contaminations are detectable such as C1s and O1s. The Ag MVV Auger structure is displayed as an inset in the figure.

Figure 3.10. Ag3d spectrum in 30 mbar N₂ atmosphere using the 0.3 mm front cone was possible to acquire within a few hours with good statistics.
3.2.4 HP-HAXPES

As mentioned HP-HAXPES can be used to increase the IMFP and reduce the scattering losses when measuring at higher pressures. At the bending magnet beamline 9.3.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory a HP-HAXPES end station is installed. In Figure 3.11, a part of the analysis chamber is shown. The exchangeable cone has a 0.3 mm opening into the HiPP-2 spectrometer to ensure measurements up to 25 mbar. The entire chamber can be filled with a gas through a needle valve or the sample can be dipped in the beaker shown in the figure creating a liquid film. The photon energy used in data presented in this thesis was 4000 eV. The 9.3.1 end station is used for data presented in Paper VI.

![Figure 3.11. Photograph from the analysis chamber at beamline 9.3.1 with the HP-HAXPES end station. The cone has an opening of 0.3 mm into the spectrometer. The beaker contains water and gives the possibility to dip the samples to measure on a solid-liquid interface. Visible next to the sample is a platinum electrode, which is used if a bias is applied on the sample.](image)
3.3 Solar cell characterization

3.3.1 IV

The most basic way to determine how much solar power is converted to electrical power by a solar cell is to take an IV-curve to determine the short circuit current ($J_{SC}$) and the open circuit voltage ($V_{OC}$) and then calculate the efficiency and the fill factor ($FF$) from Equation 3.9 and 3.10. The $J_{max}$ and $V_{max}$ are determined from the $P_{max}$, which is the point where the largest rectangle can be fitted under the IV curve, as indicated in Figure 3.12. $P_{in}$ is the power of the incident light.

Normally the cell is irradiated with a solar simulator imitating the terrestrial AM1.5G solar spectrum and calibrated to 1000 W/m$^2$ (1 sun) using a reference diode. The load on the cell is changed from zero to infinity to reach all points between short circuit and open circuit. An example of an IV curve is displayed in Figure 3.12.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}}$$  \hspace{1cm} (3.9)

$$FF = \frac{J_{max}V_{max}}{J_{SC}V_{OC}}$$  \hspace{1cm} (3.10)

![IV curve for a solar cell based on the dye D45 and a cobalt electrolyte.](image)

*Figure 3.12. IV characteristics for a solar cell based on the dye D45 and a cobalt electrolyte.*

3.3.2 IPCE

The incident photon to current conversion efficiency (IPCE) is a measure on how well the device converts light to current at a specific wavelength. By illuminating the cell with monochromatic light and dividing the obtained photocurrent with the photon flux from the light, a quantum yield can be calculated for a specific wavelength of the light. The wavelength is scanned over the visible range of the spectrum. An example of an IPCE spectrum can be seen in
Figure 3.13. IPCE measurements can give insights into the limiting processes in the solar cell according to Equation 3.11, which shows that IPCE is dependent on the light harvest efficiency \( (LHE) \), the injection efficiency \( (\phi_{inj}) \), the regeneration efficiency \( (\phi_{reg}) \) and the charge collection efficiency \( (\phi_{cc}) \).

\[
IPCE = LHE \phi_{inj} \phi_{reg} \phi_{cc}
\]  

(3.11)

Figure 3.13. IPCE characteristics for a solar cell based on D35 and a cobalt electrolyte.

3.3.3 Electron lifetime measurements

For DSCs, the electron lifetime measurements characterize how long time an electron can stay in the mesoporous semiconductor before it recombines with an oxidized dye molecule or ionic species in the electrolyte. The electron lifetime is obtained by measuring the photovoltage when a small square wave modulation is applied upon the bias of the illumination by a light emitting diode. The lifetime is always measured under open circuit conditions since no charge is extracted. In a similar way the charge carrier transport time can be determined by measuring the photocurrent under short circuit conditions. The lifetime and the transport time are obtained by fitting the rise and decay signals.

3.3.4 UV-vis absorption

To investigate the spectral properties of the dyes UV-vis absorption can be used. The absorbance of a dye at a certain wavelength can be calculated from the measured transmittance. From the absorbance the extinction coefficient can be obtained using Lambert-Beer’s law (see Equation 3.12) where \( A \) is the
absorbance, $\varepsilon$ is the extinction coefficient, $c$ is the concentration and $l$ is the length of the cuvette or sample. The absorbance can be measured either in solution or through a film.

$$A = \varepsilon cl$$  \hspace{1cm} (3.12)

### 3.4 Sample preparation

This thesis mainly focuses on PES studies of solar cell materials. The solar cell preparation is described in detail in other papers [4, 19]. Here follows a description how the samples were prepared for different PES measurements.

For solid samples, one layer of TiO$_2$ paste (DSL 18 NR-T) was screen printed on top of fluorine-doped tin oxide conductive glass (Pilkington TEC 15). The substrates were heated for 5 min in 120 °C and subsequently sintered at 500 °C at 30 minutes and left to cool in the oven over night. The thickness of the TiO$_2$ layer was between 2 and 6 µm. For the samples in Paper II also a light scattering layer was used on the electrodes. Before sensitization, the samples were cut into a suitable size (usually 1 cm$^2$) and heated up to 300 °C for 10 minutes and then cooled to around 80 °C. The samples were immersed into a dye solution and left for usually 12-15 h (depending on project). After sensitization, the samples were rinsed with the solvent used in the dyebath and immediately mounted on the sample holder and transferred into the vacuum system.

For liquid samples, LiI was dissolved in water, ethanol or acetonitrile to a concentration of 0.5 M. For the mixed solutions, molecular I$_2$ was added to obtain solutions with 0.25 M I$^-$ and I$_3^-$, respectively. For the I$_3^-$ solution equal amounts of LiI and I$_2$ were used. All solutions were prepared and filtered at the synchrotron facility immediately before the measurements took place.
3.5 Theoretical calculations

Theoretical calculations can be of good help in the interpretation of experimental photoelectron spectroscopy results, since it can give insights in the detailed electronic structure resembling PES spectra. Spectrum calculations can aid in the understanding of details in the valence band. Calculations on solvation structures can shed new light on the liquid jet experimental results and provide explanations for differences observed in PES spectra depending on solvent. In this thesis several different theoretical methods have been used and they will be briefly described.

