Centre for Molecular Water Science

White Paper

A pan-European Research Initiative

CMWS Centre for Molecular Water Science

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White Paper

May 2021

This White Paper describes the scope of the Centre for Molecular Water Science (CMWS), a collaborative, cross-disciplinary research initiative that shall use a highly dedicated laboratory infrastructure, the most advanced experimental techniques, leading theory/simulation tools and forefront photon facilities to answer the most important questions in molecular water science. The key scientific challenges, preliminary work, objectives, methodologies and infrastructural needs for five major scientific research areas (pillars) have been identified during the past three years by a group of more than 140 scientists from more than 15 countries. The results are compiled and summarised in this document.

This task would not have been possible without the continued support from the host laboratory Deutsches Elektronen-Synchrotron DESY in Hamburg (Germany). Special thanks to the Chairman of the DESY Board of Directors, Prof. Helmut Dosch, and the Director in charge of Photon Science, Prof. Edgar Weckert.

CMWS Coordination and Editorial Team

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Executive Summary

Water, Energy, Health and Environment are strongly interconnected. Addressing the challenges that humanity faces today, such as climate change, the need for carbon-free energy production via green hydrogen, pandemic diseases and the need for universal access to clean water, is key for the survival of our societies and our planet. The detailed molecular understanding of the role of water in the underlying physical, chemical and biological processes is prerequisite for sustainable solutions.

The Centre for Molecular Water Science (CMWS) brings together key experts from Europe and across the world, and from different areas of water-related sciences, with the common goal of delivering a detailed molecular understanding of the various structures, phenomena and dynamic processes in water and water interfaces that are relevant for green-energy technologies, health and environment. In a series of workshops and general meetings, the science concept has been developed by the CMWS consortium consisting of more than 140 scientists worldwide. The results and conclusions have been aggregated in this White Paper.

CMWS science is organised within five strategic pillars (Fundamental Properties of Water, Water in Climate-, Astro-, and Geo-Sciences, Water in Energy Research and Technology, Real-Time Chemical Dynamics, Water in the Molecular Life Sciences) which define both intra-pillar challenges as well as crucial inter-pillar topics to be addressed by CMWS in a cross-disciplinary approach that is unique worldwide: Bringing together researchers from different disciplines with a dedicated laboratory infrastructure directly connected to world-class research infrastructures, such as photon, neutron and NMR facilities.

CMWS today is a pan-European consortium of European and international partners where more than 45 groups have expressed their continued interest via Letters of Intent (LoI). Scientific collaborations have already been started within an Early Science Programme (ESP) co-funded by DESY and the CMWS partners. Closer collaborations are in the process of being defined via Memoranda of Understanding (MoU), collaboration contracts, the build-up of a CMWS preparation and characterisation laboratory on the Bahrenfeld Science Campus, and the implementation of the first infrastructure hubs.

A declared goal of the initiative is to locate a central part of the science activities in a new Research Centre on the Bahrenfeld Campus in Hamburg, Germany, under the leadership of DESY as host laboratory and coordinating partner. It will provide space for about 15 research groups and a dedicated laboratory infrastructure. The Centre will be surrounded by de-centralised infrastructure hubs on other sites providing complementary or further specialised capabilities, like e.g. NMR and laboratory-based spectroscopy techniques. Pivotal to the concept is access to the state-of-the-art photon facilities (PETRA III/IV, FLASH and European XFEL) in Hamburg. Young Investigator Groups (YIGs) will be working at the interfaces between the pillars. Knowledge, innovation and technology transfer as well as the cooperation with industrial partners will be established and organised together with the DESY Innovation and Technology Transfer Office.

CMWS thus aims to be a worldwide unique platform, where researchers from different disciplines will work together in a new way, having access to a highly dedicated laboratory infrastructure and forefront photon science facilities to create new knowledge necessary to tackle the most relevant and urgent challenges in molecular water science.

I. Introduction

Water is key to life on our planet and plays a central role in a large number of environmental and technological processes starting from the complex aqueous contents of cells, to clouds in the atmosphere and aqueous catalytic cycles in industry. Climate change and environmental degradation are pressing existential threats to our planet and life as we know it. Any strategy to address these threats needs to deal with multiple challenges, such as the need for carbon-free energy production and the need for clean water. To address these challenges, we need a vastly improved understanding of the underlying physical, chemical and biological processes involved. This, in turn, means we need a molecular-scale understanding of water and the role it plays in all aspects of life, chemistry and the environment.

To give a current example, our ability to effectively counteract pandemic diseases depends on detailed molecular knowledge of how bio-relevant (macro-)molecular complexes interact with drug molecules in the presence of water and how the binding of individual water molecules can tip the balance towards specific functional outcomes. In addition, it is now clear that an understanding of small aqueous droplets (aerosols) is not only

Figure I.1: Water is an anomalous liquid. It displays, e.g., a density maximum at 4 °C and a solid phase (ice) that is less dense than the liquid making the iceberg float on water. Sea ice is listed as one of the 13 essential climate variables and subject to intense research (see e.g. the 2019 POLARSTERN expedition: www.awi.de/science/climate-sciences/sea-ice-physics.html).

relevant for environmental and climate research but is in fact crucial for controlling the spreading of air-borne diseases. However, our ability to deliver the knowledge needed by establishing a molecular view of water is a non-trivial task since even some of the most basic properties of water remain poorly understood. For example, we know that water is very efficient in forming hydrogen bonds, and it is believed that this hydrogen-bond network is responsible for its complex and anomalous behaviour. However, we are still uncertain about its exact microstructure, i.e., exactly how water molecules arrange themselves in the liquid form, at surfaces and around (bio-)molecules and the molecular dynamics associated with these interactions. The following paragraphs are intended to remind us of some of the mysteries of water, introduce current challenges in different areas of water research and point towards strategies to address these with the help of theory, simulation and experiments with a particular focus on photon-based techniques.

> *"Life on earth as we know it would not exist if water was a regular liquid."*
>
> A. Kananenka and J. L. Skinner, Physical Chemistry Chemical Physics, 22 18124-18131 (2020).

The three-dimensional structure of liquid water has fascinated scientists for decades. When supercooled to below -40 °C, many of water's thermodynamic properties, such as heat capacity or isothermal compressibility, begin to soar, a sign that its density is fluctuating wildly at the molecular scale, indicating the possibility of some kind of phase transition. Already in the early 1990's it was hypothesised that this observation is indicative of a putative second critical point (in addition to the liquid–vapour critical point at 373.946 °C and 220.64 bar). At temperatures below this second critical point water might actually exist in two distinct liquid phases of different

density. If true, this two-phase model would provide an explanation for the many anomalies observed in water, which also affect its properties at ambient conditions. The solid phase of water is equally mysterious, displaying a multitude of crystalline and amorphous ice phases with at least two rather peculiar amorphous solid forms that also show a significant density difference, reminiscent of the postulated two fluid phases. Thus, our understanding of both the liquid and the solid phases are now ripe for a thorough research effort on the molecular scale to obtain a unified picture of water across the entire phase diagram.

Besides understanding the fundamental behaviour of water, it is also important to know how water interacts with technologically relevant materials at solid surfaces or interfaces. This concerns in particular processes in which water is actively involved as a reacting species – ranging from corrosion, water as a catalyst to (photo-) electrochemical processes, photo-conversion and energy storage. One prominent example is the production of molecular hydrogen gas (H_2) from water via photo-splitting (green hydrogen), for use as a fuel, which has the future potential to be a more climate friendly alternative to the production and use of fossil fuels. Since the solar energy to hydrogen conversion efficiency is low (1–2 %) and materials used in the process are costly, new materials with higher photocatalytic activity and efficiency are needed. However, for further progress, a detailed molecular understanding of the catalytic water splitting process is necessary.

An important question is which role molecular water plays in biology, e.g. in processes such as macromolecular folding, molecular recognition, and biological transport processes. For this we need to understand the interplay between bulk-water activity (influenced by co-solutes, pressure and temperature) and the formation of the solvation shells which envelope macromolecules and – especially in the case of DNA and RNA – their counter ions. This topic is currently witnessing a paradigm change, where molecular water in the biological context is no longer regarded as just a "passive" solvent but rather as an "active" participant.

Figure I.2: By screening thousands of drugs and synthetic mini-antibodies called sybodies, scientists have identified candidates that might stop SARS-CoV-2 from infecting human cells. Using DESY's X-ray light source PETRA III, the teams identified protein structures with binding sites to the virus and unravelled how the sybody interacts with the virus. T. F. Custódio et al., Nat. Commun. 11, 5588 (2020); S. Günther et al., Science (2021), DOI: 10.1126/science.abf7945.

Most viral and bacterial infection events and processes occur in aqueous environments. A better understanding of the role of molecular water in these processes, beyond water's role as a solvent, is a necessary pre-requisite for rapid and efficient drug design. A thorough understanding of the role of water in protein–ligand interactions is needed in order to rationally develop better antivirals, e.g. for the pressing issue of treating infectious diseases like COVID-19 and antibiotics.

Hydrogen as an essential component of the energy transition

Germany and the European Union aim to be climate-neutral by 2050. This should be achieved while ensuring that the population has a reliable energy supply and that industry remains competitive. To ensure Germany achieves its energy transition goal, technologies for producing, storing, distributing, and using hydrogen (H_2) need to be developed and made commercially available on a large scale.

Kompetenzatlas Wasserstoff in der Helmholtz-Gemeinschaft

https://www.helmholtz.de/fileadmin/user_upload/01_forschung/01_Energie/Wasserstoffatlas_Handout_englisch_V02.pdf

Infection Research

The current COVID-19 pandemic is caused by the novel coronavirus SARS-CoV-2.
A research focus within CMWS is to understand the role of water in protein–ligand interactions in order to help in developing better antivirals. At a more general level, revealing the interactions between molecular water and other molecules is a research aim of relevance in all research pillars of the CMWS, and the respective findings and developments will also reflect back to biological aspects.

In the atmosphere, aerosols partially counteract the greenhouse effect by reflecting solar radiation, thus playing an important role for the habitability of our Earth. Here, in particular, the formation of aerosol particles and their respective interface effects are yet to be fully understood. This can be achieved by studying aerosol growth and molecule pick-up on all relevant time and length scales, from just a few molecules to full-grown droplets.

Water will play a pivotal role in the EU Green Deal Policy areas, particularly for the policy areas Clean Energy, Sustainable Industry, Biodiversity, From Farm to Fork and Eliminating Pollution.

https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en

Molecular water in all its facets plays a major role in a variety of planetary and interstellar processes. Ice polymorphs are essential for understanding atmospheric and astrochemical processes, including the radiative balance and hydrological cycle, as well as in the chemical dynamics of the Earth's and other planets' atmospheres. In the solid Earth, significant amounts of molecular water are stored in the crystalline structure of minerals and melts as H_2O molecules, stoichiometric OH-groups or as defects. Cycling of this molecular water from the surface to the deep Earth is essential to plate tectonics, resulting in volcanism and earthquakes at convergent boundaries and the formation of continental crust.

Astrochemistry is an exciting field, with more than 200 different molecular species detected in interstellar space so far. The chemical reactions resulting in this richness of molecules are not well understood to date. One of the important scenarios for molecule formation in interstellar space proceeds via chemical processes on ice grains, which are formed of silicaceous and carbonaceous materials surrounded by icy mantles. In these ice mantles, molecules can adsorb, meet and react, while exposed to radiation. One of the holy grails of astrochemistry is to identify molecular building blocks of life in space, such as amino acids or sugars, which could be formed on these grains. Their identification would contribute to the open question of how life originated.

Chemical reactions often take place in liquid water and occur on time scales from femtoseconds to minutes. A real-time characterisation of the underlying processes has to address both, the response

Figure I.3: Dense molecular clouds as depicted here consist of a plethora of particles and atomic and molecular species, which are the basics of a rich chemistry. Dust grains in dense interstellar molecular clouds are coated with a mantle of ice that contains a variety of molecules. Infrared spectra indicate that the ices are generally dominated by H_2O, but also host, e.g. methanol, carbon monoxide, carbon dioxide, ammonia, methane and others. These ices are exposed to various forms of high-energy photons and particles (such as cosmic rays and UV light) that can break chemical bonds of the molecules in the ices, resulting in the production of new chemical compounds.

of the electronic structure and the positions of the reacting molecules. A prominent example is the radiolysis of water by intense ionising radiation. If liquid water is ionised, the cationic hole of H_2O^+ reacts with another water molecule to form an OH radical and H_3O^+. The involved transfer of a proton (H^+) happens here on an ultrafast 50 fs timescale.

When it comes to unravelling the microstructure of water, i.e. exactly how water molecules arrange themselves in the liquid form, at surfaces, or around biomolecules, it is X-ray methods that can provide the necessary high spatial resolution. Currently the most powerful 4th generation synchrotron radiation light source, the ESRF-EBS (Extremely Brilliant Source) in Grenoble (France) has just restarted operation, preceded by MAX IV (Lund, Sweden) and soon to be followed by most of the synchrotron radiation sources worldwide. The particular characteristics of the planned PETRA IV synchrotron in Hamburg promise to provide the ultimate X-ray microscope.

Knowing how the molecular microstructure evolves in time is even more challenging, since liquid water is extremely dynamic in nature with hydrogen bonds that form and dissolve on sub-picosecond timescales. Answering such questions on molecular length and ultrafast timescales thus calls for the most advanced experimental tools, such as those that have recently become available with the start of operation of the most advanced X-ray Free-Electron Laser in the world, the European XFEL in Schenefeld near Hamburg. Soft X-ray laser radiation able to probe similar time-scales is provided by the FLASH facility on the campus.

By joining forces with our partners both on campus and beyond, enabling complementary techniques (NMR, (optical/vibrational) spectroscopies, neutron and electron diffraction/spectroscopy) and by using the most advanced experimental sample preparation and handling capabilities (nanofluidics, micro and nanojets), we are uniquely in a position to address the most relevant scientific challenges on water that nature has left us to explore.

Figure I.4: The European XFEL generates ultrashort (< 100 fs) X-ray flashes – 27 000 times per second with a brilliance that is a billion times higher than that of the best storage ring X-ray sources.

PETRA IV

PETRA IV is DESY's future ultra-low emittance synchrotron radiation source. Its high brightness and degree of coherence will be ideal for X-ray microscopy and dynamics studies by correlation spectroscopies.

This will enable researchers to image microscopically heterogeneous samples and biological, chemical and physical processes under realistic conditions, enabling their investigation on length scales from atomic dimensions to millimetres and on process-relevant time scales. In particular, fundamental questions can be addressed about the unusual behaviour of water and water as a solvent, the role of water in biological systems or for various technological applications, such as corrosion or catalytic water splitting.

PETRA IV: Upgrade of PETRA III to the Ultimate 3D X-ray Microscope. Conceptual Design Report (Nov. 2019, DOI: 10.3204/PUBDB-2019-03613/)

II. The Centre for Molecular Water Science (CMWS)

The Centre for Molecular Water Science (CMWS) is a pan-European consortium of key international partners from different fields of science (physics, chemistry, biology) with the common goal of achieving a detailed molecular understanding of water. The CMWS consortium has developed a science programme centred around five strategic research pillars (Figure II.1):

i) Fundamental Properties of Water

ii) Water in Climate-, Astro-, and Geo-Sciences

iii) Water in Energy Research and Technology

iv) Real-Time Chemical Dynamics

v) Water in the Molecular Life Sciences

Each of the five strategic pillars employs scientists from different fields to address not only very (pillar) specific topics but also overarching questions, taking advantage of the synergy and interdisciplinarity between the pillars.

The CMWS consortium is interconnected via a framework of Letters of Intent (LoI) and, if appropriate, by collaboration contracts defining the common goals of the partners on the basis of this White Paper. The consortium is open to new members and new research topics within the research field of molecular water science. It collaborates not only in science related questions but also explores funding channels for research activities, a PhD and postdoc programme, networking activities and outreach. A strong interaction with the DESY Host Laboratory ensures prime relations to the Hamburg Light Sources Environment. The central activities of CMWS will be located in a research building (office and laboratory) on the Bahrenfeld Campus in Hamburg. It is planned to provide space for 15 research groups and a total of about 150 staff. The Centre will be surrounded by decentralised infrastructure hubs, providing complementary or additional capabilities and expertise (NMR spectroscopy, soft X-ray radiation, lab-based characterisation techniques) not available on the Bahrenfeld campus. Each pillar will operate with 1–3 core research groups. Young Investigator Groups (YIGs) will be located at the interfaces between the pillars. Science projects will be based on collaborations with local/on-site, European and international cooperation partners. A research hostel will enable external groups to spend research time at the centre even for

CMWS Research Pillars

Fundamental Properties of Water	Climate, Astro & Geo Sciences	Energy Research & Technology	Real-Time Chemical Dynamics	Molecular Life Sciences
• anomalies • structure and dynamics • glass transition • crystallization • polyamorphism	• aerosols • ice as reaction centers • confinement • high-pressure effects	• corrosion • catalysis • water splitting • green chemistry • photo-/electrochemistry	• solvation dynamics • hydrolysis • charge-migration • radiolysis • energy transfer • elementary reactions	• water's active role in protein structure and function • biochemical reactions • biological interfaces

Infrastructure & Technologies:
Hamburg Light Source Environment: PETRA III, FLASH, European XFEL

CMWS Cooperations / Partners

European/International	Infrastructures	Local / on site
Universities and Research Institutes	NMR (KU Leuven) Soft X-rays (ELETTRA, SOLEIL, BESSY II)	UHH, CFEL, CSSB, CHyN, HARBOR, CUI, EMBL, TUHH, European XFEL

Figure II.1: Schematic organisation chart of the research of CMWS.

extended periods. The centre will enable, foster, and encourage the establishment of cross-disciplinary research projects between various internal and/or external partners. Specific instrumentation (characterisation and analysis techniques) and sample infrastructures (liquid jets, nanofluidics, ice laboratories and others) will be established (see also section VI.2). As a special asset, compatibility with and access to the local light source facilities (PETRA III/IV, FLASH, European XFEL) will be established from the very beginning. Contact to other national projects (ELBE/DALI, BESSY III) will be activated. A knowledge, innovation and technology transfer strategy will be established early on with the existing DESY innovation and technology transfer (ITT) office.

