

Chapter 1

Introduction

Over the last decade a lot of effort has been devoted to investigations of fundamental properties, basic concepts, and model systems in order to achieve better understanding or even make prediction of the behavior of respective systems. In recent years, however, much interest focuses on 'real world systems' in contrast to model systems. 'Bridging the gap' between simplified model systems and more complex realistic systems became a focus in many fields from surface science over catalysis to life sciences. In this thesis, the study of ions, molecules and polymers in a liquid environment makes a step into the same directions. Allowing conventional ultra high vacuum (UHV) techniques like near edge x-ray absorption fine structure (NEXAFS), extended x-ray absorption fine structure (EXAFS), x-ray photoelectron spectroscopy (XPS) and others to be applicable to liquid samples is of paramount interest to a broad variety of scientists in several research areas.

The importance of investigating the liquid phase using synchrotron radiation can not be overstated, reaching from fundamental, environmental, chemical, as well as to industrial applications. Nevertheless, introducing the liquid phase to soft x-ray experiments is delayed compared to other material phases due to the need of vacuum soft x-ray experiments. Very recently studies of liquid samples by soft x-ray spectroscopy [1–11], have increased significantly. Liquid samples in many techniques have been investigated behind membranes in a vacuum chamber, or in a high pressure liquid jet with a very small diameter (1 μm) in vacuum.

During this research, I developed a new end-station which allows to investigate liquid samples in helium as well as under vacuum. Details about this system will be discussed in section 3.2. This end-station is designed for NEXAFS

and EXAFS spectroscopy for liquids, and out-gassing samples. In other setups, resonant inelastic x-ray scattering (RIXS), as well as XPS have been used to investigate ions, molecules, and polymers in solution or wet environment. In addition to the experimental techniques, many theoretical techniques were used to analyze the experimental data, in order to model possible geometric structures.

Chapter 2 introduces the experimental as well as the theoretical methods that have been used in this thesis, and starts with a brief discussion in the first section 2.1 explaining the NEXAFS, EXAFS, RIXS, and XPS techniques. In the second section 2.2 the theoretical packages which have been used in this thesis are introduced.

In chapter 3 a short introduction to synchrotron radiations, as well as beam lines is given. I will not go into details in these parts, since details about such facilities have been published in many books and articles. On the other hand, details about the end-station LIQUIDROM are discussed in section 3.2. Moreover, since in this study two other end-stations are used for XPS and RIXS, I explained them briefly in section 3.4, and 3.3 respectively. The XPS end-station has been build by *Dr. Manfred Faubel* (Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Germany), and *Dr. Bernd Winter* (Max-Born-Institut für nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Germany). The EXAFS experiment applied at BESSY (KMC2-beamline); where, supported by *Prof. Alexei Erko*, we measured EXAFS for several transition metal ions in aqueous solution as a function of concentration and pH. The experiment done in atmospheric air environment, and there was no special end-station for this technique. Part of this investigation will be discussed in detail in section 4.4. Using the RIXS setup at the Advance Light Source (ALS), Berkeley lab, USA in collaboration with *Dr. Jinhua Guo* corroborated our NEXAFS investigations using the LIQUIDROM on the behavior of ions in solution. This will be discussed in detail in section 4.4 as well. Chapter 5.1 will then address XPS investigations, used in this context to understand protonation processes in aqueous solutions.

The thesis has three main chapters for results and discussion, chapters 4, 5, and 6 presenting ions, molecules (amino acids), and polymers in wet environment, respectively. In chapter 4, NEXAFS of Na^+ ions depending upon concentration (section 4.1), solvent (section 4.2), and pH (section 4.3) is presented. The effect of concentration as well as the solvent is analyzed by the means of density functional theory (DFT) using the StoBe package [12]. *Prof. Lars G. M.*

Pettersson (University of Stockholm, Stockholm, Sweden) familiarized us with this package and with analyzing the output of the simulations. In particular, the effect of pH is noteworthy and for this investigation we collaborated with *Prof. Pavel Jungwirth* (Institute of organic chemistry and biochemistry, Academy of Science of the Czech Republic, Prague, Czeck Republic) to complement our experimental observations with molecular dynamic (MD) simulations. In section 4.4, the investigation focuses on transition metal ions in water (mainly Ni^{2+}). In this section NEXAFS, EXAFS, and RIXS are used to investigate the direct-ion interaction versus the indirect interaction (solvent-shared ion pair) for $NiCl_2$ electrolyte solution as a function of concentration. *Dr. Frank de Groot* (Department of chemistry, Utrecht university, Netherlands) has supported us in using the Cowan multiplet package [13] in order to simulate the experimental output theoretically.

In chapter 5, the investigations shift from the behavior of ions in solution to molecules. Many types molecules have been studied during my research, investigating the charge transfer and complex formation between molecules and ions as well as molecules and molecules in aqueous environment. In this chapter, the focus will be on the behavior of amino acids in aqueous solution. In section 5.1, the lysine molecule is investigated in water as a function of pH using the XPS technique. The results have been discussed by the means of molecular orbital calculations using Gaussian03 [14]. In section 5.2, the effect of cysteine and histidine upon complex formation with Zn^{2+} is investigated by the means of NEXAFS technique. A microscopic picture for the complex formation between the Zn^{2+} and these two amino acids is drawn.

In chapter 6, the charge transfer between poly(3-hexylthiophene) (P3HT) and tetrafluoro-tetracyanoquinodimethane (F4TCNQ) has been investigated in wet environment. This project was done with *Dr. Norbert Koch* (Humboldt-University Berlin, Institute of Physic, Berlin, Germany), and *Dr. Antje Vollmer* (BESSY). The experimental output have been analyzed using Gaussian03, as well as StoBe DeMon packages. *Prof. D. Neher* (Potsdam-University, Institute of Physic, Potsdam, Germany) working group, has complemented our study by conductivity measurements for the same system. An English and German summary of the thesis is presented in chapter 7.