Quantum chemical methods are needed to calculate electronic structures of molecules, since classical methods are not adequate to describe electronic degrees of freedom. The basis for many quantum calculations is the time independent Schrödinger equation where $H$ is the Hamiltonian operator describing the total energy of the system, e.g. a sum of kinetic and potential energy operators, $\Psi$ is the wavefunction and $E$ is the total energy of the system [71] as described in Equation 3.13. The stationary solutions of the Schrödinger equation are the wavefunctions with their corresponding energies for the states, which describe the system.

$$H\Psi = E\Psi$$  (3.13)

The calculations of the electronic structure can be simplified using the Born-Oppenheimer approximation, where the heavier nuclei and the lighter electrons are assumed to not be coupled to each other [72, 73]. To limit the calculation efforts it is assumed that electrons are independent of each other - that they only feel the average field created by the other electrons in the system, and that each electron is associated with a particular energy level. One method that uses these simplifications is the Hartree-Fock (HF) method where the wavefunction is described by a Slater determinant. When the determinant is solved, self consistent field (SCF) molecular orbitals with certain orbital energies are generated. These can be related to the Koopmans energy, where the negative HF orbital energy is approximated as the binding energy without relaxation effects. To access the electronic correlation - missing in the independent particle approximation - a multi-configurational (many determinants) wavefunction can be used but at a higher cost.

3.5.1 DFT

Alternatively, to study the electronic structure, density functional theory (DFT) can be used to incorporate the correlation energy. Instead of dealing with a multi-dimensional many electron wavefunction, as in the methods described below, DFT uses that: for a given electron density there is a single corresponding energy of the system. The lowest energy configuration is described by
three functions describing the systems potential energy, kinetic energy and exchange correlation interaction energy [74]. By extracting the density of states (DOS) for different elements, PES spectra can be simulated. DFT is used in Paper I to describe the electronic structure of two different dye molecules.

3.5.2 Quantum mechanical methods

Now we are turning to the more demanding multi configuration wavefunction methods. To overcome errors induced by the approximations mentioned above, the complete active space SCF (CASSCF) can be used [75]. Here the orbitals are divided into active (unfilled) and inactive (filled) orbitals, in order to generate and optimize a large number of determinants in the wavefunction that improves the description of both the electronic ground and excited states. CASSCF gives both occupied and unoccupied levels, which are interesting for photoactive materials. When introducing a second order perturbation where dynamic electron correlations are included, the method is denoted CASPT2. CASPT2+SO refers to when spin orbit interactions have been included in the calculations, usually by first calculating the spin free part of the Hamiltonian and then by adding a spin and momentum coupling contribution. CASSCF are used in Paper III and IV, while CASPT2 is used in Paper III to simulate PES spectra.

3.5.3 Solvation effects

The interactions between a molecule or ion and its surroundings (such as solvents) are normally too demanding to handle with a quantum mechanical approach. Instead molecular dynamics (MD) are used to simulate the dynamics of the solution. In MD simulations, the nuclear motion is described with the classical Newtonian equations of motion. The forces between the different particles are calculated, then the particles are allowed to move for a short time and the forces are recalculated. Classical MD simulation is used in Paper III.

In classical MD simulations, fixed force field parameters are used, and the atoms are propagated as classical particles. With these approximations, changes of the electronic structure due to bond breaking or formation will not be described adequately. In ab initio MD simulations these electronic interactions are taken into account successively when calculating the forces, since the potential is calculated in every time step using a quantum chemical calculation. In Paper IV, ab initio MD is used to account for the geometrical change of $I_3^-$ in different solvents.

MD simulations can be used for spectrum sampling, where geometries (or snapshots) from the simulation are extracted and treated with quantum chemical methods, e.g as is done for water clusters in ref. [76]. This is done by
taking several small clusters from the simulation and perform quantum chemical calculations on the clusters.

From MD simulations radial distribution functions (RDFs) can be obtained by analyzing the MD results in terms of the likelihood of finding certain inter-particle distances. RDFs will be described more in the Results section.

Instead of using explicit solvent molecules, a continuum defined by the dielectric constant of the medium can represent the solvent, simplifying the calculation, while quantum chemistry is used to simulate the solute. This method is called polarizable continuum model (PCM) [77] and is used in Paper III.

3.5.4 Spectrum calculations

To facilitate the interpretation of the experimental PES spectra, theoretical spectra can be calculated using different methods. As with all calculation chemistry, different degrees of approximations may be employed. In Paper I, DFT calculations are used to extract PES valence level spectra by using the negative orbital energies as binding energies (i.e. via Koopmans’ theorem). This does not take internal relaxations in the final state into account, and the spectrum has to be shifted in the binding energy scale for comparison with experimental spectra.

A PES spectrum can be modeled by simply calculating the final state energy and the initial state energy as described in Equation 3.3. When the total energies for those states are calculated separately, the binding energy is described as the difference between these, and hence relaxation effects are taken into account. Since the process of photoionization may be considered to be very fast, the internal geometry is assumed to be fixed, while the electronic structure is allowed to relax. The calculated binding energy will hence consist of electronic but not nuclear relaxations. This method is used in Paper III and Paper IV.
4. Summary of results

This discussion of the results will be divided into three parts; each covering results from different experimental setups and thus different interface are studied. First some results on changes in the structure of dye molecules on surfaces probed with vacuum based PES will be presented. These data give, in combination with solar cell characteristics and theoretical modeling, new insights in how structural changes affect the solar cell. Thereafter, some experimental and theoretical data on electrolytes (liquids with dissolved salts) using the liquid jet technique on the iodide/triiodide system will be discussed. Finally some results from HPXPS will be presented where electrode-water and electrode-electrolyte interfaces have been studied for energy applications, ultimately directed for examining the complete interface in the DSC.