The science portfolio and the organisation structure of CMWS is unique on a world-wide scale since:

- It addresses a wide variety of the fundamental questions in molecular water-based sciences.
- It builds on the combined expertise of an unprecedented number of key experts from different areas (physics, chemistry, biology) of water-related sciences.
- It is based on and fosters strategic cooperation (cross-area projects, research hostel).
- It is located around and provides access to the unique photon science infrastructure (PETRA III/IV, FLASH and European XFEL) in the Hamburg metropolitan area including their large-scale data handling facilities.
- It provides sample preparation and sample characterisation facilities (within the centre or via partner facility hubs).
- It integrates a unique environment of local research institutions: CFEL, UHH (CHyN, HARBOR), CSSB, CUI, TUHH, EMBL, European XFEL.
- It includes a Knowledge, Innovation and Technology-Transfer strategy (cooperation with on-site technology-transfer office, applied science partners).

II.1 The Science Portfolio of CMWS

The following section will give an overview on the five CMWS research pillars and identify cross pillar topics in science and methodology.

Pillar 1: Fundamental Properties of Water

Understanding the structure and dynamics of the hydrogen-bonding (H-bonding) network in water is essential for many problems in chemistry, physics, biology and geoscience. The ability to form up to four directional H-bonds in addition to the non-directional interactions seen in normal liquids leads to many quite unusual properties, such as increased density upon melting, decreased viscosity under pressure, a density maximum at 4 °C, high surface tension and many more. Water is special in that it seems to exist in at least 19 crystalline polymorphs and two rather different amorphous solid forms, low-density amorphous (LDA) and high-density amorphous (HDA) ice, with a density difference of 20% between them. There is debate about the possible existence of different liquid forms at low temperature, namely the low-density liquid (LDL) and high-density liquid (HDL). However, water crystallisation has made measurements of the bulk liquid phase below the homogeneous nucleation temperature of $T_H \approx 232\,\text{K}$ and above $\approx 160\,\text{K}$ extremely challenging, leading to a "No-man's land" largely devoid of experimental results. Exploring this "Terra Incognita", in particular understanding the properties and anomalies of water by studying its structure and dynamics, is one of the central goals to be addressed within the centre.

Pillar 2: Water in Climate-, Astro-, and Geo-Sciences

Molecular water in all its facets plays an important role in a variety of planetary and interstellar processes. Ice polymorphs are essential for understanding atmospheric and astrochemical processes, including the radiative balance and hydrological cycle, as well as in the chemical dynamics of the Earth's and other planets' atmospheres. Molecular water ice grains are understood to be central for astrochemical processes, while their formation and the actual

chemistry happening at their surfaces are not yet well explored. Another, on the first sight subtle, effect is the ratio between ortho/para water in space, which can give hints to processes so far unconsidered. In the atmosphere, aerosols partially counteract the greenhouse effect by reflecting solar radiation, thus playing an important role for the habitability of our Earth. Here, in particular, the formation of aerosol particles as well as their respective interface effects are yet to be fully understood. In the solid Earth, significant amounts of molecular water are stored in the crystalline structure of minerals and melts as H_2O molecules, stoichiometric OH-groups or as defects. The presence of super-critical aqueous fluids in the crust is responsible for ore formation. Water ice and molecule/water ice mixtures are highly abundant in giant planets such as Uranus or Neptune where high-pressure and high-temperature polymorphs might cause magnetic field generation. Thus, molecular water is a key ingredient for many cosmic and planetary processes, and it is our aim to unravel water's role at the molecular level as part of the CMWS portfolio.

Pillar 3: Water in Energy Research and Technology

Water, the sustainable chemical of excellence, plays a prominent role in energy research and technology. On the one hand, it passively guides energy and/or reaction pathways in chemical and physical processes – statically through tuning its highly polar character and dielectric properties – or dynamically through dielectric relaxation as a Debye or near-Debye-type liquid. On the other hand, the oxygen–hydrogen bond in water is among the strongest single bonds known in chemistry and allows efficient energy storage and transformation, converting heat or photon energy into chemical energy, by water splitting or association. Challenges in this field include the detailed study of the structure and dynamics of processes in which water is actively involved as a reacting species – ranging from corrosion over water as catalyst ("on-water" chemistry or water-splitting) to (photo-)electrochemical processes, photo-conversion, and energy storage. Nano-confinement and nano-structuring may enable tuning of the physical properties and chemical reactivity of water, which is especially important for water as a molecular-level solvent and for membrane technologies (purification and desalination).
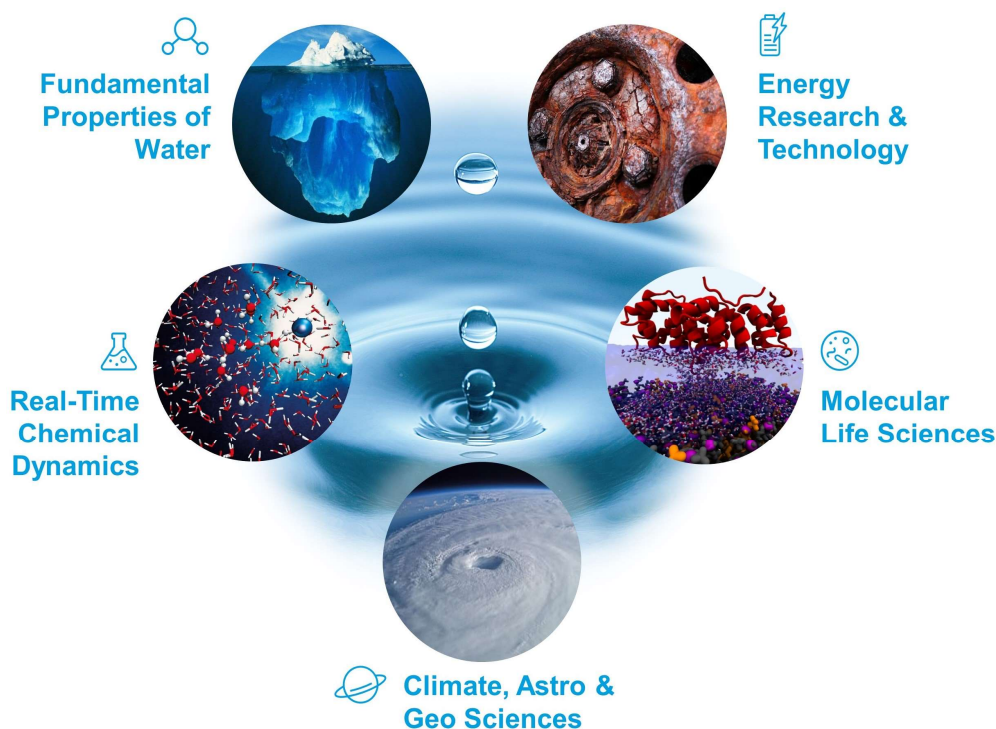
Figure II.2: Water is key to a variety of fundamental processes and technologies, addressed within the five research pillars of CMWS.

Pillar 4: Real-Time Chemical Dynamics

Many, if not most, of the important chemical reactions take place in liquid water. These processes occur on multiple time scales, ranging from femtoseconds to minutes. Therefore, it is a central objective to provide a real-time characterisation of the fundamental processes occurring in this ubiquitous solvent. Such a characterisation has to address the temporal evolution of both the electronic structure and the atomic positions. This is because the electronic structure determines the forces acting on the atoms, and the atomic positions in turn affect the properties of the electronic states. Another recurring aspect is the influence of solvation on chemical properties and transformations, addressing the question of how solvation is initiated on the microscopic level, and changes the properties of the reactants, the intermediates and transition state(s), the products, and even the solvent itself. Knowing how the solvent changes the properties of electronic states, the solvent alters the reaction pathway or the products and to what extent solvent molecules are spectators, catalysts, or participants in chemical reactions are important questions to answer.

Pillar 5: Water in the Molecular Life Sciences

Water is the molecule of life, ubiquitous in biological environments and indispensable for biochemical reactions. Living cells contain about 60–70% water, and evolution has optimised the sophisticated biological processes that determine life to function in an aqueous environment. One of the most striking challenges is correlating water's intrinsic physical properties – hydrogen bonding, polarisability and collective vibrational states – with its spontaneous capacity to generate frustrated order out of apparent chaos. Understanding the interplay between the bulk-water activity that is influenced by co-solutes, pressure and temperature, and the formation of the solvation shells which envelope macromolecules and, especially in the case of DNA and RNA, their counterions is crucial for understanding structure and the structural dynamics of biological systems. The influence of water on the association states of proteins, RNA, DNA, lipids and carbohydrates is also of the highest interest. The formation of higher-order assemblies consisting of multiple components are fundamental to all intracellular

processes and are associated with a number of disease states. Therefore, the role of water in biomolecular structure, be it defined and ordered or intrinsically disordered, and the link that water provides between structure, bio-catalysis, regulation and molecular transport will be the focal points for biochemical and biological function research in CMWS.

Inter-Pillar Topics and the Big Data Challenge

There are important cross-area topics that in fact concern several pillars. They are of scientific, methodological and/or technological character:

i)   Complex sample environments and sample delivery systems

ii) Novel X-ray methods

iii) Overarching science questions:

- Hydrogen-bond network,
- Climate challenges
- Food-energy-water nexus

iv) Multimodal approaches

i) Complex sample environments and sample delivery systems

There are overarching questions in pillars 1–5 concerning the properties of water in confined geometries (in liquid jets, droplets, nanofluidic environments, pores and channels) or under reduced dimensionality (at surfaces, interfaces). If water molecules are confined they can exhibit novel and surprising properties. Water molecules can pass through filters or biological membranes with nanopores just slightly bigger than themselves faster than through membranes with much bigger pores. This has profound impact on the development and design of novel filter technologies. Many of these nanofluidic effects arise from the very peculiar properties of the hydrogen-bonding network and are barely understood on the molecular level. Understanding the arrangement of water at extended surfaces and interfaces, the role of surface charge and counter ions, and transport mechanisms at interfaces is of critical importance for predicting reactivity (electrocatalysis, electrochemistry) and transport (membranes).

In order to address such questions, the respective sample environments have to be developed and/ or adapted. This involves, for example, the lithographical design of nano and microfluidic devices for studying transport processes for technology, chemical and life sciences. Furthermore, surface modifications of nanoporous materials will allow tuning of the pore–water interaction that is used for designing new model interfaces.

Nowadays, liquid jet, liquid droplet and aerosol injectors have become standard devices for studying structure and dynamics in liquids. For instance, injection of nano to micrometre sized droplets into vacuum results in fast cooling of the liquid. This gives access to deeply supercooled water. The adaption of these sample environments to different measurement techniques, e.g. the synchronisation of droplet injection with the pulse structure of an XFEL, as well as tailor-made jets and droplets will be needed for the research in all pillars.

Water is also special in that it seems to exist in at least 19 crystalline polymorphs and two rather different amorphous solid forms. The crystalline and amorphous polymorphs of ice are typically found at extreme conditions, e.g. low temperatures and high pressures. Therefore, production, storage and provision of these phases need to be handled via the dedicated ice laboratory and flexible sample environments that will be developed in CMWS.

ii) Novel X-ray methods

Since conventional scattering methods only yield ensemble-averaged information, novel methods based on coherent X-rays and higher order correlation functions have been developed by CMWS researchers. X-ray Photon Correlation Spectroscopy (XPCS) can provide information about equilibrium and non-equilibrium dynamic processes even on ultrashort timescales if appropriate optics are applied. X-ray Cross Correlation Analysis (XCCA) is sensitive to local symmetries and thus gives information on local order beyond the information from pair-correlation functions.

The study of local order and dynamics in heterogeneous systems is relevant for all pillars. Many disordered systems including complex liquids (colloidal suspensions, protein solutions or water) display spatiotemporal fluctuations in their local dynamical behaviour. It is believed that this behaviour is linked to the appearance of local, transient order, that is, to the existence of patches or domains in which single-particle displacements are correlated. XPCS and XCCA allow one to gain information on local order and dynamics in disordered systems such as water.[1] A primary goal is to address the controversy about the potential two liquid phases HDL/LDL of water. Another question concerns how hydration water, i.e. water molecules at the protein interface, leads to different local order and (fast) dynamics. Here, coherent X-ray techniques can provide useful additional information and support the modelling and interpretation of conformational heterogeneities.

Forefront imaging techniques (Coherent Diffraction Imaging, Ptychography, Fourier Transform Holography and others) benefit from the ever-improving properties of the 4th generation synchrotron light sources, e.g. PETRA IV, providing nanometre resolution and acting as true real-space microscopes. These techniques will allow one to take real-space images of solid state and biological materials.

The availability of high-energy X-rays at the modern light sources such as PETRA III/IV combined with novel high-pressure environments enables a better understanding of different aspects of molecular water. For instance, the measurement of pair-distribution functions throughout the phase diagram of water and ice will shed light on the kinetics of the particular phase transitions, covering atomic to several nanometre length scales. Furthermore, the water cycle within the Earth will be accessed across its history by investigating the stability of H_2O-bearing mineral phases as well as establishing the equations of state of H_2O ices at conditions similar to those found in the interior of water-rich planet.

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[1] see: F. Perakis et al., Nat. Commun. 9, 1917 (2018); F. Lehmkühler et al., Sci. Adv. 6, eabc5916 (2020).

Gas dynamic virtual nozzle: Liquid water is focused into a microjet by a coflowing sheath gas, e.g. nitrogen. Micrometre-sized droplets are produced.

European XFEL: The 3.4 km accelerator energises electrons up to 17.5 GeV generating ~50 fs long X-ray pulses with MHz repetition rate.

AGIPD detector: 1 Megapixel detector, up to 352 scattering images at 6.5 MHz (one image every 154 ns)

Ultrafast pump laser: Pulse length 100–10 fs Wavelength e.g. 800 nm Power up to 3 mJ per pulse

evaporative cooling

ultrafast heating

amorphous ice

Stable liquid water

Supercooled water

Homogeneous nucleation line

No-man's-land

273

232

LDL   HDL

Amorphous ices

LDA   HDA

Temperature (K)

Pressure

Figure II.3: Schematic illustration of an X-ray experiment in "No-man's-land" (see temperature and pressure diagramme) requiring sophisticated sample manipulation and state-of-the-art X-ray technologies.

iii) Overarching science questions

Hydrogen-bond network

The hydrogen-bond network of water is responsible for many of the unique properties and anomalies. At the surface of ice and water, and at the interface with other molecules or materials, this network is interrupted, giving rise to yet other fascinating properties, such as the very high surface tension of water. As a result of this the importance of water across many disciplines of science and engineering cannot be overstated. The recent advent of novel approaches for studies of the hydrogen-bond network, both theoretical and experimental, with the ability to describe the structure and dynamics of water in complex systems at the molecular level, is at the very centre of the increased interest in investigating water at the molecular level across several disciplines.

Climate challenges

The water–surface interaction plays an important role in several pillars. It is particularly relevant for the surfaces of nano and microparticles, either on the particle surface or when immersed or dissolved inside droplets. It also plays a very important role, e.g. for cloud formation and climate research in general. X-rays from synchrotron radiation sources have been a crucial tool in recent years to unravel the structure of water solution droplets containing organic material. With this understanding, scientists will be able to formulate new theoretical models providing a much-improved description of the formation and transformation of water solution droplets in the atmosphere. In the coming years, the collaborative effort within CMWS will radically transform our understanding of air pollution, climate effects of airborne nanoparticles and cloud droplets, as well as the transmission of particle and droplet-borne pathogens.

Food–energy–water nexus

The food–energy–water (FEW) nexus is ultimately defined via resource trade-offs. Water is an essential input to produce both food and energy while also serving many other purposes. At least in the short run when technologies and the allocation of water for other uses are fixed, allocating more water to produce more food implies that less will be available for energy. Similarly, more "water for energy" leaves less "water for food", and obtaining more water for other uses takes resource away from both food or energy. These trade-offs comprise the so-called trilemma of FEW resources, which is only expected to intensify in the future because of long-term global trends including population growth, income growth and climate change. This perspective for the FEW nexus motivates the need for research that can conserve resources through more efficient technologies. There is a direct connection to the activities in research pillar 3, while also the fundamental properties of molecular water studied in pillar 1 will be relevant to address the FEW trilemma.[2]

iv) Multimodal approaches

The need for cross-topical technologies and multiple experimental approaches is illustrated more explicitly in Figure II.3 for the example of studying water under deeply supercooled conditions. Exploring "No-man's land" (see phase diagram) requires mastering either the super-cooling of small water droplets, e.g. via a gas dynamic nozzle (GVDN) to produce small droplets that supercool upon expansion in a vacuum vessel, or the heating (with ultrashort high-power laser pulses) of specially prepared (pressure, temperature) amorphous ice phases. Measuring the structure and dynamics of supercooled water requires ultra-short coherent X-ray pulses from a FEL such as the European XFEL as atomic displacements are to be investigated. Such data require the most sophisticated 2-D detection schemes as provided by the Adaptive Gain Integrating Pixel Detector (AGIPD) with one million pixels acquiring up to 3520 images per second. Such experiments also require the

handling of very large data quantities and corresponding processing power. Interpretation of data involves comparison with theory and simulation, such as using a molecular dynamics (MD) approach.

The extended use of large Megapixel detectors acquiring data at Megahertz rates (up to 4.5 MHz for the case of the European XFEL) is reaching petabyte data volumes comparable to the ones known from particle physics, e.g. from the Large Hadron Collider (LHC) at CERN in Geneva. Meeting this challenge of big data requires increasing efforts in machine learning and artificial intelligence to generate computation and resource-efficient algorithms for searching through data to find and mine relevant or pertinent information. CMWS will thus reach out to initiatives such as the DFG Priority Programme BIG DATA (SPP1736) or the initiatives of the BMBF (see https://www.bmbf.de/foerderungen) addressing, e.g. Künstliche Intelligenz (KI)/ Artificial Intelligence (AI).