4.1 Molecular-electrode interfaces

4.1.1 Changes in the D-π-A structure

A common way of designing organic dyes for DSCs is to distinguish between three different parts of the dye molecule namely the donor, the linker and the acceptor units (see Figure 4.1). The donor unit is usually where the HOMO is located and the electron is upon excitation transferred to the LUMO, which is located on the acceptor unit close to the semiconductor surface. To prevent recombination and tune the spectral properties, longer or shorter π conjugated linker units are used to separate the donor and acceptor. The optoelectronic properties of the molecule can be tuned by chemical modifications or substitutions to the donor or acceptor units. The HOMO level can be tuned by changes in the donor unit while modifications in the acceptor unit will shift the LUMO level. The LUMO should preferably be spread over the entire molecule to ensure good electron transport and also couple well with the conduction band of the semiconductor via the anchoring group on the acceptor unit. The linker can also affect the absorption spectrum in different ways [78–81]. By introducing groups on the donor unit to obtain steric hindrance, the recombination can be lowered by blocking the approach of electrolyte molecules to the surface, which is needed for the use of Co-based electrolytes. Introduction of these bulky alkoxychains on the donor unit can in addition to lower the recombination also prevent dye aggregation. Longer and larger donor and linker units can however affect the binding angle of the dye and by that the surface coverage and in addition lower the photocurrent [82–90]. In Paper I, a change in the donor unit is investigated and in Paper II the linker unit is altered.
**Figure 4.1.** An illustration of the Donor-π linker - Acceptor dye design system. For an n-type DSC the anchoring group is usually located on the acceptor unit.

**Figure 4.2.** The two organic dye molecules D35 and D45 are compared in Paper I. The only difference is the length of the alkoxy chains, located on the donor unit.

**Figure 4.3.** The five dyes D35 and LEG1-4 are compared in Paper II. The linkers are changed while the donor and acceptor units are the same.
In Paper II, the linker unit was changed to broaden the absorption range to higher wavelengths [91]. Four different new linkers compared to the D35 dye were introduced and are shown in Figure 4.3. For the solar cells, PEDOT counter electrodes were used as well as a Co-based electrolyte. The solar cell characteristics are summarized in Table 4.1 and compared to the original D35 dye. LEG4 performs best under the conditions used in Paper II, yielding the highest efficiency as well as the highest $J_{SC}$ while the $V_{OC}$ is rather low. These improved properties are attributed to a large extinction coefficient and a red shift in the absorption spectrum (the lower $V_{OC}$ will be discussed later). Also for LEG2 based solar cells the $V_{OC}$ is lower than expected and this is attributed to dye aggregation, which does not seem to be a problem for LEG4. In Figure 4.4 the electron lifetimes are summarized. The shorter lifetimes for LEG2 and LEG4 can be one reason for the lower $V_{OC}$ observed for these dyes. LEG3 shows both the longest electron lifetime and the highest $V_{OC}$.

PES measurements can aid in the understanding of these differences in solar cell performance. The surface coverage is estimated by comparing the S2p intensities when normalized to the corresponding substrate Ti2p signal, as displayed in Figure 4.5. The dye coverage is here lowest for LEG4 and highest for LEG1. Also the binding morphology can help in the efforts to understand the differences observed in electron lifetimes and can be estimated using the N1s spectra as described previously, see Equation 3.5. By using values of 6 Å for and 8 Å for the IMFP for photon energies of 540 eV and 758 eV [15, 92], respectively, the binding configurations are calculated from the corresponding N1s intensities. LEG4 has the shortest N-N distance (average distance normal to the surface) and is therefore assumed to have a rather small binding angle compared to the surface while LEG1 seems to be standing up and the binding configurations for LEG2 and LEG3 are somewhere in between. The method is crude but useful as an indication for average distances. The bulkier unit introduced, the lower the binding angle observed for the dye molecules. The binding angle will essentially affect the surface coverage and as seen in

<table>
<thead>
<tr>
<th>Dye</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D35</td>
<td>0.86</td>
<td>9.4</td>
<td>0.69</td>
<td>5.6</td>
</tr>
<tr>
<td>D45</td>
<td>0.81</td>
<td>8.8</td>
<td>0.68</td>
<td>4.8</td>
</tr>
<tr>
<td>LEG 1</td>
<td>0.88</td>
<td>7.6</td>
<td>0.62</td>
<td>4.2</td>
</tr>
<tr>
<td>LEG 2</td>
<td>0.80</td>
<td>7.9</td>
<td>0.65</td>
<td>4.1</td>
</tr>
<tr>
<td>LEG 3</td>
<td>0.92</td>
<td>8.9</td>
<td>0.68</td>
<td>5.5</td>
</tr>
<tr>
<td>LEG 4</td>
<td>0.85</td>
<td>10.8</td>
<td>0.71</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Figure 4.5, the binding morphology estimated and the surface coverage are proportional where a smaller binding angle leads to a lower coverage. The short electron lifetime for LEG4 can be attributed to smaller dye coverage due to a smaller binding angle to the surface preventing a sufficient blocking effect resulting in increased recombination with the electrolyte and lower $V_{OC}$.

Figure 4.4. The electron lifetimes for injected electrons in TiO$_2$ with different dye molecules. Left: D35 and D45. Right: LEG1-4.

Two well studied and well performing organic dye molecules for DSCs are D35 and D45 [93, 94]. The structures are displayed in Figure 4.2. The only difference is the hydrophobic chain length at the donor unit of the molecules. This difference largely affects the electron lifetime of the electrons in the mesoporous TiO$_2$ (as seen in Figure 4.4), but also the current and the voltage where D35 based solar cells show higher values. To deduce the origin of these differences in solar cell performance, a PES study complemented with theoretical DFT calculations have been performed accounting for both geometric and energetic characteristics of the system.

Starting with a geometrical approach, the surface density was investigated with DFT and by comparing the S2p signal from the dyes, see Figure 4.5. The calculations showed a 47 % larger maximum coverage for D45 while PES indicated 30 % increased coverage. The results are not very surprising since D45 is significantly smaller. Another factor that could influence the lifetime (see Paper II) is the binding angle. By using the same approach as for the LEG series, the N1s spectra showed in Figure 4.6 indicate a similar binding angle for both dyes with a standing molecule. This is supported by DFT calculations where the standing configuration is showed to be more energetically favorable compared to a more flat configuration.