II.2 The Role of CMWS in the European Landscape

One of the key features of the CMWS is the strong involvement of the partners to form a pan-European network addressing water-related science in all dimensions, and establish complementary infrastructure hubs outside of Hamburg. This pan-European ambition manifests itself in the distribution of partners and partner institutions that have expressed their support by a Letter of Interest (LoI). Figure II.4 shows a map illustrating the geographical distribution of the present LoI partners.

The role of CMWS within the European Landscape is thus at least fourfold:
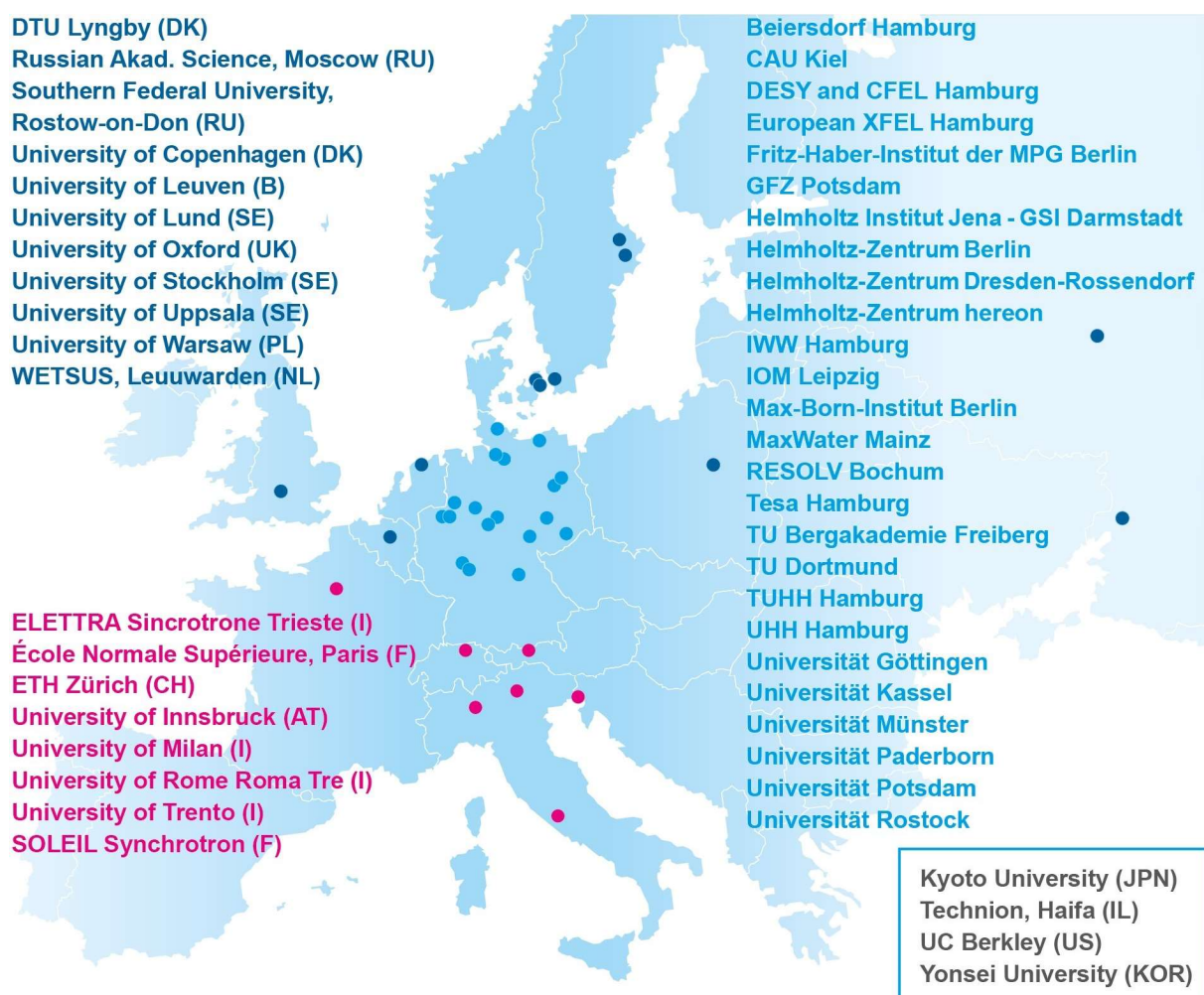
- CMWS will continue to act as the scaffold for a pan-European network of academic and industrial partners addressing questions of molecular water research. It will continue to

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[2] Competition for Water, edited by J. R. Ziolkowska and J. M. Peterson; Elsevier (2017) DOI: 10.1016/C2014-0-03820-8.

welcome new partners and new capabilities within the network.

- CMWS will pursue, support and coordinate science and science programmes between the CMWS partners. CMWS science is in many aspects commensurate with HORIZON EUROPE. The CMWS science portfolio, as illustrated in Figure II.1 and laid out in detail in section III, lists several subtopics addressed in the HORIZON EUROPE pillar 2 clusters [https://ec.europa.eu/info/sites/info/files/research_and_innovation/ec_rtd_he-presentation_062019_en.pdf]. This holds in particular for activities in the CMWS pillars pillar 5 Water in the Molecular Life Sciences, pillar 3 Water in Energy Research and Technology and pillar 2 Water in Climate-, Astro-, and Geo-Sciences, which connect to the HORIZON EUROPE clusters > *Health,* >

Digital, Industry and Space, and > Climate, Energy and Mobility.

- An Early Science Programme (ESP, see section II.3) financed by DESY and partners started in 2019 and currently supports students from eight different European partner countries. This programme is expected to be extended with support from European funding such as Horizon Europe MSCA-doctoral networks-cofund-staff-exchange.
- CMWS will promote, coordinate and facilitate the access to the CMWS infrastructure such as the DESY-CMWS preparation and characterisation laboratory but also to European research infrastructures (European XFEL, PETRA III, SOLEIL, ELETTRA and others). This involves also access to hub infrastructures, such as the NMR facility at KU Leuven, or priority programmes for water-

DTU Lyngby (DK)
Russian Akad. Science, Moscow (RU)
Southern Federal University,
Rostow-on-Don (RU)
University of Copenhagen (DK)
University of Leuven (B)
University of Lund (SE)
University of Oxford (UK)
University of Stockholm (SE)
University of Uppsala (SE)
University of Warsaw (PL)
WETSUS, Leuuwarden (NL)

Beiersdorf Hamburg
CAU Kiel
DESY and CFEL Hamburg
European XFEL Hamburg
Fritz-Haber-Institut der MPG Berlin
GFZ Potsdam
Helmholtz Institut Jena - GSI Darmstadt
Helmholtz-Zentrum Berlin
Helmholtz-Zentrum Dresden-Rossendorf
Helmholtz-Zentrum hereon
IWW Hamburg
IOM Leipzig
Max-Born-Institut Berlin
MaxWater Mainz
RESOLV Bochum
Tesa Hamburg
TU Bergakademie Freiberg
TU Dortmund
TUHH Hamburg
UHH Hamburg
Universität Göttingen
Universität Kassel
Universität Münster
Universität Paderborn
Universität Potsdam
Universität Rostock

ELETTRA Sincrotrone Trieste (I)
École Normale Supérieure, Paris (F)
ETH Zürich (CH)
University of Innsbruck (AT)
University of Milan (I)
University of Rome Roma Tre (I)
University of Trento (I)
SOLEIL Synchrotron (F)

Kyoto University (JPN)
Technion, Haifa (IL)
UC Berkley (US)
Yonsei University (KOR)

Figure II.4: Map of CMWS Letter of Intent (LoI) Partners in Germany (light blue), northern and eastern Europe (dark blue), central and southern Europe (magenta) and overseas (grey).

related research presently being discussed at the European XFEL in Hamburg.

- Since science at synchrotron radiation and free-electron laser (FEL) facilities plays an important role for CMWS the League of European Accelerator-based Photon Sources (LEAPS) [https://leaps-initiative.eu/] is a prime partner for CMWS.
- CMWS will reach out to other communities active in advanced water research. Here neutron-based techniques are of particular importance and the League of advanced European Neutron Sources (LENS) is a prime partner (www.lens-initiative.org).

II.3 The Early Operation Phase

An Early Science Programme (ESP) was launched in 2019 supporting PhD projects in molecular water science between different CMWS partners. The programme is financed by DESY and CMWS partners with equal contributions. There are presently six active projects with ESP funding and three associated projects without ESP funding. A second call was launched in February 2020 and ten new projects will start in 2021.

A preparation and characterisation laboratory with basic characterisation capabilities (Raman and FTIR spectrometers) has been installed on the DESY campus and is available for CMWS partners.

The CMWS Office started operation in January 2020 supporting the ESP and working on an outreach programme. This involves:

A website

www.cmws-hamburg.de

Lead articles in the DESY research magazine femto

www.desy.de/femto (Issue 02/20)
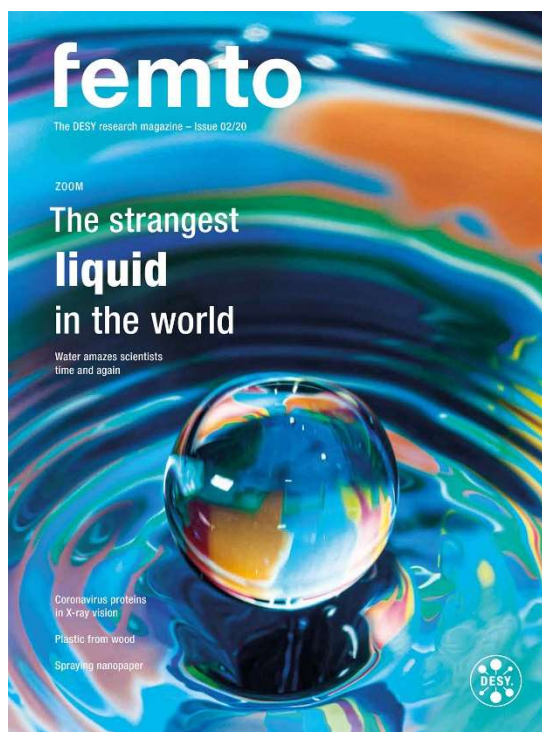
A series of workshops and schools

XVII. DESY Research Course 2018 Trends in Water Research:

http://researchcourse2018.desy.de/

2nd Workshop "Centre for Molecular Water Science":

https://indico.desy.de/e/CMWS_Workshop2

DESY WATER WEEK 2020:

https://indico.desy.de/indico/e/waterweek2020

CMWS DAYS 2021:

https://indico.desy.de/e/cmwsdays2021

Public Lecture:

https://fortbildung.desy.de/e109/e295296/e296348/

III. The Science Case for CMWS

CMWS Pillar 1: Fundamental Properties of Water

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III.1 Fundamental Properties of Water

## III.1.1 Scientific Challenges and State of the Art

Understanding the structure and dynamics of the hydrogen-bonding (H-bonding) network in water is essential for many problems in chemistry, physics, biology, and geoscience. The ability to form up to four directional H-bonds in addition to the non-directional interactions seen in normal liquids leads to many quite unusual properties [1.1], such as increased density upon melting, a density maximum at 4 °C, decreased viscosity under pressure, high surface tension and many more. Water properties are also affected by various solutes and through interactions at interfaces. Furthermore, water exists in at least 19 crystalline polymorphs and two rather different amorphous solid forms, low-density amorphous (LDA) and high-density amorphous (HDA) ice [1.2,1.3], with a density difference of 20% between them. There is also an on-going debate relating to the nature of the experimentally observed glass transition(s), indicating the possible existence of two different liquids at low temperature, namely the low-density liquid (LDL) and high-density liquid (HDL) [1.4]. However, water crystallisation has made measurements of the bulk liquid phase below the homogeneous nucleation temperature of $T_H \approx 232$ K and above ≈ 160 K extremely challenging, leading to a "No-man's land" largely devoid of experimental results (see Figure III.1.1).

The overarching goal in the field is to understand the molecular-scale origin of the various anomalies of water in its bulk form as well as at interfaces and their connection to the structural and dynamic properties of this liquid.

Challenge 1: Interplay between Anomalies, Structure and Dynamics in Liquid Water

Despite more than 100 years of research, the structure of liquid water remains one of the unsolved problems in condensed matter physics. Its structure is in particular responsible for the huge number of anomalies, ranging from thermodynamic and structural properties of liquid water to the complex phase diagram of its solid phase. The origin of the observed anomalies of the bulk phases of water lie in the physics of the many-body interactions between individual water molecules. Therefore, a thorough and precise description of the hydrogen bonding between few water molecules will be one of the foci of the CMWS within
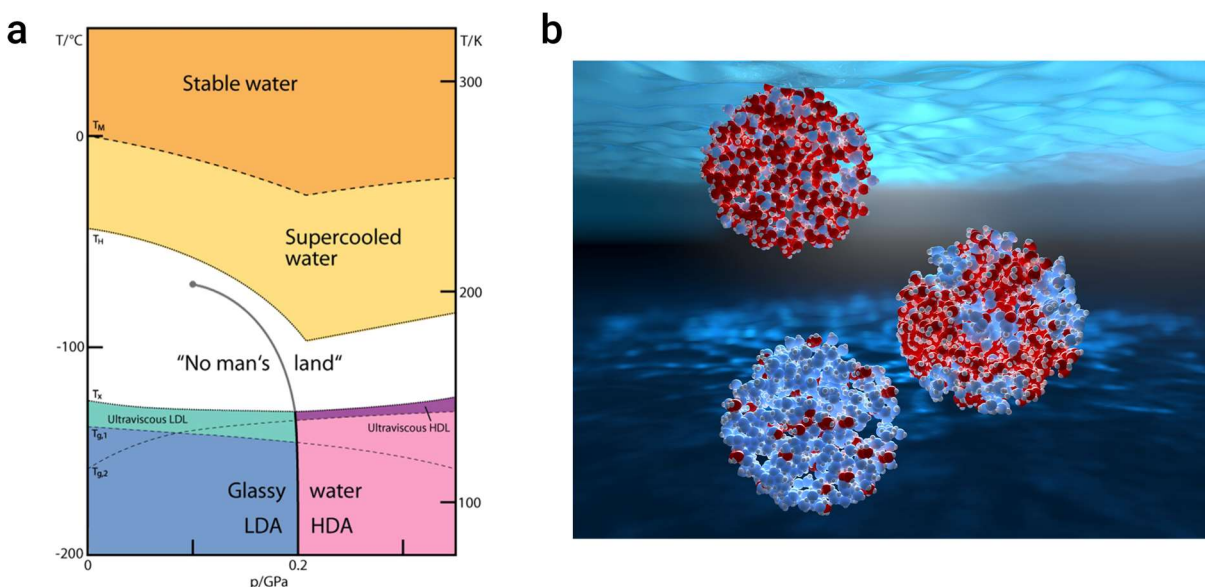
Figure III.1.1: (a) Phase diagram of the non-crystalline states of water, as proposed by Mishima and Stanley, adapted from [1.4]. (b) Illustration of LDL and HDL regions in water droplets (cover image from Phys. Chem. Chem. Phys. 21, issue 1 (2019)).

pillar 1. H-bonding is now understood as mainly electrostatic, but with significant contributions from competing short-range charge-transfer and exchange-repulsion interactions that are inherently quantum mechanical in their nature. The deceptive complexity of the associated effects, such as quantum delocalisation and quantum tunnelling, make the definitive characterisation of the H-bond very challenging. The overarching question here is to understand these characteristics based on a detailed understanding of interactions and dynamic processes in systems of water molecules with increasing complexity. Starting from the properties of individual water molecules changes will be clarified once water molecules are surrounded by other water molecules in crystalline like structures towards the dynamic interactions in liquid water.
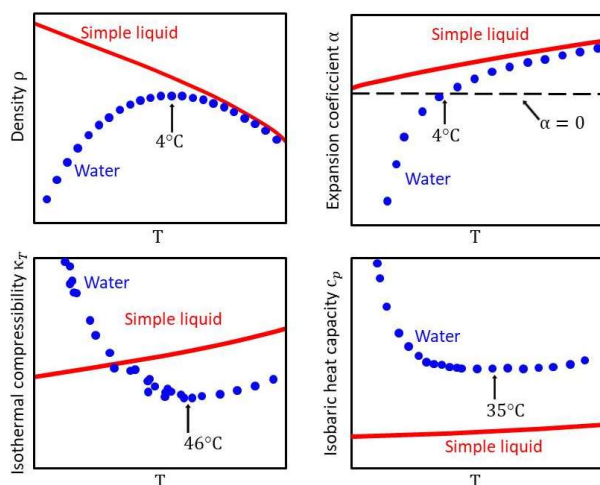
Figure III.1.2: Schematic comparison of the trends of the density and thermodynamic response functions of water with those of other simple molecular liquids. Adapted from [1.8].

Many of water's anomalies become dominant in the supercooled state [1.1]. Experiments and theory indicate in fact that thermodynamic response functions such as density and compressibility diverge in the supercooled regime around 228 K (see Figure III.1.2). This suggests the existence of a liquid–liquid critical point and consequently two liquid states: high-density liquid (HDL) and low-density liquid (LDL) water. However, water crystallisation challenges measurements of the supercooled liquid phase in the region between 160 K and 232 K. While recent studies [1.5-1.7] support the hypothesis of the existence of two states of liquid water, little is

known on the actual structure and dynamics of the transient and fluctuating water structures as well as the exact location of the proposed liquid–liquid critical point (LLCP).

As water's anomalies extend to ambient temperatures, the question arises how structural motifs – even if transient in nature – rule the properties of liquid water. In the framework of this so called "two-liquids hypothesis" liquid water is understood as a fluctuating mixture of LDL and HDL on the nanoscale. This raises the question on the "nature" of liquid water in clusters built up from few molecules up to nanometre scales and in nano-confinement. Due to recent experimental progress, the answer to this question comes within reach.