When turning to the C1s spectra, displayed in Figure 4.7, some differences are seen. Noteworthy, the D35 dye contains almost 30 % more carbon and therefore the signal should be 30 % more intense if all other parameters are fixed. One should also have in mind that we have somewhere in the order of 30-47 % (experimentally and theoretically) more dye molecules on the surface in the case of D45. Taking the total amount of carbon in each sample.
Figure 4.5. To determine the surface coverage the S2p signal for the different dyes normalized vs. the Ti2p signal are showed. The top spectra show data from Paper I and the bottom spectra are data from Paper II. As seen, the relative amount of dye is largest for LEG1 and smallest for D35 and LEG4.

Figure 4.6. N1s spectra for D35 and D45 measured with different photon energies (758 eV and 540 eV). The N in the donor and acceptor units are chemically shifted and by comparing the intensities a binding geometry can be estimated.

into consideration, the D35 and D45 C1s intensities are expected to be about the same. At higher photon energy (758 eV), i.e. less surface sensitive measurements, the intensities are approximately equal when intensity normalized at the corresponding Ti2p signal. However, when probed with lower photon energy (454 eV), the D35 C1s signal is 29 % stronger. From this information we can conclude that the butoxy chains are located at the very top layer of the dye molecule probably forming an entangled alkoxy layer preventing the
electrons injected into the TiO$_2$ from recombining with the Co$^{3+}$ complexes. This would explain the longer lifetime observed for D35 based solar cells.

![Figure 4.7](image)

*Figure 4.7.* C1s spectra for D35 and D45 measured with different photon energies. The lined spectra are measured with photon energy 758 eV (left axis) and the dashed spectra are measured with photon energy 454 eV (right axis).

![Figure 4.8](image)

*Figure 4.8.* Left: The valence bands from D35 and D45 measured with a photon energy of 150 eV. The two spectra show strikingly similar spectral shapes and levels. Right: Experimental N1s-NEXAFS, also similar for both dyes.

One other plausible explanation for the changes in solar cell performance is that the energy levels are shifted. In the left part of Figure 4.8, the outermost part of the valence bands of D35 and D45 are shown with the HOMO levels visible. The two spectra show strikingly similarities. Also the N1s-NEXAFS spectra showed in the right part of Figure 4.8 are very similar. Hence, the alkoxy chains do not change the energy levels on neither an atomic nor a molecular level. This also indicates that the triarylamine unit will be unaffected in geometry by changing the chains. The experimental spectra are supported by theoretical DFT calculations (presented in Paper I). The conclusion in Paper I is that only geometrical factors due to the longer alkoxy groups will be the explanation for the quite large changes in the solar cell performance when the donor unit is changed in the D35 dye.
4.2 Solute-solvent interfaces

The iodide/triiodide electrolyte system is the classical system used for DSCs and a detailed understanding of energy levels and organization of the ions is of importance to understand the solar cell. Iodine and iodide are also used in a number of other applications such as medicine, biology etc [22, 95–97]. Triiodide in solution have been studied before using PES with focus on spectroscopic features [98]. Before going into the details from the iodide/triiodide results some general discussion about solvation will follow.

4.2.1 Solvation- molecular interactions in liquids

A solid can be viewed as structured and ordered while gases on the other hand are assumed to be disordered with little interactions between different molecules. Liquids are in the middle and behave differently from solids and gases. When a solid (solute) is dissolved in a solvent, different events will occur depending on the properties of both the solvent and the solute. These differences and changes can largely be attributed to intermolecular forces both on a macroscopic and a microscopic scale. These can be added into the macroscopic dielectric constant, which is included in the Born solvation model discussed below. The Born solvation model is one of the simplest models to study solvation and it gives a surprisingly good measure on the solvation in terms of changes in Gibbs energy upon solvation of an ion in a solvent.

The Born solvation energy is the contribution to Gibbs energy due to solvation of ions in a solvent, which means the energy it takes to transfer an ion from vacuum into the solvent. The solvent is considered to be a dielectric continuum while the ion is a sphere inside a cavity. By using the expression in 4.1 one can estimate the change in Gibbs energy when ions are dissolved and also the shift in the PES spectrum, here denoted as $SIBES_{BORN}$ (solvent induced binding energy shift) based on the Born model. It is important to note that the Born model only includes the ion-solvent interactions and completely neglects interactions between ion-ion and solvent-solvent.

$$SIBES_{BORN} = (Z_i^2 - Z_f^2) \frac{(\frac{1}{\varepsilon} - 1)e^2}{8\pi\varepsilon_0 r},$$

where $\varepsilon$ is the dielectric constant for the solvent, $\varepsilon_0$ is the vacuum permittivity, $Z$ is the ion charge (before and after ionization) and $r$ is the cavity radius [99].

The Born solvation model takes into consideration the charge of the initial and final state of the ionized ion; hence a positive ion will have a negative change in energy when dissolved while a negative ion will have a positive change. The charge will also affect the magnitude of the energy change upon solvation. For example, I$^-$ will go from a -1 state to a non charged state leading to a change in energy towards higher binding energy while Li$^+$ will go from a +1 state to a +2 state leading to a -3 times change in energy towards lower
binding energy. Noteworthy is that only the initial state will contribute in the case of a single negatively charged ion. For a neutral species only the final state will contribute. Despite the many rough assumptions in the Born model, it can give an approximation of solvation energies. However, our experimental results show that when a large influence on hydrogen bonding is involved in the solvation this model is not able to model changes in a reliable way. The Born model can be attributed to follow the electronic contributions to solvation without taking any nuclear relaxation into consideration.

A common way to examine solvation is to study (or model) the organization of solvent molecules around a specific ion, usually denoted as solvation cage or solvation shells. The solvent molecules will usually arrange themselves in shells around the ion. These can be examined by calculating the radial distribution function (RDF). The RDF is defined as the probability of finding another molecule at a distance \( g(r) \) from another molecule. The minima in these RDFs define the solvation shells and the size of these shells can be estimated. The RDFs can be obtained by classical MD simulations. The thermodynamic view on solvation is described in the following textbooks [100, 101].

### 4.2.2 Solvent induced binding energy shift- SIBES

We define, as mentioned above a spectroscopic measure on the solvation shift named SIBES as an acronym for solvent induced binding energy shift which is the difference between the experimentally determined binding energy and the theoretical binding energy for a gas molecule calculated with CASPT2+SO.

The first experiments and calculations were performed on LiI dissolved in water, ethanol and acetonitrile. The PES structure of I4d is a doublet due to a spin-orbit split in the d-orbitals of 1.7 eV. As presented in Figure 4.9, the binding energy of the I4d spectra are shifted for I\(^-\) in the different solvents and hence the SIBES will be different. The values are summarized in Table 4.2. These differences in SIBES cannot be attributed to the difference in dielectric constants for the different solvents: \( \varepsilon = 78.39 \) (water), \( \varepsilon = 24.55 \) (ethanol) and \( \varepsilon = 36.64 \) (acetonitrile). Hence, the Born solvation model does not capture the local structure of the solvents as it is too crude to describe the results. Instead the influence of hydrogen bonding is a more likely explanation. Water forms a hydrogen bonding network around the ions that will lead to a higher solvation shift while acetonitrile does not form hydrogen bonds at all. Ethanol can form these bonds to some extent. This statement is supported by radial distribution functions (RDFs) extracted from MD simulations.
Figure 4.9. I4d spectra of LiI on different solutions. The difference between the binding energy of the I4d core level and the calculated spectrum in gas phase is denoted SIBES (solvent induced binding energy shift). As seen in the figure, SIBES is highest for water and smallest for acetonitrile.

Table 4.2. The experimental binding energies (in eV) for LiI dissolved in water, ethanol and acetonitrile. The calculated theoretical value is used as a reference. The SIBES are calculated from the difference of experiments and calculations and derived from the Born model.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Ethanol</th>
<th>Acetonitrile</th>
<th>Gas (theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I⁻ (I4d₅/₂)</td>
<td>53.8</td>
<td>53.2</td>
<td>53.0</td>
<td>49.59</td>
</tr>
<tr>
<td>I⁻ SIBES (Experimental)</td>
<td>4.2</td>
<td>3.6</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>I⁻ SIBES (Born with r=2.30 Å)</td>
<td>3.09</td>
<td>3.00</td>
<td>3.04</td>
<td></td>
</tr>
</tbody>
</table>

To extend the discussion, we move to the larger and more complex I₃⁻ ion in solution. I₃⁻ was measured in two different ways: in a solution containing only I₃⁻ and Li⁺ dissolved in ethanol; and in solutions containing both I₃⁻ and I⁻ (with a concentration ratio of 1:1) as well as Li⁺ dissolved in ethanol, acetonitrile or water. A symmetric and linear I₃⁻ ion is assumed in the organic solvents ethanol and acetonitrile. In Figure 4.10 (left) both the theoretical (gas phase) and experimental I4d spectra (in ethanol) of I₃⁻ are found. The I4d I₃⁻ spectrum can be fitted into four contributions (two spin-orbit doublets). The binding energies of the contributions from the terminal atoms (atoms with only one bond to another iodine atom) and the central atom (bound to two different iodine atoms) are separated by approximately 1.1 eV, with terminal I4d found at higher binding energy. Both the center and the terminal I atoms are affected by the solvation, although the solvation is clearly stronger (almost 1 eV) for the terminal atoms. The difference in SIBES between the terminal and center...
atoms can be attributed in the Born model since the charge of the different parts in the ion is different. Just taking that into consideration, the SIBES should be at least twice as large for terminal atoms compared to center atoms. This is supported by the calculations (gas phase) where the shift between the terminal and center I4d contribution is larger than the experimental value indicating a larger solvation for terminal atoms.

*Figure 4.10.* Left: (a) The theoretical I4d spectrum of I$_3^-$ calculated with CASPT2+SO. The spectrum is divided in center and terminal contributions. (b) The experimental spectrum of I$_3^-$ obtained from a LiI$_3$ solution in ethanol. The SIBES is indicated in the figure. Right: Spectra in ethanol (a) and acetonitrile (b) with a 1:1 ratio of I$^-$ and I$_3^-$. At higher binding energies the Li1s peak is overlapping with a shake-up feature from terminal I$_3^-$. 

In Figure 4.10 (right), I4d spectra from mixed solutions are presented. The de-convolution of the spectra was performed using data taken from the single ion spectra. The smaller SIBES observed for cI3- compared to I$^-$ can be understood in relation to the Born model since the cavity radii are assumed to be different for the different ions and also the charges are different with a more negative charge for I$^-$. One would therefore expect that I$_3^-$ would be less solvated compared to I$^-$ which is in accordance with the experimental data as seen in Table 4.3.

Turning to the difference in the different solvents, the Born model was shown not to be valid for I$^-$. The dielectric constant is smaller for ethanol compared to acetonitrile and a smaller SIBES in ethanol is therefore expected, which is in accordance with the experiments for I$_3^-$. The macroscopic properties seem to play a more important role in the case of I$_3^-$ due to a less localized
charge compared to $\Gamma^-$ where hydrogen donating bonds affect the different SIBES.

As a summary, the relative $I_{4d}$ binding energy difference between $I_{4d}$ core levels for $\Gamma^-$ and terminal-$I_{3}^-$ is 0.3 eV in ethanol and 0.8 eV in acetonitrile. This difference is related to two different phenomena where the binding energy of $\Gamma^-$ depends on the capability of hydrogen bond formation while the binding energy of $I_{3}^-$ contributions are less affected by hydrogen bonding but more by the electronic properties (dielectric constant). These findings are presented in Paper III.

Table 4.3. Experimental binding energies and derived SIBES (in eV) extracted from the spectra of the mixed solutions presented in Figure 4.10.

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Acetonitrile</th>
<th>Gas (theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy $\Gamma^-$ ($I_{4d_{5/2}}$)</td>
<td>53.3</td>
<td>53.1</td>
<td>49.59</td>
</tr>
<tr>
<td>Binding energy $I_{3}^-$ (terminal $I_{4d_{5/2}}$)</td>
<td>53.6</td>
<td>53.9</td>
<td>51.87</td>
</tr>
<tr>
<td>Binding energy $I_{3}^-$ (center $I_{4d_{5/2}}$)</td>
<td>54.7</td>
<td>55.0</td>
<td>53.83</td>
</tr>
<tr>
<td>Difference $\Gamma^-$ vs. $I_{3}^-$ (terminal $I_{4d_{5/2}}$)</td>
<td>0.3</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>SIBES $\Gamma^-$</td>
<td>3.7</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>SIBES $I_{3}^-$ (terminal $I_{4d_{5/2}}$)</td>
<td>1.7</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>SIBES $I_{3}^-$ (center $I_{4d_{5/2}}$)</td>
<td>0.9</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

4.2.3 Hydrogen bonding affecting the geometrical structure of $I_{3}^-$

Turning to the $I_{3}^-$ in water, the fitting procedure of the experimental data was not straightforward and an unsymmetric ion was therefore assumed. *Ab initio* MD simulations were performed to shed some light on this unsymmetric structure and its background. In Figure 4.11, the MD simulation results for the internal geometry of the $I_{3}^-$ ion in aqueous environment are presented. The terminal atoms are denoted left and right, and as can be seen in the figure, large bond length fluctuations are observed over time.