Furthermore, nuclear quantum effects play an important role for water properties. Compared to normal water (H_2O), heavy water (D_2O) is known to have different physical properties, such as higher freezing and boiling points and differs significantly in its thermodynamic response functions. Although these properties have been studied for years, little is known on their origin on the atomic and molecular level [1.1].

With respect to understanding the time-dependent anomalies of water the electrodynamics of water and ice play an important role. Although the mechanical properties of ice and water differ, they are remarkably similar in their electrodynamic response and have common molecular dynamics, but appearing at different time scales. This might point to the essential role of fast, sub-picosecond proton exchange [1.9]. The nature and details of the proton exchange is thus an important part of the water dynamical structure puzzle.

Challenge 2: The Nature of Water's Glass Transition and Crystallisation

Whether or not the amorphous states of water, LDA and HDA, are connected by a glass–liquid transition to the two hypothesised liquid states, LDL and HDL, has been considered most controversial over the last 35 years [1.3,1.10,1.11]. The glass transition in amorphous ice was first investigated in the 1980s, leading to a heated and still ongoing debate about the nature of the observed glass transition [1.11]. Instead of a true

glass–liquid transition involving diffusive translational motion, some experiments rather indicate reorientational dynamics to be the active mechanism around 130 K [1.12], as either a precursor for a potential glass-liquid transition at higher temperatures or not related at all to the liquid state [1.13]. Recently, X-ray photon correlation spectroscopy experiments at DESY [1.5] have been able to demonstrate that HAD ice shows diffusive dynamics on the nanometre scale already at temperatures before it transforms to the low-density state, indicative of a liquid–liquid transition. Still, the underlying mechanism within the hydrogen bond network during the liquid-liquid transition on different length scales remains unclear. Owing to rapid crystallisation at around 160 K when heating amorphous ice at a moderate rate, the potential ultra-viscous liquid can only be studied within a small temperature range using traditional experimental methods. Modern X-ray sources like the European XFEL open new possibilities to measure the liquid states at even higher temperatures or, using next generation storage-ring sources such as PETRA IV, at different time and length scales. While the transition between HDL and LDL appears to be first-order-like at ambient pressure, little is known on how the HDA state and the third amorphous state, very-high-density amorphous ice (VHDA), are related at elevated pressures. Recently, it was reported that both HDA and VHDA reach the same HDL state at intermediate pressures of 0.1–0.3 GPa [1.14]. However, still no direct information about the diffusivity at elevated pressures is available. In order to use the full capabilities of modern X-ray and electron sources to study these different forms of ice and ultraviscous water, further development of sample preparation and sample environments is necessary.

Besides the glass-transition, also the crystallisation behaviour, both upon cooling the liquid state as well as upon heating the amorphous ice or the ultra-viscous liquid still lacks a full understanding. A major question concerns the role of transient structural precursors of crystallisation and the role of the H-bonding network. Crystallisation can be avoided by studying suitable water–salt solutions (*challenge 4*) or studying water in confinement (*challenge 5*), accompanied by the question if and how the properties of water in

these systems can be compared to bulk water. In this context, important tasks are also to further investigate the role of crystallisation agents and finally the comparison of water's phase diagram to the ones of other liquids.

Challenge 3: Polymorphism of Ice

The Bernal-Fowler ice rules allow for a large range of H-bond topologies, 19 of which are known in ice polymorphs today [1.15], see Figure III.1.3 [1.16]. These polymorphs may be ordered in terms of only the oxygen atoms ("frustrated crystals") or, at low temperatures, both in terms of oxygen and hydrogen atoms ("ideal crystals"). The H-ordering process is not yet fully understood – some ice phases, such as H-disordered ice II or H-ordered ice IV are known in computer simulations, but have remained elusive in experiments. The kinetics of the H-ordering process, its isotope effect and the extent to which quantum effects such as proton tunnelling play a role still need to be elucidated in order to guide the way to the experimental characterisation of such ice phases. Especially since the H/D-isotope effect tends to prevent the ordering in D_2O-samples, there is a need to study the structure and dynamics of H_2O-samples using X-ray, neutron and electron scattering, especially in the presence of point defects that accelerate the H-exchange. The questions addressed in *challenge 3* are closely connected with pillar 2, because the high-pressure ice phases are also of astrophysical importance.

In order to use the full capabilities of modern X-ray and electron sources to study these different forms of ice, further development of sample preparation and sample environments is necessary.

Beside the crystalline polymorphs, additionally three polyamorphs of ice exist, namely LDA, HDA and VHDA, as already discussed in *challenge 2*. The amorphisation process is suggested to be caused by different mechanisms at different temperatures, but the role of kinetics remains unclear [1.13]. While mechanical collapse results in the formation of unannealed HDA (uHDA) at low temperatures [1.17], thermal melting seems to be involved at higher temperatures. Recent experiments using slow compression are consistent with the picture of HDA at low temperatures being a metastable intermediate state, kinetically arrested between ice I and the

Figure III.1.3: (a) Phase diagram of ice consisting of liquid water (red), the hydrogen-disordered (orange), and hydrogen-ordered (blue) phases of ice as well as the "polymeric" ice X (green). (b) Ice polymorph networks. [1.16].

high-pressure ice phase XV [1.18], or ice IV [1.16]. These studies challenge the view of amorphous ice as a glassy state of water and show the importance of a better understanding of the amorphisation process, as well as amorphous–amorphous and other solid–solid transitions in ice.

Challenge 4: Water as Solvent

Water is the most important solvent in research and everyday life. Thus, this challenge represents a cross-pillar activity of the CMWS. Within pillar 1, the research will be focused on fundamental questions of water's role in solvation processes. Understanding water as a solvent is important for electrochemistry, as well as for studies of colloids, nanoparticles, biological systems and liquid crystals. It is therefore necessary to study the interactions between individual water molecules and other molecules starting from one water molecule interacting with another molecule up to truly solvated molecules in bulk liquid.

In general, the interactions of water molecules with solute components are significant for the properties of the resulting solution. In aqueous solutions a chemical element interacts, not only with water, but particularly with all other elements in that solution forming a variety of chemical compounds, called speciation. Influences on speciation include temperature, pH, concentration and available ligands. Especially the pH-value has an immense relevance for the hydration and the structure of the resulting speciation/complex structure. Such effects lead to significant

influences on technical applications regarding the selective separation of elements/components from fluid streams [1.19].

Another issue is the salt-induced precipitation of solutes known as Hofmeister series. Depending on the type of salt used as co-solute, the solubility of, e.g. proteins is significantly reduced. This may be connected to a potential strengthening or weakening of the H-bond network as observed for some co-solutes [1.20], especially in ternary solutions, however the mechanism behind the properties of different solved salts is still unclear. Furthermore, the role of water as a solvent in the formation of clathrate hydrates [1.21] is of tremendous environmental and industrial importance. Such clathrates are solid ice-like inclusion compounds and form in the presence of many dissolved gas molecules such as methane and carbon dioxide. Clathrates occur at seabed both naturally and during oil field drilling where natural gas interacts with seawater under high pressure and low temperature conditions.

Challenge 5: Structure and Dynamics of Water and Ice Surfaces and Interfaces

Water surfaces and interfaces play an important role in a wide variety of different scientific disciplines. Due to the lack of symmetry at any two-dimensional interface, many exciting effects are observed. At water–solid, water–gas and water–liquid interfaces specific interactions (surface charge, polarity, van der Waals interactions and H-bonding) can lead to different structural and dynamic behaviour of water compared to that in

the bulk [1.22, 1.23, 1.24], including layering and growth of liquid-crystalline ordered layers [1.25]. The properties of the interface become especially important for nanoconfined water [1.26], which exhibits properties very different from bulk water, e.g. reduced melting point, that are still poorly understood and continue to create controversy. Furthermore, interactions between two surfaces with distances in the sub-micrometre to nanometre range mediated by water or aqueous solutions determine the mobility of micro and nanoparticles used in current lab-on-a-chip concepts when the particles are moving close to a surface.

A particularly intriguing effect observed at surfaces and near solids is interface-induced ice melting. Here, a quasi-liquid layer (QLL) wets the ice surface well below its bulk melting point [1.27]. While the structure and dynamics of this QLL prewetting film is still unknown, there are first indications that the structure of the QLL is linked to the hypothesised high-density liquid phase. Therefore, new experimental studies might allow the linkage of interfacial water structures and interfacial segregation to either of the postulated HDL and LDL water forms (challenge 1).

Understanding dynamics at liquid interfaces is a huge challenge. For instance, absorption of ions in water can affect the capillary wave behaviour at interfaces, which is of current controversy. While previous simulations predicted a decrease of the capillary wave fluctuations at the interface [1.28], a very recent simulation study indicates an increase in fluctuations [1.29]. Previous X-ray scattering studies of liquid surfaces have focused on the time-averaged structure using, e.g. X-ray Photon Correlation Spectroscopy and on the equilibrium dynamics of capillary waves in the low-q regime and at time scales ≥ microseconds [1.30]. These studies revealed a range of ordering phenomena at liquid surfaces such as atomic layering [1.31] and surface freezing [1.32]. Spectroscopic studies of liquid interfaces and liquid jets indicate that the dynamics for orientation-relaxation, diffusion, solvation, and intermolecular energy transfer are influenced by the presence of the interface [1.33]. Since these processes are central to every interface reaction, a detailed knowledge of these effects ranging from molecular to continuum length scales is required to understand important natural and technological processes, e.g. the role of capillary waves at liquid interfaces over many length scales, which has been inaccessible so far [1.34].

III.1.2 Preliminary Work and Competences

Addressing the described challenges requires a combined experimental and theoretical approach probing structure and dynamics of such water-based systems on molecular length and time scales. The groups and partners contributing to the research in pillar 1 provide a broad expertise of the necessary methods and techniques with special attention on fundamental properties of water and related aqueous systems.

In order to investigate structure and dynamics of liquid water in water on femtosecond timescales over a large temperature range, as described in challenges 1 and 4, the usage of FEL sources has become important over the last years [1.6,1.35]. Therefore, usage of sample injection systems such as liquid microjets and aerosol injectors have become crucial for such experiments. Most importantly, the evaporation of microdroplets injected to vacuum enabled us to reach new record of supercooling water [1.7,1.36] which is crucial to study and understand many of water's anomalies. We operate various of such devices, starting from molecular jets for gas-phase experiments, over sources for homogeneous water clusters and heterogeneous water plus "X" clusters to liquid jets, all of them being used in spectroscopy X-ray scattering experiments. We have been among the first groups developing and investigating liquid water microjets in vacuum with FEL sources [1.7]. We found that deep supercooling down to 230 K is possible using micrometre-sized water droplets generated by such jets (see Figure III.1.4) [1.7, 1.36]. Furthermore, we developed aerosol injectors producing clusters of water molecules. With such injectors, we performed the first photon-electron spectroscopy experiments on water droplets of 100 nm size [1.37] and measured proton transfer and intermolecular Coulombic decay in water clusters built up from 5 to 250 water molecules on femtosecond time scales [1.38]. We also contribute to a variety of detection techniques such as single-photon dispersed-fluorescence detection [1.39] and in electron-

electron as well as electron-photon coincidence [1.40]. One of the preliminary results is the observation of a spectrally broad UV fluorescence upon irradiation of liquid water with soft X-rays. The discovered broad liquid-phase emission band is regarded as a new spectroscopic fingerprint of electronically excited liquid water which can be utilised in the search for water in the liquid phase in interstellar space [1.41].
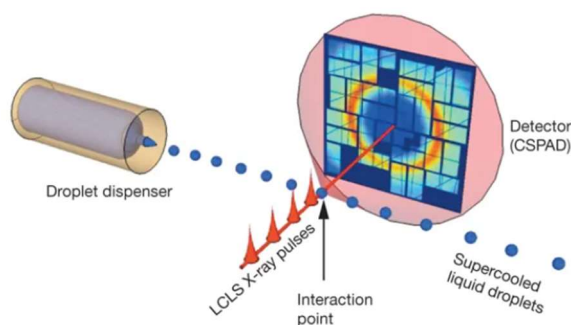
Figure III.1.4: Principle of a liquid jet experiment at an FEL source. A train of droplets propagates in vacuum synchronised to the fs-long X-ray pulses [1.7].

We have performed pioneering X-ray scattering and spectroscopy experiments probing the local structure and dynamics of water [1.1] (*challenges 1, 2* and *4*) and developed many techniques studying structure and dynamics of liquid samples. Using inelastic X-ray scattering and absorption spectroscopy, we measured many properties of water during the last 20 years, for instance viscoelastic properties of water [1.42] and H-bonding in water, different ices and clathrates [1.42-1.48]. By generation of supercooled water droplets from microjets and ultrafast probing at FEL sources, we measured maxima in the thermodynamic response around 230 K indicating the existence of a Widom line and thus a liquid–liquid critical point at supercooled conditions [1.6]. By making use of the coherence properties of modern X-ray radiation sources, structure beyond pair-correlations can be accessed by means of X-ray Cross Correlation Analysis. We applied this technique by studying the local order and phase transitions in different samples such as liquid crystals [1.49] and colloids [1.50]. Furthermore, by modifying the X-ray pulse lengths at FEL sources we demonstrated ultrafast X-ray speckle visibility spectroscopy in the femtosecond regime, probing molecular dynamics of liquid water in real

time [1.35]. We were able to extend this time range recently to the nanosecond scale using split-and-delay devices [1.51].

We are the world-leading groups in preparing high-pressure ice phases (*challenge 3*), i.e. different crystalline phases as well as amorphous ices as made via pressure-induced amorphisation at liquid-nitrogen temperatures [1.10,1.17]. Furthermore, we have studied amorphous ice made by vapor deposition [1.52] as well as by hyperquenching liquid droplets [1.53]. The investigation of the proposed glass transition in amorphous ice is a major focus of research [1.11,1.12,1.54,1.55]. We measured the onset of the glass transition in LDA at 136 K and for HDA at 116 K using differential scanning calorimetry and dielectric spectroscopy [1.54], neutron scattering and nuclear magnetic resonance [1.11]. We recently studied the transition from HDA to LDA using X-ray scattering and X-ray photon correlation spectroscopy at PETRA III and found evidence for the appearance of the corresponding liquid states HDL and LDL around 130 K [1.6]. We have experience in studying the H-ordering process using calorimetry, dielectric and Raman spectroscopy [1.10]. With this techniques several studies have been performed on the isotope effect in water and how point defects influence phase transitions as well as proton ordering [1.55].

Interfaces of water and water at interfaces *(challenge 5)* play a key role for all pillars of the CMWS. We have extensive experience of surface and interface-sensitive X-ray scattering studies as well as surface-specific vibrational spectroscopy [1.56]. X-ray studies across the hydrophobic solid-water interface allowed us to identify different mechanisms on the molecular length scale that are contributing to the narrowing of the "hydrophobic gap" [1.57]. With the aim to understand the surface structure of ice premelt, we showed that a quasi-liquid layer exists below water's freezing temperature [1.27]. We described the role of water as a polar liquid in electrochemical systems for the liquid–liquid mercury-electrolyte interface [1.30]. We developed a dedicated liquid X-ray scattering setup at PETRA III (LISA) [1.58], where we have shown that water plays a role in strain-free nucleation and growth of liquid-crystalline structures at liquid–liquid interfaces [1.25]. Furthermore, we have investigated

structure formation at solid–vapor interfaces [1.59] such as the *in situ* formation of carbon-dioxide clathrates [1.60].

We have a broad expertise on studies of nanoconfinement properties of water [1.61,1.62], including synthesis of different nanoporous materials as well as temperature-dependent X-ray diffraction, dynamic mechanical analysis [1.62], dielectric spectroscopy and quasi-elastic neutron scattering. In particular, we could show in that the molecular mobility of nano-confined water in mesoporous organosilicas is influenced by the polarity of the organic moiety [1.63,1.64].

The research in pillar 1 within the CMWS will be based on a profound interplay of experiments and simulation work. We can build on broad molecular dynamics (MD) expertise on water systems [1.1,1.35]. We developed different computational methods focusing on *ab initio* simulations. These schemes have been applied to model experimental results from water, e.g. using X-ray absorption spectroscopy, NMR, IR and Raman spectroscopy. Further studies using these methods suggested that liquid water forms on average four hydrogen-bonds, but that there is a significant asymmetry in the energy of these contacts [1.65] and demonstrated the impact of nuclear quantum effects on the low-temperature protonated water dimer [1.66]. Recently, we found a linear relationship between the OH stretch frequency and the charge and energy transfer due to hydrogen bonding in liquid water [1.67].

III.1.3 Objectives

The central objective of the research in pillar 1 is to obtain a fundamental understanding of bulk, surface, interface and confined water with special attention on its anomalies by investigating water's structure and dynamics. Therefore, the availability of sample environments that enable controlled access to extreme conditions, such as extreme supercooling and high pressures, are essential for the research in pillar 1. We will address the challenges by combining scattering and spectroscopy experiments both laboratory and facility-based, together with theory and simulations of liquid water and aqueous solutions across their phase diagrams. The objectives of pillar 1 will build on modern X-ray studies of structure and dynamics

with molecular resolution and covering more than 18 orders of magnitude in time.

An essential part of modern experiments on liquid water, in particular at storage ring and FEL sources, is the development and improvement of injection systems as sample environments. Consequently, this represents a cross-challenge objective within pillar 1. This comprises liquid jet and droplet injection systems for studying water and aqueous solutions over a wide temperature range as well as aerosol injections generating water clusters built up from few molecules to larger clusters to understand the nature of the H-bond network.

Addressing the scientific challenges of pillar 1 demands a joint experimental and theoretical approach. Therefore, the development and adaption of theory and molecular dynamics (MD) simulations represents as well a cross-challenge objective of pillar 1. Our goal is to acquire the ability to accompany the respective experiment with tailor-made MD simulations and theory.