*Figure 4.11.* During the MD simulation of $I_{3}^-$ in water, large asymmetry fluctuations were observed. This asymmetry can be visualized by plotting the distribution of the longer and shorter I-I bonds over time.
To confirm the MD simulations and easier compare with the experimental data, theoretical I4d spectra where extracted from the snap shot simulations with different bond lengths (short and long), and are presented in Figure 4.12. When the molecule is distorted (with different bond lengths), the doublet corresponding to photoemission from the terminal atom involved in the elongated bond gradually shifts to lower binding energy, while the binding energy of the other terminal atom increases. When the negative charge is increased on the terminal atom involved in the longer bond, the electrons will be less tightly bound and hence appear at a lower binding energy. The terminal atom involved in the shorter bond will on the other hand approach neutral and therefore get higher binding energy. The contribution from the central atom will be more or less fixed since it is not involved in the charge delocalization.

![Figure 4.12](image-url). Left: The calculated I4d spectra for I$_3^-$ with different bond asymmetry. Data are from MD simulations of LiI$_3$ in water environment. The most symmetric ion is found in the bottom of the figure and the almost separated ion is at the top. The charge will be distributed depending on the bond distance with a symmetric division when the ion is symmetric. Right: Experimental I$_3^-$ spectra in water, acetonitrile and ethanol. In ethanol and acetonitrile the structure of the spectra resembles that of the calculated symmetric ion while the spectrum collected in water appears unsymmetric. Note that the I$_3^-$ contributions in water and acetonitrile are subtracted out from spectra of mixed solutions, see Figure 4.10.
In Figure 4.12, the experimental spectra of I₃⁻ are presented. In the case of ethanol, I₃⁻ was measured on its own in the solution (including counter ion), but in the case of water and acetonitrile subtractions of the I⁻ spectra were performed to obtain the structures for I₃⁻. As can be clearly seen in the figure, and as discussed above, when the ion is dissolved in an organic solvent, the results indicate a symmetric and linear structure while the spectrum in aqueous solution resembles that of a more distorted structure when compared to the simulated spectra.

To get a reliable explanation for these differences in behavior depending on solvent we again turn to RDFs extracted from the MD simulations. The terminal atom with a long bond is shown to have a larger probability of having a bond distance to a hydrogen atom, which is likely to be of hydrogen bond character. The terminal atom with a shorter bond as well as the center atom does not show the same tendencies. Hence, we conclude that the asymmetry observed in the I₃⁻ ion is due to hydrogen bonding. These results are presented in Paper IV.
4.3 Electrode-electrolyte interfaces

As a step towards studies of complete DSC devices with PES techniques, HPXPS have been used to study electrode-water and electrode-electrolyte interfaces. Paper VI focuses on structural and energetical changes of a dye molecule in water vapor atmosphere and Paper VII discusses a new sample transfer technique for measuring electrode-electrolyte samples without exposing the sample to air or vacuum before measurements in high pressure.

4.3.1 In-situ probing of H$_2$O effects

Effects from water in the DSC system is specifically interesting since the use of water based electrolytes would further reduce the environmental footprint of DSC production. The performance of purely water based solar cells is, however, generally less efficient than state-of-the-art systems which are based on organic solvents. Some traces of water will always be present and during long-term use, water will leak in through the sealing. Effects on current and voltage have been observed for solar cells containing water as well as limitations in stability [102–104]. One problem with water based electrolytes is desorption of the dye molecules, by introducing hydrophobic chains this problem can be partly overcome [102, 105]. The dye Z907 (see Figure 4.13) is a hydrophobic molecule that has previously been studied using vacuum based PES [20]. In Paper VI, the effects on Z907 with a water atmosphere present during measurements were investigated.

![Figure 4.13. The structure of the dye Z907 used in Paper VI.](image)

To demonstrate the pressure evolution the O1s spectra from the water and the TiO$_2$ sample are shown for 3 different pressures (vacuum, 11 mbar, and 25 mbar) in Figure 4.14. The spectra are intensity normalized to the substrate TiO$_2$ peak intensity to show the evolution of a new feature around 533 eV. This is attributed to adsorbed water on the organic material on the surface [106]. The new feature is estimated to be 4 times larger than the small contribution corresponding to carboxyl oxygen from the dye molecule, hence there is at least one order of magnitude more water than dye molecules on the surface.
To probe the effects from this water adsorption both core levels (S1s, C1s and Ru3d) and the valence band were investigated. Starting with the S1s level, clear changes after water subjection were observed as seen in Figure 4.15. The displayed spectra have been measured in vacuum and 11 mbar H₂O atmosphere at ALS and are intensity normalized to the corresponding Ti2p signal but since the kinetic energy of the photoelectrons from S1s and Ti2p will be significantly different, the attenuation of the two peaks due to scattering will be different. In the upper part of Figure 4.15 no corrections for these changes are made but in the lower part the electron cross section is accounted for. In both cases a decrease in the S1s signal is observed after subjection to water vapor. The observed reduction of the intensity of the 11 mbar spectrum compared to the vacuum spectrum suggests either dye desorption or a ligand change due to the presence of water. As seen in Figure 4.16A, the intensity of the Ru3d feature remains unaffected by water and the C1s peak is even increasing slightly which rules out dye desorption. The other plausible explanation for the observed decrease of the S1s signal is that the NCS-ligands are partly replaced by H₂O-ligands or converted to cyano (CN)-ligands. The NCS-ligand replacement will change the light absorption spectrum for the dye molecules [107]. The UV-vis absorption spectra taken from electrodes exposed to liquid water for different times are shown in Figure 4.16B. As observed, the absorbance maxima will be more and more blueshifted with longer exposure time indicating a ligand change. From literature it is known that the absorbance maxima of similar Ru-complexes are shifted depending on the ligand, for CN-ligands (493 nm), H₂O-ligands (500 nm) and NCS-ligands (534 nm), respectively [107, 108].

Figure 4.14. O1s spectra recorded at different pressures with 4000 eV photon energy. The spectra are normalized to the substrate peak around 530 eV. The peak at 537 eV is from gaseous water and the emerging peak around 533 eV is from adsorbed water.
Figure 4.15. Ti2p and S1s spectra measured with 4000 eV. The upper Ti2p spectra are only normalized vs. number of sweeps and an attenuation of the intensity is observed. The upper S1s spectra are intensity normalized to the corresponding Ti2p signal. In the lower spectra the change in cross section for collisions with the surrounding H₂O molecules are considered. The decrease in S1s signal is then less prominent but clearly there.

Figure 4.16. A. C1s and Ru3d spectra recorded with 4000 eV in vacuum and 11 mbar H₂O. No change in intensity for the Ru3d peak is observed. The C1s intensity is increasing with pressure possibly due to contaminations over time. B. UV-visible absorption spectra for Z907 samples subjected to liquid water for different times. A blueshift is observed depending on the exposure time.

To disentangle which ligand change that is more likely to occur one can turn to the valence bands, presented in Figure 4.17. Valence band and HOMO-level
are practically unaffected by the presence of 2 mbar water vapor, however, when the pressure was increased to 25 mbar a shift of 0.2 eV towards lower binding energy is observed. When probed with high energies (here 4000 eV), the HOMO spectrum will mainly have a Ru4d character, due to the higher cross section for the 4d level compared to p levels of lighter elements, even though the HOMO level is known to be a mixture of molecular orbitals from the NCS-group and Ru [109]. A decrease in the HOMO level can be understood as a decrease in redox potential for the dye. As reported, the redox potential for Z907 will decrease if the ligand is changed to H2O and increase when replaced by CN [107]. The shift in the HOMO-level suggests a partly exchange from NCS-ligands to H2O when the electrodes are subjected to water atmosphere.

![Figure 4.17. A. Valence spectra of Z907 adsorbed to TiO2. The upper spectra are measured using AlKα radiation in vacuum and 2 mbar water vapor while the lower spectra are measured at ALS using 4000 eV in vacuum and 25 mbar water vapor. The peak around 1 eV binding energy is the HOMO level of the dye while the larger feature between 2 and 8 eV stems from the substrate. At higher binding energy is the contribution from the gaseous water. The large difference in the position of the water is due to changes in the surface work function when the pressure is changed. B. Pure Gaussian fits of the HOMO-peaks measured in vacuum and with 25 mbar are shown.](image)

A shift in the HOMO level of 0.2 eV could largely affect the solar cell performance since the energy matching between the different components is crucial for the kinetics in the solar cell system. The HOMO level is involved in the regeneration of the dye molecules by the electrolyte. The driving force for regeneration would therefore be reduced and this could slow down the electron transfer from the electrolyte to the oxidized dye [10, 11].
4.3.2 Sample transfer system for electrolyte measurements

In Paper VII, a sample transfer system was developed to transfer samples into the HiPP-2 system (described in Paper V). Two main advantages compared to conventional sample transfer were obtained using the new method. The first being that air or water sensitive samples were transferred from a glove box without exposure to air ahead of measurements. Further (and more importantly), the exclusion of the pump-down step to UHV before HPXPS measurements allowed for measurements on an actual liquid droplet. The system was tested for battery samples since they are highly sensitive to air and water contaminations [110]. The electrode used was a silicon and carbon black based electrode and the electrolyte was 1.0 M LiClO₄ dissolved in propylene carbonate (PC) [111].

![Diagram of HiPP-2 system](image)

**Figure 4.18.** A schematic picture of the HiPP-2 system with the gas inlets marked and the valve separating the load lock and the analysis chamber. The valve is opened when equal gas pressures are obtained on both sides. The glove bag is attached to the load lock chamber.

In short the sample transfer was performed as follows. A glove bag was mounted on the load look and a vacuum sealed bag (sealed in the glove box) containing the sample was opened and the electrode was positioned on the manipulator inside the load lock. A drop of electrolyte was placed on the pristine electrode, followed by a fast pump down to 2 mbar. As seen in the schematic setup presented in Figure 4.18, there are N₂-gas inlets both on the analysis chamber and on the load lock. The pressure was, after sample injection, adjusted to be equal on both sides of the valve separating the two chambers. The valve was subsequently opened and the sample was moved to measurement.
position. With this procedure the sample was never exposed to high vacuum conditions, and thus the electrolyte was still present as a liquid drop on the electrode.

HPXPS measurements were performed at different sample positions to evaluate the possibility to actually measure on the electrode-electrolyte interface. Figure 4.19 shows Si2p and C1s spectra obtained from the reference electrode, the interface and the liquid droplet. By translating the sample, an ideal spot can be found for measuring the actual interface. The large C1s contribution around 285 eV in the reference sample stems from the carbon black and the smaller features at higher binding energy are from the PC [112].

![Figure 4.19](image)

*Figure 4.19.* By changing the measurement spot (moving the manipulator up and down) the substrate, solvent and the interface can be measured. The Si2p feature from the substrate is decreasing when the electrolyte propylene carbonate is appearing as seen in the C1s spectra.

PC has a low vapor pressure, but the pumping through the analyzer front cone will reduce the amount of liquid present over time. To evaluate this, the integrated relative intensities of the C1s signal from the PC contribution over time at different background pressures are presented in Figure 4.20. A faster attenuation is seen with a background pressure of 0.7 mbar compared to 2 mbar. These observations are in line with solvent evaporation leading to a reduced droplet thickness and thus decreased solvent signal intensity. The presented measurement technique enables HPXPS measurements of the electrode-electrolyte interface at stable conditions in the timeframe of 1 hour for this specific system investigated.