In order to address *challenge 1*, we will determine the local order and dynamics of water through the phase diagram. We will start with investigating deeply supercooled states of liquid water by performing single-shot coherent X-ray scattering measurements on water droplets. We will cover length scales from molecular dimensions to tens of nanometres, i.e. the predicted size of potential LDL/HDL domains. Liquid water is believed to show a variety of locally ordered structures that are transient in nature. Experiments accessing such structures will be performed using ultrashort pulses generated at modern hard X-ray FEL facilities. Therefore, we will develop and apply coherent X-ray scattering methods such as X-ray cross correlation analysis for low-intensity data.

Measuring the relation between structure and dynamics will help us to understand H-bond fluctuations, possibly revealing the nature of the proposed HDL and LDL phases as shown in Figure III.1.5. We will connect structural and dynamical properties of both H_2O and D_2O to thermodynamic response functions and extend the currently accessible temperature range using new injection systems. This will allow us to locate the potential liquid–liquid critical point as well as the Widom line in the supercooled regime, as
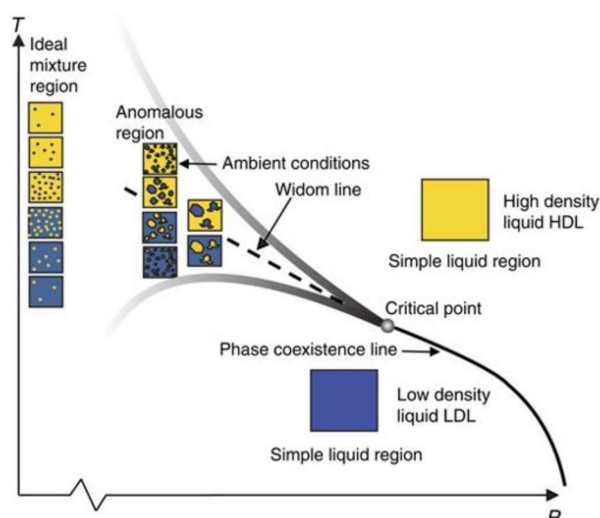
Figure III.1.5: Scheme of the hypothetical phase diagram of liquid water [1.1].

demonstrated recently by first experiments [1.68, 1.69].

Another route to address structure formation of water will be studies from small water clusters up to bulk-like environments using liquid droplets and aerosol injectors. The ultimate goal will be the answer to the question what the nature of liquid water actually is and how far we can go in temperature while still staying in a liquid state.

Challenge 2 focuses on the nature of crystallisation and glass transition of water. Studies of crystallisation and glass transition under extreme conditions will benefit from the development of sample environments at modern X-ray sources as discussed above. The investigation of the nature of water's glass transitions will be closely connected to *challenge 1* where we will focus on how high- and low-density amorphous solids (HDA and LDA) can possibly form the proposed counterparts HDL and LDL as liquid phases. We will localise the glass transitions and crystallisation conditions using different pressure and temperature route. The role of crystallisation agents and inhibitors will be addressed by investigating in which way they change the characteristics of structure and dynamics and thus the phase behaviour. In particular, differences between the different glass transitions of water and to other common glass formers will be a key objective of *challenge 2*.

The objective of *challenge 3* will be to understand the polymorphism of crystalline ice in particular, and its relation to the amorphous forms. Special

attention will be paid on studying H-order–disorder transitions to reveal the mechanism and driving forces of the H-ordering process. The combination of modern light sources with state-of-the art high-pressure and low-temperature sample environments will enable *in situ* studies on structure and formation kinetics of different ices. Characterisation of both crystalline and amorphous states after different pressure and temperature quenches from liquid water and other solid water states will solve the question of the complex polymorphism of crystalline and amorphous ice. Such experiments will provide valuable input for simulation and theory to understand why water can form so many different solid phases.

The main focus of *challenge 4* will be set on revealing the role of solutes on the H-bonding network of liquid water. We will study systematically, in which way solutes affect the structure and dynamics of liquid water. In particular, their influence on the anomalies of liquid water will be investigated. For instance, different salts are typically used to reduce the melting point of water, however, this may also change different water properties rising the question to which extent solvent water resembles bulk water. This includes the interaction of water with various ions, (biological) macromolecules, polymers and different colloidal systems. Another objective will be the role of different co-solutes in ternary aqueous solution. These are believed to strengthen or weaken the hydrogen bond network of water and thus stabilise the third constituent, e.g. protein molecules. Closely connected to *challenge 1*, the solution process will be studied on different length scales, ranging from bulk solutions to single molecular levels using small water clusters. Furthermore, the formation processes of ice-like clathrates where solute molecules are enclosed in ice-like water networks will be part of *challenge 4*. We plan to use pump-probe schemes to study the kinetics of the solute-solvent interactions in bulk solutions as well as at aqueous surfaces and interfaces.

To address *challenge 5* we will investigate the impact of the symmetry breaking at two-dimensional interfaces or in nanoconfinement on the structure and dynamics of water. This will involve measurements of structure, electronic structure and fluctuations of water surfaces by

capillary waves over different length scales covering collective dynamics as well as molecular level dynamics. This will involve as well water molecules and films at charged, hydrophobic and biological interfaces. Furthermore, studies of ice interfaces and the characteristics of the quasi-liquid layer will extend the objectives of *challenge 3*. In close connection to *challenge 2,* revealing the nature of the heterogeneous crystallisation at water interfaces will be a goal of *challenge 5*. Furthermore, we aim to understand the phase behaviour of water in nanoconfinement as a function of pore size and water-pore interaction as well as free-flowing or cavitating nano-bubbles and compare it to the phase behaviour of bulk water.

III.1.4 Methodologies

The investigation of fundamental properties of water requires a combination of state-of-the-art experimental, theoretical and molecular dynamics and Monte Carlo simulation approaches. Especially the structure and dynamics of liquid water, ices, solutions and aqueous interfaces will be investigated down to molecular length scales and between femtoseconds and hours. This is perfectly covered by the unique Hamburg light-source environment. The European XFEL enables experiments on femto to microseconds timescale with molecular resolution [1.70]. This is complemented by the soft X-ray FEL FLASH providing ultrafast spectroscopy and experiments on longer length scales as well as the storage ring source PETRA III to long time scales. The objective of pillar 1 will especially benefit from the planned upgrade of PETRA III to the diffraction-limited storage ring PETRA IV that will provide a significant increase of brilliance and thus enable new experiments completing the accessible time range of the FEL sources seamlessly to more than 18 orders of magnitude.

Liquid jet and microdroplet injectors are inherent to the research in pillar 1. Microscopic liquid water jets in vacuum on FEL sources [1.7] have become the standard tool for investigation of not only biomolecules but also liquid and supercooled water by evaporating microdroplets, see Figure III.1.6. In order to address the scientific objectives in pillar 1, research on new injection devices and

a continuous improvement of the existing technology will be performed. This comprises different types of liquid jet designs, as well as aerosol, cluster injectors and new liquid cell technology that produces submicron thick jets of liquid water layers. We will implement and further develop methods to characterise jet and droplet size such as demonstrated by means of Raman scattering [1.36] and aim to reduce the droplet size significantly below 1 μm to reach even lower temperatures at deeply super-cooled conditions. Furthermore, we will extend the injection systems to routinely study aqueous solutions. These devices will in particular be optimised for experiments at XFEL and storage ring sources, which are outlined in the following paragraphs.

In connection to *challenge 2* and *3* high-pressure devices will be used to prepare different crystalline polymorphs of ice as well as high-density amorphous ices. Bulk samples can be prepared using a piston-cylinder setup, applying pressures up to 2 GPa in the temperature range between 77 K and RT. Those ice-sample can be recovered to ambient pressure and studied *ex situ* using various lab-based methods, such as calorimetry [1.54], Raman, Infrared and UV-Vis spectroscopy. As demonstrated by us earlier, those
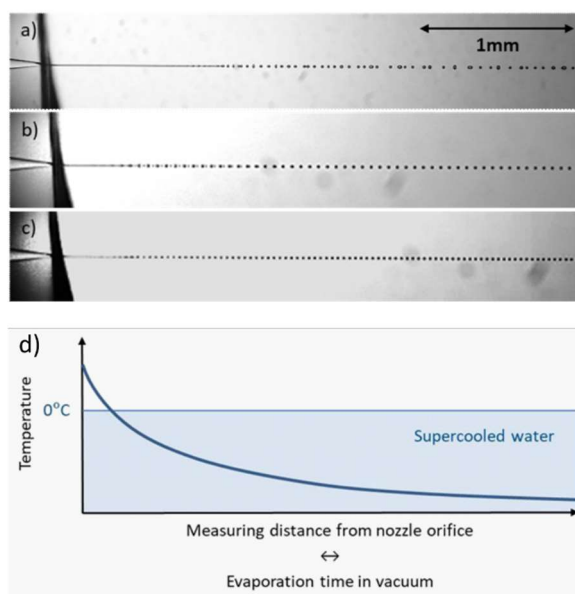
Figure III.1.6: Shadow images of a nozzle producing a 10 μm thick water jet and trains of water droplets due to Rayleigh break-up (a) and different external triggers (b, c). The droplets cool down by evaporation reaching supercooled temperature as a function of travelling time (d) [1.71].

samples can also be studied by Neutron scattering [1.17], at storage ring sources [1.5] as well as XFELs. In order to study high-pressure ice phases and phase transitions at elevated pressures, a Diamond anvil cell [1.13] as well as the Paris-Edinburgh cell [1.18] will be used. These devices will also be used in order to investigate the challenges described in pillar 2, and the development of entirely new experimental setups that can be used in terms of high-pressure pump-probe schemes at, e.g. XFELs are of broad interest across the pillars.

In order to measure the structure of water, aqueous solutions, nanoconfined water and various ice phases, a first part will be the measurement of Pair Distribution Functions (PDF) using X-ray, electron and neutron scattering. Precise measurement of these PDF is challenging, and the effect of systematic errors and noise is hard to track. In the framework of the CMWS, the combined approach will help to overcome disadvantages of the different techniques, e.g. weak scattering cross section for X-ray, significant inelastic scattering for neutron, and multiple scattering for electrons. Diffraction-based methods will be complemented by X-ray spectroscopic structural characterisation of water and aqueous solutions. X-ray diffraction and spectroscopy experiments will be carried out at the most modern storage rings, e.g. PETRA III and PETRA IV, or XFEL sources (such as the European XFEL), as well as at REGAE as a source of relativistic electrons. Combined with new analysis techniques based on machine learning and Bayesian statistics, partial-PDF will be determined with unprecedented accuracy mapping out the hydrogen bond network in water and its time-dependent correlations.

To access water's local order, we plan experiments using short coherent light pulses from FEL sources and analysis in terms of higher-order correlation functions beyond the study of pair correlations. Dynamics in the supercooled/pressurised liquid and the amorphous and crystalline ice regime need experimental tools that span time regimes from ps to ms. X-ray Photon Correlation Spectroscopy (XPCS), X-ray Speckle Visibility Spectroscopy (XSVS) as well as X-ray Cross Correlation (XCCA) techniques can provide critical information when carried out at modern X-

ray light sources. Combined with ultrashort pulses and split-and-delay techniques, we will be able to access dynamics in water and ice at molecular length scales over more than 18 orders of magnitude in time, ranging from femtoseconds to several 1000 s with such correlation techniques.

For investigating the two-dimensional structure and dynamics of liquid–liquid and liquid–gas interfaces down to atomic scale resolution we foresee experimental campaigns at dedicated instruments, such as LISA at beamline P08 of PETRA III, giving access to interfaces without sample movement [1.25,1.30,1.58]. Access to the dynamics at liquid interfaces with nanosecond time resolution will be obtained by a femtosecond laser allowing optical pump-X-ray probe studies, which has been developed at LISA. One alternative approach for investigating liquid interfaces will be to measure X-ray reflectivity from a liquid drop by superimposing many single-shot profiles [1.72]. Emission of shock-waves and jets by cavitation bubbles is studied using single-pulse XFEL holography in a pump-probe scheme with temporal resolutions down to 100 fs. The quantitative contrast allows to extract e.g. the time evolution of the density profile close to the vapour-liquid interface.

The X-ray-based techniques will be complemented by state-of-the-art bulk and surface specific optical spectroscopy methods to be located at CMWS laboratories. For example, IR and Raman spectroscopy are common probes to investigate the vibrational properties of water and ice, especially the complex band shape of the intramolecular OH-stretch. Probing in the THz-frequency region can directly access intermolecular vibrations and thus the H-bonds in water and aqueous solutions. With surface-sensitive vibrational spectroscopy we are able to study the water–vapor or ice–vapor interface [1.56]. 2D-IR as a non-linear spectroscopy method allows us to probe hydrogen bond dynamics [1.73], as well as explore the coupling and energy pathways between high frequency intramolecular vibrations to low frequency intermolecular modes [1.74]. Changes in the vibrational band profile, i.e. bimodal shape, frequency, frequency width and intensity are connected to changes in the present distribution of intra and intermolecular bond

lengths and might even indicate structural transitions upon variation of temperature, pressure and concentration. The sensitivity of the OH-stretch band of water makes probes like Raman spectroscopy an ideal tool to monitor contactless the sample temperature. This is for example important for the localisation of with X-ray methods measured structural and dynamical properties of samples under extreme conditions like rapidly evaporating and cooling liquid jets in vacuum.

To study electrodynamic properties of water and ice, we will use dielectric, microwave, infrared and optical spectroscopies at various temperatures and pressures, as well as other methods that supplement the Hamburg light source experimental facilities. The frequency dependence of the dielectric parameters of liquid, solid, or confined water will help us to understand its dynamical structure on both bulk and local-molecular levels. The measurements are planned in the frequency range from 1 Hz to 50 GHz, as well as the infrared region. The total frequency interval covers the set of atomic-molecular motion, such as, e.g. hopping, drift, twinkling and vehicle-like migration, as well as includes long-term static dynamics.

The connection between experiments and theory, in particular MD simulation within one centre will be a key characteristic of the CMWS. Within pillar 1, state-of-the art simulations will strengthen the understanding of water structure and dynamics over the whole phase diagram. Experimental results obtained at the new light sources will set benchmarks for simulations, both classical and *ab initio* MD. Thus, we foresee to further develop different MD simulation schemes to improve our understanding of molecular water.

III.1.5 References

[1.1]   A. Nilsson and L. G. M. Pettersson, The Structural Origin of Anomalous Properties of Liquid Water, Nat. Commun. 6, 8998 (2015).

[1.2]   O. Mishima, L. D. Calvert, and E. Whalley, An Apparently First-Order Transition between Two Amorphous Phases of Ice Induced by Pressure, Nature 314, 76 (1985).

[1.3]   O. Mishima and H. E. Stanley, The Relationship between Liquid, Supercooled and Glassy Water, Nature 396, 329 (1998).

[1.4]   P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, Water: A Tale of Two Liquids, Chem. Rev. 116, 7463 (2016).

[1.5]   F. Perakis, K. Amann-Winkel, F. Lehmkühler, M. Sprung, D. Mariedahl, J. A. Sellberg, H. Pathak, A. Späh, F. Cavalca, D. Schlesinger, A. Ricci, A. Jain, B. Massani, F. Aubree, C. J. Benmore, T. Loerting, G. Grübel, L. G. M. Pettersson, and A. Nilsson, Diffusive Dynamics during the High-to-Low Density Transition in Amorphous Ice, Proc. Natl. Acad. Sci. 114, 8193 (2017).

[1.6]   K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, K. H. Nam, T. Katayama, and A. Nilsson, Maxima in the Thermodynamic Response and Correlation Functions of Deeply Supercooled Water, Science 358, 1589 (2017).

[1.7]   J. A. Sellberg, C. Huang, T. A. McQueen, N. D. Loh, H. Laksmono, D. Schlesinger, R. G. Sierra, D. Nordlund, C. Y. Hampton, D. Starodub, D. P. DePonte, M. Beye, C. Chen, A. V. Martin, A. Barty, K. T. Wikfeldt, T. M. Weiss, C. Caronna, J. Feldkamp, L. B. Skinner, M. M. Seibert, M. Messerschmidt, G. J. Williams, S. Boutet, L. G. M. Pettersson, M. J. Bogan, and A. Nilsson, Ultrafast X-Ray Probing of Water Structure below the Homogeneous Ice Nucleation Temperature, Nature 510, 381 (2014).

[1.8]   P. G. Debenedetti, Supercooled and glassy water, J. Phys.: Cond. Matt. 15, R1669-R1726 (2003).

[1.9]   V. G. Artemov, A unified mechanism for ice and water electrical conductivity from direct current to terahertz, Phys. Chem. Chem. Phys. 21, 8067 (2019).

[1.10] K. Amann-Winkel, R. Böhmer, F. Fujara, C. Gainaru, B. Geil, and T. Loerting, Colloquium: Water's Controversial Glass Transitions, Rev. Mod. Phys. 88, 011002 (2016).

[1.11] C. A. Angell, Insights into Phases of Liquid Water from Study of Its Unusual Glass-Forming Properties, Science 319, 582 (2008).

[1.12] J. J. Shephard and C. G. Salzmann, Molecular Reorientation Dynamics Govern the Glass Transitions of the Amorphous Ices, J. Phys. Chem. Lett. 7, 2281 (2016).

[1.13]   C. Lin, X. Yong, J. S. Tse, J. S. Smith, S. V. Sinogeikin, C. Kenney-Benson, and G. Shen, Kinetically Controlled Two-Step Amorphization and Amorphous-Amorphous Transition in Ice, Phys. Rev. Lett. 119, 135701 (2017).

[1.14]   J. Stern, M. Seidl-Nigsch, and T. Loerting, Evidence for high-density liquid water between 0.1 and 0.3 GPa near 150 K, Proc. Natl. Acad. Sci. 116, 9191 (2019).

[1.15]   T. M. Gasser, A. V. Thoeny, A. D. Fortes and T. Loerting, Structural characterization of ice XIX as the second polymorph related to ice VI, Nat. Commun. 12, 1128 (2021).