Even though the system for electrode-electrolyte measurements was tested for battery samples, this new setup opens up possibilities for interfacial solar cell measurements with a dye-sensitized interface with an electrolyte (includ-
Figure 4.20. Attenuation curves for the PC C1s signal (electrolyte) over time with different pressures in the chamber. As seen the intensity is decreasing faster with lower pressure, hence, the liquid is evaporating faster.

The solvation effects on the adsorbed dye molecules would then possibly be measured and the influence of different salt mixtures could be evaluated. If the sample is assumed to be stable in air the procedure including the glove bag could be excluded. By choosing a solvent with lower vapor pressure, a longer time window for measurements is expected. As seen in the results, the pressure in the chamber largely affects the time window for possible measurements on the interface. By increasing the gas pressure it would enable measurements on liquids also with higher vapor pressures as well as for longer times.

Two setups for measurements on solid/liquid samples have been the discussed in the framework of this thesis (Paper VI and VII). The first one enables dipping of the sample in a beaker containing the liquid in the analysis chamber and the other being introduction of a droplet on the solid sample and subsequently avoiding pump-down. Which of these methods that is to prefer largely depends on the nature of the interface of interest. For harmful electrolytes, the method with a droplet might be preferable, since less sample is needed, while measurements with water or similar liquids could be performed using the beaker.
5. Outlook

In this thesis different interfaces in the photoelectrochemical DSC system have been studied using different branches of PES. For each different technique that has been introduced new insights on the molecular and geometrical interfacial properties of the solar cell have been obtained.

Going back to the figure in the Solar cell chapter (replicated and updated in Figure 5.1 below) where the different interfaces are indicated, one important interface has not been studied; the complete interface containing the oxide substrate the dye and an electrolyte. However, looking ahead the same setups as used in this thesis could be used also for targeting this challenge. Moreover, by introducing a solar simulator in a HPXPS or HP-HAXPES system it would be possible to investigate all interfaces simultaneously under working conditions (in operando). This may be accomplished for both configurations discussed in Paper VI and VII by introducing a counter and reference electrodes but requires a continued methodology development in line with that presented in the thesis. After realizing such a setup it would be possible to probe the interface with PES while collecting the current and voltage produced and relate these two measurements with the vision of obtaining structure function relationships at an atomic level.

*Figure 5.1. A schematic picture of a complete DSC measured in operando with a solar simulator and an electron spectrometer.*
6. Populärvetenskaplig svensk sammanfattning

6.1 Energianvändning

Den största delen av världens energikonsumtion kommer från icke förnybara energikällor såsom fossila bränslen. Dessa bränslen (olja, gas och kol) omvandlas till bland annat koldioxid när de förbränns. De ökande utsläppen av koldioxid är ett stort problem och en ökad andel förnybara energikällor är därför önskvärd. Förnybara energikällor är sådana som inte bidrar till koldioxidutsläpp eller annan kraftig miljöpåverkan. Till förnybara energikällor räknas vind-, sol- och vattenkraft samt geotermisk utvinning. I hela världen kommer nästan 70 % av elektriciteten från fossila bränslen och andelen förnybara källor står för strax under 20 %. I Sverige är siffran annorlunda på grund av den stora andelen kärnkraft och vattenkraft som finns (kring 40 % vardera av den totala produktionen). Vindkraft står för ungefär 7 % av elektricitetsproduktionen medan solkraft endast står för 0.03 %. I dessa siffror är inte transportsektorns energikonsumtion inräknad som består till absolut största del av fossila bränslen.

6.2 Färgämnessensiterade solceller


![Figure 6.1. Bilden visar en schematisk översikt över en färgämnessensiterad solcell. Solen lyser på färgämnet som absorberar en foton och därmed kan en elektron lyftas till en högre energinivå. Denna elektron injiceras in i titandioxidfilmen och vandrar sedan ut i en krets där ett arbete kan utföras. Färgämnet får tillbaka en elektron från electrolyten och kan då exciteras igen. Elektrolyten får i sin tur tillbaka elektronen från kretsen.](image)
6.3 Fotoelektronspektroskopi
Fotoelektronspektroskopi (XPS eller PES) är en ytkänslig och elementspecifik mätmetod som kan ge detaljerad information om en ytas egenskaper. Genom att lyssa på ett material med röntgenljus kommer elektroner att emitteras och få en kinetisk energi som går att mäta. Om energin (våglängden) på röntgenljuset är känd kan den elektroniska bindningsenergin för den specifika elektronen beräknas. Denna energi är specifik för en viss sorts atomer och även för olika orbitaler (energinivåer inom en atom eller molekyl). Röntgenljuset kan fås antingen från en labbkälla, då ofta AlK$\alpha$ strålning används, eller en synkrotron där mer intensivt ljus med olika våglängder kan produceras.

![Diagram](image)

*Figure 6.2.* Bilden visar principen för XPS. Tv: När röntgenljus lyser på materialet emitteras en elektron. Genom att mäta energin på elektronen och hur många elektroner som emitteras med en viss energi kan ett spektrum ritas. Th: Ett Ti2p spektrum mätt med en fotonenergi på 758 eV.

6.4 Resultat
I den här avhandlingen har olika typer av solcellsmaterial studerats med hjälp av elektronspektroskopi. För att kunna studera olika gränsskikt har olika typer av metoder använts. Den största skillnaden mellan de olika teknikerna har varit trycket i analyskammaren. Färgämnen som är bundna till titandioxidytan kan studeras med hjälp av vakuumbaserad XPS. Information så som exempelvis mängd färgämne på ytan, bindningsvinklar för molekylerna samt energimatchning mellan olika komponenter kan erhållas. Denna typ av studier finns presenterade i Artikel I och II.

Genom att använda en vätskejet är det även möjligt att mäta XPS-spektrum på vätskor och i det här fallet har jodid och trijodid som är lösta i olika lösningsmedel (en elektrolyt) studerats. Vi har kunnat se att olika lösningsmedel
påverkar jonerna på olika sätt både vad gäller energinivåer och geometri. Resultaten från vätskeexperimenten finns i Artikel III och IV.


Sammanfattningsvis har projekten lett till en ökad förståelse för geometriska och energetiska strukturer för olika solcellsmaterial. Vi har kommit flera steg närmare målet att kunna mäta en komplett fungerade solcell med XPS-tekniker.
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