[1.16]   C. G. Salzmann, Advances in the experimental exploration of water's phase diagram, J. Chem. Phys. 150, 060901 (2019).

[1.17]   T. Loerting, K. Winkel, M. Seidl, M. Bauer, C. Mitterdorfer, P. H. Handle, C. G. Salzmann, E. Mayer, J. L. Finney, and D. T. Bowron, How Many Amorphous Ices Are There?, Phys. Chem. Chem. Phys. 13, 8783 (2011).

[1.18]   C. A. Tulk, J.J. Molaison, A.R. Makhluf, C.E. Manning, and D.D. Klug, Absence of amorphous forms when ice is compressed at low temperature, Nature 569, 542 (2019).

[1.19]   A. Werner, A. Rieger, M. Mosch, R. Haseneder, J.-U. Repke, Nanofiltration of indium and germanium ions in aqueous solutions: Influence of pH and charge on retention and membrane flux, Separation and Purification Technology 194, 319-328 (2018).

[1.20]   F. Lehmkühler, Y. Forov, M. Elbers, I. Steinke, C. Weis, N.Tsuji, M. Itou, Y. Sakurai, A. Poulain, and C. Sternemann. Temperature dependence of the hydrogen bond network in Trimethylamine N-oxide and guanidine hydrochloride - water solutions. Phys. Chem. Chem. Phys. 19, 28470 (2017).

[1.21]   E. D. Sloan Jr. and C. A. Koh, Clathrate Hydrates of Natural Gases, 3rd ed. (CRC Press, 2007).

[1.22]   R. A. Livingstone, Y. Nagata, M. Bonn, and E. H. G. Backus, Two Types of Water at the Water–Surfactant Interface Revealed by Time-Resolved Vibrational Spectroscopy, J. Am. Chem. Soc. 137, 14912 (2015).

[1.23]   R. Khatib, E. H. G. Backus, M. Bonn, M.-J. Perez-Haro, M.-P. Gaigeot, and M. Sulpizi, Water Orientation and Hydrogen-Bond Structure at the Fluorite/Water Interface, Sci. Rep. 6, 24287 (2016).

[1.24]   A. P. Gaiduk, T. A. Pham, M. Govoni, F. Paesani, and G. Galli, Electron Affinity of Liquid Water, Nat. Commun. 9, 247 (2018).

[1.25]   J. Haddad, D. Pontoni, B. M. Murphy, S. Festersen, B. Runge, O. M. Magnussen, H.-G. Steinrück, H. Reichert, B. M. Ocko, and M. Deutsch, Surface Structure Evolution in a Homologous Series of Ionic Liquids, Proc. Natl. Acad. Sci. 115, E1100 (2018).

[1.26]   K. Wu, Z. Chen, J. Li, X. Li, J. Xu, and X. Dong, Wettability Effect on Nanoconfined Water Flow, Proc. Natl. Acad. Sci. 114, 3358 (2017).

[1.27]   M. A. Sánchez, T. Kling, T. Ishiyama, M.-J. van Zadel, P. J. Bisson, M. Mezger, M. N. Jochum, J. D. Cyran, W. J. Smit, H. J. Bakker, M. J. Shultz, A. Morita, D. Donadio, Y. Nagata, M. Bonn, and E. H. G. Backus, Experimental and Theoretical Evidence for Bilayer-by-Bilayer Surface Melting of Crystalline Ice, Proc. Natl. Acad. Sci. 114, 227 (2017).

[1.28]   V. Venkateshwaran, S. Vembanur, and S. Garde, Water-Mediated Ion-Ion Interactions Are Enhanced at the Water Vapor-Liquid Interface, Proc. Natl. Acad. Sci. 111, 8729 (2014).

[1.29]   Y. Wang, S. Sinha, P. R. Desai, H. Jing, and S. Das, Ion at Air–Water Interface Enhances Capillary Wave Fluctuations: Energetics of Ion Adsorption, J. Am. Chem. Soc. 140, 12853 (2018).

[1.30]   A. Madsen, T. Seydel, M. Sprung, C. Gutt, M. Tolan, and G. Grübel, Capillary Waves at the Transition from Propagating to Overdamped Behavior, Phys. Rev. Lett. 92, 096104 (2004).

[1.31]   A. Elsen, B. M. Murphy, B. M. Ocko, L. Tamam, M. Deutsch, I. Kuzmenko, and O. M. Magnussen, Surface Layering at the Mercury-Electrolyte Interface, Phys. Rev. Lett. 104, 105501 (2010).

[1.32]   X. Z. Wu, B. M. Ocko, E. B. Sirota, S. K. Sinha, M. Deutsch, B. H. Cao, and M. W. Kim, Surface Tension Measurements of Surface Freezing in Liquid Normal Alkanes, Science 261, 1018 (1993).

[1.33]   K. R. Siefermann, Y. Liu, E. Lugovoy, O. Link, M. Faubel, U. Buck, B. Winter, and B. Abel, Binding Energies, Lifetimes and Implications of Bulk and Interface Solvated Electrons in Water, Nat. Chem. 2, 274 (2010).

[1.34] C. Gutt, O. Leupold, and G. Grübel. Surface XPCS on nanometer length scales — What can we expect from an X-ray free electron laser? Thin Solid Films 515, 5532 (2007).

[1.35] F. Perakis, G. Camisasca, T. J. Lane, A. Späh, K. T. Wikfeldt, J. A. Sellberg, F. Lehmkühler, H. Pathak, K. H. Kim, K. Amann-Winkel, S. Schreck, S. Song, T. Sato, M. Sikorski, A. Eilert, T. McQueen, H. Ogasawara, D. Nordlund, W. Roseker, J. Koralek, S. Nelson, P. Hart, R. Alonso-Mori, Y. Feng, D. Zhu, A. Robert, G. Grübel, L. G. M. Pettersson, and A. Nilsson, Coherent X-Rays Reveal the Influence of Cage Effects on Ultrafast Water Dynamics, Nat. Commun. 9, 1917 (2018).

[1.36] C. Goy, M. A. C. Potenza, S. Dedera, M. Tomut, E. Guillerm, A. Kalinin, K.-O. Voss, A. Schottelius, N. Petridis, A. Prosvetov, G. Tejeda, J. M. Fernández, C. Trautmann, F. Caupin, U. Glasmacher, and R. E. Grisenti, Shrinking of Rapidly Evaporating Water Microdroplets Reveals Their Extreme Supercooling, Phys. Rev. Lett. 120, 015501 (2018).

[1.37] R. Signorell, M. Goldmann, B. L. Yoder, A. Bodi, E. Chasovskikh, L. Lang, and D. Luckhaus, Nanofocusing, Shadowing, and Electron Mean Free Path in the Photoemission from Aerosol Droplets, Chem. Phys. Lett. 658, 1 (2016).

[1.38] C. Richter, D. Hollas, C.-M. Saak, M. Förstel, T. Miteva, M. Mucke, O. Björneholm, N. Sisourat, P. Slavíček, and U. Hergenhahn, Competition between Proton Transfer and Intermolecular Coulombic Decay in Water, Nat. Commun. 9, 4988 (2018).

[1.39] A. Hans, P. Schmidt, C. Ozga, G. Hartmann, X. Holzapfel, A. Ehresmann, and A. Knie, Extreme Ultraviolet to Visible Dispersed Single Photon Detection for Highly Sensitive Sensing of Fundamental Processes in Diverse Samples, Materials 11, 869 (2018).

[1.40] A. Hans, T. Miteva, X. Holzapfel, C. Ozga, P. Schmidt, H. Otto, G. Hartmann, C. Richter, N. Sisourat, A. Ehresmann, K. Gokhberg, U. Hergenhahn, and A. Knie, Electronic Decay of Singly Charged Ground-State Ions by Charge Transfer via van der Waals Bonds, Phys. Rev. Lett. 123, 213001 (2019).

[1.41] A. Hans, C. Ozga, R. Seidel, P. Schmidt, T. Ueltzhöffer, X. Holzapfel, P. Wenzel, P. Reiß, M.N. Pohl, I. Unger, E. F. Aziz, A. Ehresmann, P. Slavíček, B. Winter, and A. Knie, Optical Fluorescence Detected from X-ray Irradiated Liquid Water, J. Phys. Chem. B 121, 2326 (2017).

[1.42] G. Monaco, A. Cunsolo, G. Ruocco, and F. Sette, Viscoelastic Behavior of Water in the Terahertz-Frequency Range: An Inelastic X-ray Scattering Study, Phys. Rev. E 60, 5505 (1999).

[1.43] Ph. Wernet et al., The Structure of the First Coordination Shell in Liquid Water, Science 304, 995 (2004).

[1.44] J. S. Tse, D. M. Shaw, D. D. Klug, S. Patchkovskii, G. Vankó, G. Monaco, and M. Krisch, X-Ray Raman Spectroscopic Study of Water in the Condensed Phases, Phys. Rev. Lett. 100, 095502 (2008).

[1.45] H. Conrad, F. Lehmkühler, C. Sternemann, A. Sakko, D. Paschek, L. Simonelli, S. Huotari, O. Feroughi, M. Tolan, and K. Hämäläinen, Tetrahydrofuran Clathrate Hydrate Formation, Phys. Rev. Lett. 103, 218301 (2009).

[1.46] T. Pylkkänen, V. M. Giordano, J.-C. Chervin, A. Sakko, M. Hakala, J. A. Soininen, K. Hämäläinen, G. Monaco, and S. Huotari, Role of Non-Hydrogen-Bonded Molecules in the Oxygen K-Edge Spectrum of Ice, J. Phys. Chem. B 114, 3804 (2010).

[1.47] C. J. Sahle, C. Sternemann, C. Schmidt, S. Lehtola, S. Jahn, L. Simonelli, S. Huotari, M. Hakala, T. Pylkkänen, A. Nyrow, K. Mende, M. Tolan, K. Hämäläinen, and M. Wilke, Microscopic Structure of Water at Elevated Pressures and Temperatures, Proc. Natl. Acad. Sci. 110, 6301 (2013).

[1.48] F. Lehmkühler, Y. Forov, T. Büning, C. J. Sahle, I. Steinke, K. Julius, T. Buslaps, M. Tolan, M. Hakala, and C. Sternemann, Intramolecular Structure and Energetics in Supercooled Water down to 255 K, Phys. Chem. Chem. Phys. 18, 6925 (2016).

[1.49] I. A. Zaluzhnyy, R. P. Kurta, N. Mukharamova, Y. Y. Kim, R. M. Khubbutdinov, D. Dzhigaev, V. V. Lebedev, E. S. Pikina, E. I. Kats, N. A. Clark, M. Sprung, B. I. Ostrovskii, and I. A. Vartanyants, Evidence of a First-Order Smectic-Hexatic Transition and Its Proximity to a Tricritical Point in Smectic Films, Phys. Rev. E 98, 052703 (2018).

[1.50] F. Lehmkühler, F. Schulz, M. A. Schroer, L. Frenzel, H. Lange, and G. Grübel, Heterogeneous Local Order in Self-Assembled Nanoparticle Films Revealed by X-Ray Cross-Correlations, IUCrJ 5, 354 (2018).

[1.51] W. Roseker, S. O. Hruszkewycz, F. Lehmkühler, M. Walther, H. Schulte-Schrepping, S. Lee, T. Osaka, L. Strüder, R. Hartmann, M. Sikorski, S. Song, A. Robert, P. H. Fuoss, M. Sutton, G. B. Stephenson, and G. Grübel, Towards Ultrafast Dynamics with Split-Pulse X-Ray Photon Correlation Spectroscopy at Free Electron Laser Sources, Nat. Commun. 9, 1704 (2018).

[1.52] C. R. Hill, C. Mitterdorfer, T. G. A. Youngs, D. T. Bowron, H. J. Fraser, and T. Loerting, Neutron Scattering Analysis of Water's Glass Transition and Micropore Collapse in Amorphous Solid Water, Phys. Rev. Lett. 116, 215501 (2016).

[1.53] I. Kohl, L. Bachmann, E. Mayer, A. Hallbrucker, and T. Loerting, Glass Transition in Hyperquenched Water?, Nature 435, E1 (2005).

[1.54] K. Amann-Winkel, C. Gainaru, P. H. Handle, M. Seidl, H. Nelson, R. Böhmer, and T. Loerting, Water's Second Glass Transition, Proc. Natl. Acad. Sci. 110, 17720 (2013).

[1.55] V. Fuentes-Landete, L. J. Plaga, M. Keppler, R. Böhmer, and T. Loerting, Nature of Water's Second Glass Transition Elucidated by Doping and Isotope Substitution Experiments, Phys. Rev. X 9, 011015 (2019).

[1.56] M. Bonn, Y. Nagata, and E. H. G. Backus, Molecular Structure and Dynamics of Water at the Water-Air Interface Studied with Surface-Specific Vibrational Spectroscopy, Angew. Chem. Int. Ed. 54, 5560 (2015).

[1.57] M. Mezger, H. Reichert, S. Schoder, J. Okasinski, H. Schroder, H. Dosch, D. Palms, J. Ralston, and V. Honkimaki, High-Resolution in Situ X-ray Study of the Hydrophobic Gap at the Water-Octadecyl-Trichlorosilane Interface, Proc. Natl. Acad. Sci. 103, 18401 (2006).

[1.58] B. M. Murphy, M. Greve, B. Runge, C. T. Koops, A. Elsen, J. Stettner, O. H. Seeck, and O. M. Magnussen, A Novel X-Ray Diffractometer for Studies of Liquid–Liquid Interfaces, J. Synchrotron Radiat. 21, 45 (2014).

[1.59] Y. Nagata, T. Hama, E. H. G. Backus, M. Mezger, D. Bonn, M. Bonn, and G. Sazaki, The Surface of Ice under Equilibrium and Nonequilibrium Conditions, Acc. Chem. Res. 52, 1006 (2019).

[1.60] F. Lehmkühler, M. Paulus, C. Sternemann, D. Lietz, F. Venturini, C. Gutt, and M. Tolan, The Carbon Dioxide−Water Interface at Conditions of Gas Hydrate Formation, J. Am. Chem. Soc. 131, 585 (2009).

[1.61] M. Lippmann, O. H. Seeck, A. Ehnes, K. Nygård, F. Bertram, and A. Ciobanu, Experimental Observation of Crystal–Liquid Coexistence in Slit-Confined Nonpolar Fluids, J. Phys. Chem. Lett. 10, 1634 (2019).

[1.62] V. Soprunyuk, W. Schranz, and P. Huber, Dynamic Mechanical Analysis of Supercooled Water in Nanoporous Confinement, EPL Europhys. Lett. 115, 46001 (2016).

[1.63] J. B. Mietner, F. J. Brieler, Y. J. Lee, and M. Fröba, Properties of Water Confined in Periodic Mesoporous Organosilicas: Nanoimprinting the Local Structure, Angew. Chem. Int. Ed. 56, 12348 (2017).

[1.64] B. J. Mietner, M. Fröba, and R. Valiullin, Water Transport in Periodic Mesoporous Organosilica Materials, J. Phys. Chem. C 122, 12673 (2018).

[1.65] T. D. Kühne and R. Z. Khaliullin, Electronic Signature of the Instantaneous Asymmetry in the First Coordination Shell of Liquid Water, Nat. Commun. 4, 1450 (2013).

[1.66] T. Spura, H. Elgabarty, and T. D. Kühne, "On-the-Fly" Coupled Cluster Path-Integral Molecular Dynamics: Impact of Nuclear Quantum Effects on the Protonated Water Dimer, Phys. Chem. Chem. Phys. 17, 14355 (2015).

[1.67] D. Ojha, K. Karhan, and T. D. Kühne, On the Hydrogen Bond Strength and Vibrational Spectroscopy of Liquid Water, Sci. Rep. 8, 16888 (2018).

[1.68] K.H. Kim, K. Amann-Winkel, N. Giovambattista, A. Späh, F Perakis, H. Pathak, M. Ladd Parada, C. Yang, D. Mariedahl, T. Eklund, T. J. Lane, S. You, S. Jeong, M. Weston, J. H. Lee, I. Eom, M. Kim, J. Park, S. H. Chun, P. H. Poole, and A. Nilsson, Experimental observation of the liquid-liquid transition in bulk supercooled water under pressure, Science 370, 978 (2020).

[1.69]   H. Pathak, A. Späh, N. Esmaeildoost, J. A. Sellberg, K. H. Kim, F. Perakis, K. Amann-Winkel, M. Ladd Parada, J. Koliyadu, T.J. Lane, C. Yang, H. T. Lemke, A. R. Oggenfuss, P. J. M. Johnson, Y. Deng, S. Zerdane, R. Mankowsky, P. Beaud, and A. Nilsson, Enhancement and maximum in the isobaric specific-heat capacity measurements of deeply supercooled water using ultrafast calorimetry, Proc. Natl. Acad. Sci. 118, e2018379118 (2021).

[1.70]   F. Lehmkühler, F. Dallari, A. Jain, M. Sikorski, J. Möller, L. Frenzel, I. Lokteva, G. Mills, M. Walther, H. Sinn, F. Schulz, M. Dartsch, V. Markmann, R. Bean, Y. Kim, P. Vagovic, A. Madsen, A. P. Mancuso, and G. Grübel, Emergence of anomalous dynamics in soft matter probed at the European XFEL, Proc. Natl. Acad. Sci. 117, 24110 (2020).

[1.71]   C. Goy, Spektroskopie an tief unterkühlten Wassertropfen, Dissertation, Goethe University Frankfurt (2019).

[1.72]   S. Festersen, S. B. Hrkac, C. T. Koops, B. Runge, T. Dane, B. M. Murphy, and O. M. Magnussen, X-Ray Reflectivity from Curved Liquid Interfaces, J. Synchrotron Radiat. 25, 432 (2018).

[1.73]   F. Perakis, L. De Marco, A. Shalit, F. Tang, Z.R. Kann, T.D. Kühne, R. Torre, M. Bonn, and Y. Nagata, Vibrational Spectroscopy and Dynamics of Water, Chem. Rev. 116, 7590 (2016).

[1.74]   K. Ramasesha, L. De Marco, A. Mandal, and A. Tokmakoff, Water vibrations have strongly mixed intra- and intermolecular character, Nat. Chem. 5, 935 (2013).

CMWS Pillar 2:
Water in Climate-, Astro-, and Geo-Sciences

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III.2 Water in Climate-, Astro-, and Geo-Sciences

III.2.1 Scientific Challenges and State of the Art

Molecular water and its ice polymorphs play an outstanding role in atmospheric and astrochemical processes, including the radiative balance and hydrological cycle, as well as in the chemical dynamics of the Earth's and other planets' atmospheres. Molecular water ice grains are understood to be central for astrochemical processes. In our own atmosphere, aerosol particles and water droplets formed on aerosols partially counteract the greenhouse effect by reflecting solar radiation, thus being prominent for the habitability of the Earth. In the solid Earth, significant amounts of molecular water are stored in the crystalline structure of minerals and melts as H_2O molecules, stoichiometric hydroxyl (OH)-groups or as defects. Cycling of this molecular water from the atmosphere across the surface to the deep Earth is essential to plate tectonics, resulting in volcanism and earthquakes at convergent plate boundaries and the formation of continental crust. The presence of super-critical aqueous fluids in the crust is responsible for ore formation. Water ice and ice mixtures of water with other molecules are highly abundant in giant exoplanets similar to Uranus or Neptune where high-pressure and

high-temperature polymorphs might cause magnetic field generation.

Earth's climate, and its sensitivity to perturbations, is set in large part by basic properties of water. Most of what we understand about climate and climate change is rooted in our understanding of atmospheric water. The converse is also true: most of what we wish we understood is rooted in our lack of understanding of water, also with respect to its interaction with the land surface.

Thus, molecular water is a key ingredient for many cosmic and planetary processes. However, a number of grand scientific challenges in our understanding of molecular water in geo-, astro-physical and atmospheric environments remain unresolved. We discuss below five key challenges that will be addressed by the groups within the CMWS.

Challenge 1: How does Molecular Water Shape Astrochemical Processes and the Evolution of Astrophysical Environments?

Water is the third most abundant molecule in the interstellar medium (ISM) [2.1,2.2]. One of the key questions of astronomy concerns the processes that lead to the efficient formation of water in the Universe and that explains its ubiquity in different environments, from the warm gas of star formation to the cold ice grains of diffuse interstellar clouds. Once emerged in its molecular form, water can lead to the formation of molecular water ice mantles made of microporous, amorphous water,
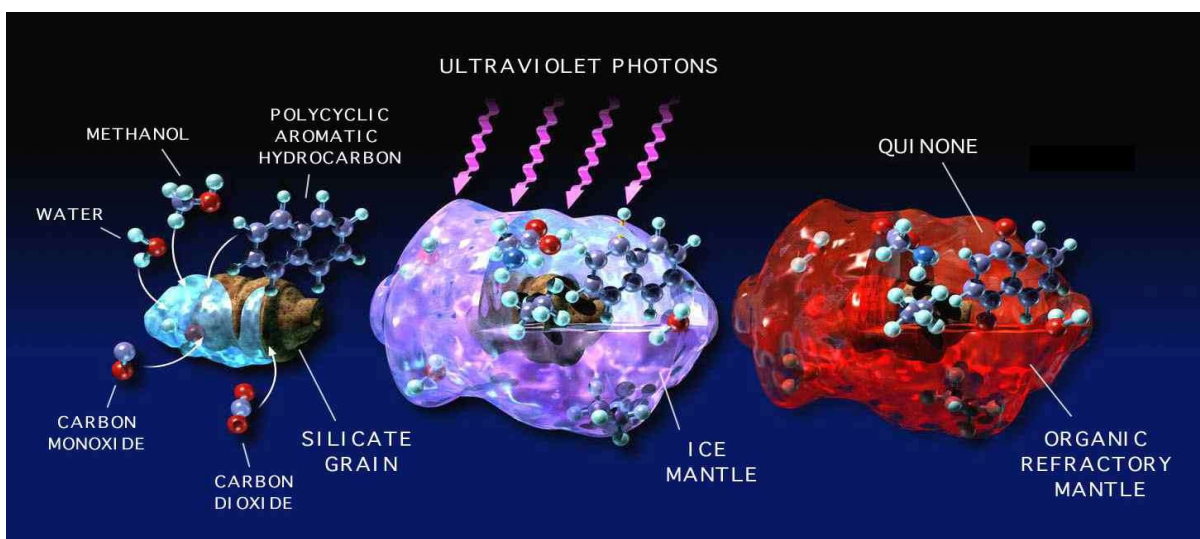

Figure III.2.1: Ice grain formation and chemical reactions in interstellar space.

surrounding carbonaceous or silicaceous inter-stellar dust particles [2.3,2.4] under the extremely low temperature and pressure conditions of the ISM. These ice mantles also contain other volatile components, such as CO, methanol or polycyclic aromatic hydrocarbons, which can undergo complex chemical reactions, especially under the influence of (V)UV irradiation or particle bombardment [2.5,2.6] (Figure III.2.1). As such, these ice grains represent the cradle for new molecules, including those that are regarded to be crucial for life, such as amino acids, but are also a shielding layer protecting labile molecules from irradiation-induced decomposition. Despite its importance, interstellar chemistry on these grains is not well understood. Elucidating the processes of molecule formation on molecular ice grains via a combination of experiments, theory and astronomical observations is crucially important in understanding the processes that lead to star and planet formation and may contribute to revealing the origin and development of life [2.7]. In addition to unravelling the molecular complexity generated on such ice grains, simple molecules such as O_2, O_3, H_2O_2 and OH are regarded as precursors of water formation in oxygen-rich ice grains [2.8], and the respective ongoing processes on these ice grains and their importance for the overall chemical richness observed in the ISM are an active area of research.

The non-thermal nuclear-spin-state distributions and deuteration levels allow for remote measurements of the temperature and reactivity in ISM water clouds. Owing to their two hydrogen nuclei, water molecules exist in *para* and *ortho* forms of the nuclear spin isomers [2.9]. The conversion between *ortho* and *para* isomers in isolated water molecules is strongly forbidden, so that their relative abundance (also known as the "*ortho/para* ratio") is believed to be conserved over time. This is intriguing to astrophysicists because the *ortho/para* ratio can serve as a key molecular signature for monitoring the evolution of matter in different kinds of astrophysical media. Nonetheless, in cold environments, the *ortho/para* conversion could take place through the internal magnetic hyperfine interaction with nuclear spins, an effect that has been hitherto disregarded. Accurate studies of the quantum nature of the nuclear spin flips and spin-exchange mechanisms

in water will be essential to disentangle the history of astrophysical environments.

The study of H_2O ices, both pure and mixed with other components such as ammonia and methane, under high pressure and temperature is crucial for our understanding of geophysical processes in the interior of icy moons (e.g. Ganymede, Enceladus, or Europa), the ice giant planets (Uranus and Neptune) and thousands of recently discovered icy exoplanets. Questions about the layering of the mantle or the possibility of sub-surface oceans can only be addressed if the phase behaviour and the physical properties for pure H_2O ice and mixtures are understood at the pressure and temperature conditions of the planet interior. For example, data on the dielectric or elastic properties of these high-pressure phases are scarce, and the conditions at which they turn from crystalline solids into liquids or amorphous solids have not yet been explored. While it is well known that pure hexagonal ice experiences pressure-induced amorphisation at pressures up to 2 GPa [2.10], it is much less clear whether H_2O ices mixed with methane, ammonia or other molecules experience the same phenomenon or, e.g. rather form clathrate hydrates [2.11-2.13]. The pressure-amorphised ices may even transform to ultraviscous liquids at low temperatures at conditions relevant to the shallow inner layers (< 2 GPa and 200 K). Moreover, these phases may become superionic at greater depths (> 50 GPa and 1000 K). It will, therefore, be essential to map the phase diagram for mixed ices over a broad range of pressure-temperature conditions for a better understanding of the dynamics and layering in the mantle of icy planetary bodies.

Challenge 2: What is the Role of Interface Effects in Cloud Physics and Aerosol Chemistry and their Relation to Earth's Climate Sensitivity?

Interface phenomena and processes are also important for atmospheric cloud and aerosol particles.

Given an Earth–Sun geometry, and the luminosity of our star, Earth's surface temperature is conditioned by (i) its albedo effect, which is largely determined by the water condensate burden in the atmosphere; and (ii) its greenhouse effect, which is additionally sensitive to the atmospheric water vapour burden. At surface temperatures above

300 K, Earth's humid atmosphere becomes opaque in the infrared, and the amount of thermal infrared radiation that escapes to space becomes insensitive to the surface temperature. This leads to a local run-away condition whereby warming shifts the effective emission height upward, but does not change the net emission. In this situation, the system must increasingly resort to other means to transport energy out of the column to achieve a balance. The opacity of the atmospheric window – whose "closing" we just described – is not understood. Knowing how the effects of absorption features accumulate, at wavelengths spectrally far from the centre of such features, or how new absorption features arise in dense vapors, would improve our understanding of the continuum absorption that closes the window, and more firmly ground our understanding of Earth's greenhouse effect.

Similarly, the condensate burden – and hence the albedo effect, which is mostly a property of the atmosphere, not the surface – is determined by the precipitation efficiency. How much it rains is determined by the atmospheric energy budget. A greenhouse atmosphere, by definition, is a net source of radiant energy, and the surface a sink. The balance is maintained by the hydrological cycle – with surface evaporation balanced by net condensation in the atmosphere. The main rain rate thus quantifies the strength of Earth's greenhouse effect. This links to the precipitation efficiency and Earth's albedo, because the ratio between the required precipitation rate and the effective lifetime of the condensate determines the condensate burden. Hence, understanding the condensate burden, and how it might change, requires an understanding of what processes determine the effective height at which condensate forms, and how effectively it aggregates. Both depend on microphysical processes, characterised by the surface physics of water's condensate phases, which affect habits of crystal growths, droplet growth rates, and particle interactions. Furthermore, there is a need to better understand ice particle growth modes, since the ice particle shape directly influences the Earth's outgoing longwave radiation, particularly in the far infrared spectral range [2.14]. This is of crucial importance both for understanding the Earth's energy balance and for making full use of upcoming satellite missions, such as FORUM by the European Space Agency ESA, where such information needs to be known beforehand. This latter aspect of ice particle growth is also strongly linked to *challenges 1* and *5* of this pillar and *challenges 3* and *5* described in pillar 1.

Aerosols are proposed to partially counteract the greenhouse effect by cooling the Earth via reflection of solar radiation (the direct effect) and promoting cloud formation (the indirect effect). According to the Intergovernmental Panel on Climate Change [2.15], the magnitude of these effects is the major uncertainty in climate change predictions, and it is crucial to constrain them better to improve climate modelling. Clouds interact with the atmospheric circulation, which greatly complicates understanding their impact on Earth's climate sensitivity. This has been selected as one of the seven current grand challenges of the World Climate Research Programme [2.16].

The main constituents of atmospheric aerosols stem from both natural and anthropogenic sources and include primary particles (sea salt, mineral dust, biogenic material, soot) and organic and inorganic secondary particles originating from gas-phase reactions. Aerosol particles play an important role by acting as cloud condensation nuclei. Cloud particles consist of liquid water or ice, and particularly the latter are still poorly understood. Ice particles grow in a plethora of shapes, and even the temperature dependence of the basic growth modes is currently not well known [2.17]. There is thus an immediate need to understand the initial steps of aerosol and cloud formation.

Due to the interaction with water vapor, aerosols form solid–vapor, solution–vapor, and solid–solution interfaces that act as sites for numerous heterogeneous reactions [2.18,2.19]. The nature of those interfaces is assumed to play a significant role in atmospheric chemistry, and new insights to these aspects are crucial to improve our molecular level understanding of atmospheric surface phenomena and processes.

Challenge 3: Does Liquid Water Form at Very Low Temperatures, and is there a Relation to Habitability?

Because all known living organisms require liquid water, the search for conditions suitable to life (i.e. habitability) of other planets is often the search for liquid water. Therefore, the occurrence of liquid water on Mars and other planets is a topic of ongoing research. Though there is evidence that Martian soils contain significant amounts of molecular water in the order of about 2–10% by weight [2.20], the existence of liquid water is not expected as Martian surface temperatures are below the triple point of water. In fact, most of the water in the Martian soil is bound in hydrated inorganic salts such as sulfates [2.21], chlorides [2.22] and perchlorates [2.23]. However, gullies found in valleys and on crater slopes suggest the presence of liquid water [2.24], which means that there must be a way to create or maintain liquid water below the triple point. One such process that lowers the freezing temperature is the increase of salinity of aqueous solutions. Alkaline earth chlorides and perchlorates and mixtures thereof have particularly low eutectic temperatures and are good candidates for stabilising brines under Martian conditions [2.25].

A second mechanism causing a significant shift of the triple point temperature is confinement, i.e. the influence of interfaces. The melting temperatures of solids decrease with decreasing crystal size due to an increasing influence of the surface energy (the Gibbs-Thomson effect). In the case of H_2O ice, melting temperatures as low as 215 K were observed in nanometre sized pores [2.26]. Recently, it was shown that the combination of the two effects, the influence of salts and of confinement, leads to particularly low freezing temperatures [2.27]. Finally, it is well known that liquid films form on solid surfaces below the melting temperature of the bulk solid. This phenomenon is known as pre-melting [2.28]. Similarly, gas adsorption leads to the formation of films on solid surfaces. Water vapor adsorption on hygroscopic surfaces such as salt crystals results in the formation of solution films on the crystal surfaces, which is known as pre-deliquescence [2.29]. Both, pre-melting and pre-deliquescence, are typical interfacial effects and are driven by the minimisation of surface energy.
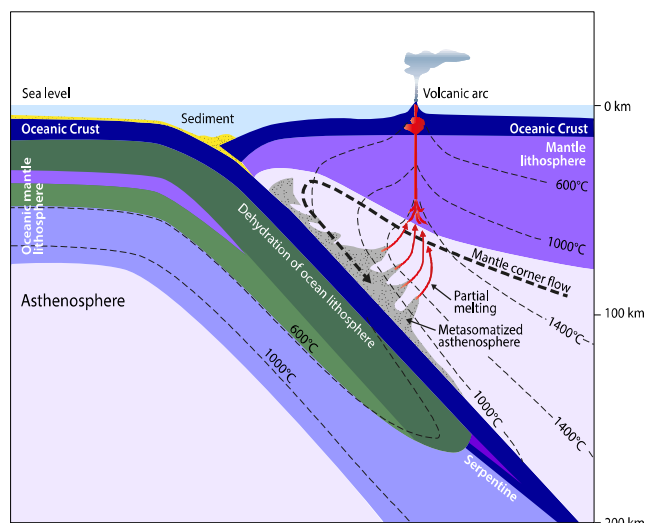
Figure III.2.2: Sketch of a subduction zone (adapted from [2.31]).

In order to fully understand the possible existence of life on other planets, a complete understanding of the formation of liquid water or water salt solutions is required. Thus, it is essential to elucidate all the effects involved in lowering the triple point of the water system that may lead to the formation of liquids. In order to identify mechanisms that extend the domain of liquid water, more complex phase diagrams have to be considered including both the presence of salt mixtures and the influence of confinement. Currently, available data are scarce. In addition to experimental investigations appropriate thermodynamic models are required, which validate the experimental data. Finally, the influence of confinement in small pores and the formation of liquid films are not well understood and require systematic studies and the development of appropriate models.

Challenge 4: What is the Role of Water in the Dynamics of Earth and Planetary Interiors across different Length Scales?

While the global distribution of H_2O during formation and evolution of planetary bodies such as the Earth remains elusive, it is clear that H_2O plays a major role in the interior dynamics of planets [2.30]. In addition to the presence of aqueous fluids at shallow depths in the Earth, H_2O may be present in many mineral phases either as interstitial molecules, stoichiometric OH-groups or as defects in nominally anhydrous phases. Since the initiation of plate tectonics in Earth's history, subduction zones have served as a major vehicle for transporting and cycling H_2O into the Earth

interior, inducing arc volcanism, earthquakes, as well as element mobilisation, enrichment and ore formation in the overlying mantle wedge, all of which are directly impacting society in one way or another. H_2O enters the newly formed crust at mid ocean ridges through the formation of hydrous minerals (Figure III.2.2) [2.32]. During subduction of the hydrated lithosphere, these minerals are subjected to high pressures and high temperatures, resulting in solid-state phase transformations to other hydrous and anhydrous phases [2.33]. Dehydration reactions within the subducted oceanic lithosphere release fluids that migrate into the overlying mantle. The presence of fluids causes localised deformation, mineral dissolution/reaction, partial melting and arc magmatism, often resulting in violent volcanism at the Earth's surface [2.34]. In addition, large volume reduction and embrittlement associated with mineral dehydration are linked to intermediate and deep focused earthquakes within subducting oceanic slabs, see e.g. [2.35]. To provide a full understanding of these large scale and macroscopic processes, a detailed knowledge of the microscopic stability and breakdown of all the possible hydrous phases present in the subducting slab and the Earth's mantle is required. This includes a full determination of the physical properties of the mineral phases such as composition, phase stability, equations of state (EoS), and elastic properties of all the candidate hydrous phases, e.g. Dense Hydrous Magnesium Silicates [2.36-2.39].

At the conditions of the deep Earth, aqueous fluids are known to transport metals very efficiently, which leads to the formation of ore deposits in the Earth's crust [2.40,2.41]. The mineral solubility in these mostly supercritical fluids, their chemical composition and structure as well as the speciation of metals in these fluids is not well understood. In addition, the relation between the thermodynamic phase stabilities and the microscopic locus where melting or exsolution of fluid starts, i.e. the influence of the intergranular region, and how these processes influence the mechanical or rheological properties requires further investigations.

Therefore, systematic studies on mineral phase stabilities, the spatial location of fluid formation in a rock assembly, and properties of fluids are essential to understanding the deep Earth H_2O cycle in order to critically evaluate the role of H_2O in the geochemical and geophysical dynamics of the solid Earth and its effect on volcanism, earthquakes and ore formation.

Challenge 5: How do Molecular Processes at Water-Mediated Interfaces Control Systems Relevant for Climate-, Astro-, and Geo-Sciences?

This overarching *challenge 5* interconnects the other four challenges of this pillar and is also an important cross-pillar topic, concerning the role of molecular processes at water-mediated interfaces in geo-, astro-, and climate-systems. At all conditions investigated, mass transfer or interaction between phases at the micro-scale represents a critical step for the dynamics of the macroscopic system [2.42], such as surface reactivity in interstellar ices and the surface influences for aerosol chemistry. This is most significant at low temperatures where the kinetics of the molecular processes at the interfaces is often rate-limiting. Even at the elevated temperatures of planetary interiors, molecular water on grain boundaries may enhance diffusive transport through bulk material by orders of magnitude compared to solid-state diffusion. In addition, their understanding is essential for other research areas such as environmental sciences, rock weathering, geochemistry, corrosion and chemical technology [2.43]. Interfaces are also relevant for the transport of complex multi-phase fluids, which can have safety, sustainability, and environmental impact, for example when it contains harmful substances. To understand such processes, a clear separation of various interfacial contributions at the solid–liquid and the liquid–gaseous interfaces is required depending on the structure and topology of the pore space. Fundamental insights gained within these research activities can then be integrated into high-level multi-physics models, for example [2.44,2.45]. Therefore, this field of interfaces will play an important role in all research challenges addressed in this pillar and will act as an important link across all pillars of the CMWS.

III.2.2 Preliminary Work and Competences

For tackling the challenges in the field of astrophysics and aerosols (*challenges 1* and *2*), we build on great experience with respect to generating and studying molecular ices [2.10,2.46,2.47], molecule-water clusters [2.48] as well as water jets [2.49-2.51]. For liquid water, we have world-leading competence on electron spectroscopy studies using clusters and liquid jets [2.52,2.53], and recently we have extended these surface-sensitive studies to free aerosol surfaces [2.54].

We have a variety of spectroscopic methods in our hands, ranging from high-resolution rotational, infrared and THz spectroscopy in the gas phase. They provide highly accurate molecular parameters and structural information, and we have great expertise in applying them to molecules and molecular clusters of different complexity. The structure-sensitive character of rotationally resolved spectroscopy allows for the unambiguous identification of structurally similar molecules, like conformers and isomers, which will be relevant for the identification of the different molecular species formed in the ice mantles. The technique was recently applied to study the structures of molecular water clusters up to $(H_2O)_{11}$ [2.55-2.57] as well as water-solute clusters [2.58,2.59].

Furthermore, there is a vast amount of expertise in the consortium to perform accurate theoretical quantum-chemical calculations to predict and analyse high-level spectra [2.60-2.62] and to astronomically observe and model the astrochemistry of key molecules involved. Recent studies on cold interstellar environments and a dedicated search for the presence of H_2O_2 molecules in star forming regions have shown that our understanding of water formation from condensed oxides is still in its infancy and far from a profound understanding [2.63].

Regarding *challenge 3*, we have long experience in the synthesis of nanoporous materials with defined pore size distributions [2.64,2.65]. Such materials can be used to study systematically the influence of confinement on phase equilibria in water–salt systems [2.66,2.67]. The materials can be synthesised with narrow pore sizes, defined pore geometries (e.g. cylindrical, spherical), with hierarchical pore structures and with varying chemical properties of their pore walls [2.68]. We

also have extensive experience in the characterisation of composite materials with salts using a variety of experimental techniques such as Raman [2.69] and NMR spectroscopy [2.70], XRD, SAXS/SANS, calorimetry and gas adsorption [2.64].

We are experienced in the use of thermodynamic models to predict phase equilibria in water–salt systems [2.65,2.66]. These models are based on equations representing the non-ideal electrolyte solution thermodynamics and have been successfully used to predict phase equilibria in complex mixed salt systems [2.67]. Such models were extended to include the influence of confinement in order to predict melting points in small pores or deliquescence of salts both in pores or as nanoparticles. These models are thus also applicable to aerosols (challenge *2*).

As relevant for challenges *3* and *4*, we have outstanding experience in using a large variety of high-pressure instrumentation capable of pressure generation up to 1000 GPa in diamond anvil cells (DAC) [2.71] < 35 GPa (WC anvils), and > 60 GPa (sintered diamond, SD anvils) in various multi-anvil presses (which can be summarised as Large Volume Presses, LVP) and up to 5 GPa in piston cylinder presses (PCP), for sample sizes from less than 0.01 mm (DAC) to more than 10 mm (PCP, LVP). The instruments are located in the different labs of the partners, and also at DESY's photon sources PETRA III and the European XFEL to perform high-level X-ray diffraction and X-ray spectroscopy experiments.

Novel *in situ* high-pressure and high-temperature synchrotron X-ray diffraction techniques are used and developed at the two Extreme Conditions Beamlines at PETRA III (P02.2 and P61B) to simulate various geothermal conditions along subduction zones to investigate mineral-volatile interactions. There is strong expertise to quantitatively study the incorporation of volatiles, including H_2O, in minerals, the high-pressure stability and the physical-chemical behaviour of these hydrous minerals, e.g. super hydrated clay minerals using the DAC up to 19 GPa [2.33] and Dense Hydrous Magnesium Silicates in multi-anvil experiments up to 20 GPa [2.27, 2.72, 2.73]. This expertise is complemented by competences for studying the mechanical behaviour and elastic properties of phases at the extreme conditions of the deep

Earth interior [2.74-2.78]. Using a Brillouin scattering instrument in combination with XRD at the Extreme Conditions Beamline (ECB) P02.2 has enabled dedicated studies on the elastic properties of minerals at extreme conditions [2.77, 2.79]. Novel capabilities for the study of highly reactive planetary H_2O-rich ice phases have been implemented at PETRA III by combining fast compression (milliseconds to seconds scale) experiments in dynamically-driven DACs (dDACs) with time-resolved X-ray diffraction techniques [2.80]. Furthermore, a new method of heating H_2O ice samples compressed in DAC using consecutive X-ray pulses of the European XFEL has been recently validated (so-called "X-ray heating"), thus opening new paths for exploring the properties and dynamics of planetary ices.

Insights into the formation of ore deposits have been achieved by X-ray absorption spectroscopy (XAS) on metals in fluids at high pressure and temperature. This technique will be enhanced in future using a new hydrothermal apparatus at beamline P65 at PETRA III. As a novel spectroscopic technique, X-ray Raman scattering can be applied for *in situ* studies of low Z elements' absorption edges such as the oxygen K-edge at extreme conditions using laser-heated or resistively heated DACs. This allowed, for example, the study of water and aqueous solutions at varying pressure and temperature [2.81]. Several prototype experiments have been performed recently at PETRA III (P01) [2.82,2.83] and will be further developed as part of the CMWS research in the near future at DESY and European XFEL.

III.2.3 Objectives

The aim of the planned research activities within this pillar 2 is to reveal and deeply understand the outstanding role of molecular water under the various conditions relevant to climate and environment, in particular geo- and astrophysics as well as aerosol physics/chemistry. These conditions include wide ranges in temperature and pressure, crystallinity/amorphicity and porosity, interaction with electromagnetic radiation, influence of composition and interaction with other fluid or solid phases as well as their interfaces. Deciphering the role of water in climate and environment is closely linked to our understanding of the fundamental properties of water (with multiple important links

to pillar 1), such as the hyperfine nuclear-spin symmetry breaking, non-covalent interactions between the molecules that influence their structures and chemical behaviour or its interaction with solid (oxides) phases and frozen volatiles through interfaces, in micropores or through incorporation into their crystal structure.

Micro and nano-sized water-solute clusters are relevant for aerosol formation and the basic processes in interstellar ice chemistry as well as key elements of climate and air pollution systems. A precise knowledge of the structures of these clusters is also of importance for understanding the influence of molecular water on conformational dynamics (pillar 4) and conformational preferences of biomolecules (pillar 5) illustrating strong cross-pillar connections, also on the methodological side. Therefore, the CMWS represents a unique platform for exchanging knowledge and techniques between individual communities in water-related research, resulting in a strong benefit for our research.

The objectives associated to *challenge 1* are fourfold and interconnected. Firstly, we aim at revealing the fundamental chemistry on ice grains, including their formation and the effect of harsh radiation, such as of short wavelengths, on these processes. It is one aim to investigate water formation and water-induced chemistry to test astrochemical models. We will focus on H_2O ices, doped with small and medium-sized molecules such as methanol or chiral molecules such as methyl oxirane. The H_2O ices will be deposited in various ways to produce a large range of porosities and amorphicity that will allow us to decipher the fundamental processes at the origin of molecule formation and gas–solid phase equilibria in interstellar ices and to understand the influence of surface effects, which will also be an objective associated with *challenge 5*. Secondly, we aim at understanding the interaction of astrochemically relevant molecules, such as polycyclic aromatic hydrocarbons, with water at the molecular level to mimic aggregation in interstellar chemistry. The obtained precise structures will provide us with important insights into the first steps of grain formation. A third objective relates to the prediction and spectroscopic detection of the nuclear spin *ortho/para* transitions in isolated water and in the presence of electric and magnetic

fields, of the kind existing in the astrophysical environments. Nuclear spin conversion in small water clusters, enhanced by mutual dipolar interactions, will also be extensively studied to explore the role of nuclear spin effects in the chemistry on ice grains. The spectroscopic data in form of precise transition frequencies will be used as first-hand information for dedicated astronomical searches for gas-phase molecules intimately linked to water and its formation processes in space. Finally, the fourth objective aims at constraining the phase diagrams and physical properties of H_2O ice and H_2O mixtures with other molecular compounds at conditions relevant for planetary interiors, > 150 GPa and 3000 K. A major focus here is the structure and thermal equations of state of unusual forms of ice stabilised under pressure, including superionic phases of H_2O ice and gas-filled H_2O clathrates and hydrates. These superionic phases have been proposed as a plausible origin for the anomalous magnetic fields detected in the ice giant planets. The new data will benchmark theoretical predictions of ice properties and will serve as input parameters for large-scale numerical models to constrain the internal structure and dynamic of ice giants and "water-rich" exoplanets, including the origin of their magnetic fields.

The chemical composition and structure of aerosols (*challenge 2*) determine their climate effects, both their efficiency as cloud condensation nuclei (CCN), and how much they scatter solar radiation. It has been proposed that due to the small size of aerosols, surface phenomena and processes become important (*challenge 5*), which shall be further explored here. First, surface-active species could affect the surface tension, which is a key parameter to understand water condensation into liquid droplets. Second, enrichment of organics into a hydrophobic surface layer may strongly influence condensation and evaporation rates and thus aerosol growth and CCN activity. Third, the surface composition could strongly affect aerosol chemical activity. Fourth, for small aerosols, which are microscopic systems, surface enrichment of a species will lead to bulk depletion, affecting macroscopic properties. Important properties of aerosols affecting climate and health are thus influenced by the composition and microscopic internal spatial distribution of chemical

species. Surface effects are, however, rarely taken into account in current climate models. It will be one of the objectives tackled with respect to *challenge 5* to improve our molecular level understanding of atmospheric surface phenomena and processes.

In order to understand the water cycle on Mars and other planets (*challenge 3*), we will study all phase equilibria involving water in different states, i.e. as vapor, as liquid (solvent) and as solid (ice, water of hydration) and the relevant salt mixtures using a variety of experimental techniques (section III.2.4). These equilibria will be considered both in bulk and in confinement where interfaces control the equilibrium behaviour. One of the main objectives of this challenge is to develop and use appropriate thermodynamics models to predict the relevant phase equilibria and to derive phase diagrams of salt–water systems under extreme temperature conditions, also considering non-ideal solution thermodynamics and the influence of confinement.

With respect to *challenge 4,* we aim to establish new phase stability diagrams of hydrous minerals, which will provide insights to their dehydration behaviour and their physical properties at conditions of the deep Earth. A new and unprecedented level of understanding of the kinetics of related phase transitions is an additional and very important aspect of this work. Overall, one important objective is to significantly improve the understanding of the stability, structure and property of hydrous silicates in order to assess their relevance to geodynamic processes. New data will help to model the effect of H_2O in larger scale geodynamic processes.

The objectives of our research with respect to the formation of ore deposits will be to experimentally determine mineral solubility and metal complexation in aqueous fluids (*challenge 4)*. In particular, the role of anionic ligands in the formation of metal species in the fluid will be assessed. The experimental results will, in conjunction with literature data, permit construction or improvement of quantitative thermodynamic models for the most important complexes of ore metals in natural hydrothermal fluids and extend the existing ones to higher temperatures. These thermodynamic models will advance our understanding of ore-

formation processes and promote the development of large-scale reactive flow models of ore-forming systems.

III.2.4 Methodologies

Since the systems under consideration stretch over several orders of magnitude with respect to temperature and pressure and also vary in density, pore structure and phase, our experimental approaches are highly diverse. They cover large areas of the electromagnetic spectrum, from the microwave frequency range to hard X-ray radiation to probe samples in different extreme environments, such as low temperatures or extremely high pressures. Ultimately, these data should be used to constrain large-scale models to get a clear understanding of the influence of H_2O in planetary and interstellar processes.

Interstellar chemistry in ice grains (*challenge 1*) will be mimicked in the laboratory by studying (i) interstellar ice analogues and (ii) gas-phase clusters of water and different solutes. The interstellar ice analogues will be produced by water vapor co-deposition of mixtures of H_2O and volatiles, resulting in compact or porous amorphous solid water with guest molecules adsorbed both to the external surfaces as well as inside the micropores. These will then be irradiated with electromagnetic radiation from the UV to X-rays, for example, to initiate chemical reactions. In this context different amorphicities, specific surface areas and microporosities will lead to transition state selectivity and different products. The products will be spectroscopically investigated, both *in situ* and in the gas phase after evaporation. For the study of water ices, surface-sensitive IR spectroscopy provides important information on the surface structure and composition (*challenge 5*). Specifically, the bulk surfaces and interface will be probed using IR/Raman-spectroscopy to reveal potential bond formation, and UV-VIS spectroscopy and electron spin/paramagnetic resonance to probe for bond dissociation and radicals. The gas phase will be probed using quadrupole mass spectrometry and microwave spectroscopy [2.48,2.59]. Astronomical observations of precursor molecules of water formation (such as O_2, O_3, H_2O_2, and OH) in the gas phase by means of millimetre wave and IR astronomy will provide a deep insight into the processes hidden in the ice grains of the ISM. For this, we will use a unique combination of experimental techniques as described here and the access to large telescope facilities such as the Atacama Large Millimeter/submillimeter Array (ALMA) and the Stratospheric Observatory for Infrared Astronomy (SOFIA). The evolution of the properties of small water clusters and nano solutions can be investigated in a bottom up approach using molecular ions, which allow an exact size selection. The element and size specificity of X-ray methods (such as using PETRA III/IV or FLASH) allows the investigation of how the electronic structure changes with the exact size and how complex phenomena emerge with size.

Water–solute clusters (ii) can mimic important interactions and reaction steps occurring on ice grains, and their reactivity can be probed with high-resolution molecular spectroscopy in advanced kinetic and dynamic experiments, which will be further developed as part of the CMWS research. Here, it is also particularly interesting to study the fundamental intermolecular interactions that shape the structures of these complexes.

Theoretical predictions for the *ortho-para* water project will be based on fully quantum mechanical simulations and consider all major electronic, nuclear motion and external field effects to a high degree of accuracy. The development of general variational approaches, such as used in the models TROVE and RichMol [2.60-2.62], offer comprehensive quantum-mechanical modelling of the nuclear spin-rovibrational motions and external-field interactions for arbitrary polyatomic molecule. Owing to the exact representation of the kinetic energy operator, the use of arbitrary curvilinear internal coordinates and the Eckart conditions to reduce couplings and minimise basis size, these are the only tools that are capable of meeting the highest accuracy demands of modern high-resolution spectroscopic and imaging experiments. The spectroscopic measurements on ortho/para water will be performed using mid-infrared frequency-comb techniques that allow traditional laser spectroscopy experiments with scanning cw-lasers to achieve unprecedented precision. Data will be collected and introduced to data bases accessible to both spectroscopists

and astronomers to improve and to test astro-chemical models of water formation and water induced chemistry in solid ice grains.

Ices under high pressure will be studied both *in situ* and after quench-recovery to ambient pressure using calorimetric, dielectric, IR/Raman spectroscopic and diffraction techniques, employing both laboratory-based X-ray experiments and the Hamburg X-ray facilities (PETRA III/IV and European XFEL). The phase diagram and structure of high-pressure icy compounds will be investigated by using novel dynamic compression experiments in DAC in conjunction with time-resolved X-ray diffraction diagnostics recently implemented at PETRA III and at the European XFEL. The Dynamic Compression Microscope proposed for PETRA IV will allow overcoming current limitations in the study of kinetics of phase transformations in icy compounds. Even higher pressure and temperature conditions (> 150 GPa and 3000 K) will be obtained by developing novel pump and probe X-ray heating experiments at the High-Energy-Density (HED) instrument of the European XFEL. Atmospherically relevant surfaces (*challenges 2* and *5*) will be studied at two levels. First, systematic studies of model aqueous solutions will be performed, carefully selected to isolate specific surface phenomena. Using surface-sensitive and chemically selective X-ray photo-electron spectroscopy (XPS) at the new FHI liquid-jet endstation at P04 at PETRA III, it is anticipated to obtain chemically selective information on the concentration and speciation at the surface as compared with the bulk and how this is affected by environmentally relevant parameters such as temperature, concentration, added salts, and pH. In a second step, surfaces of more complex and realistic systems will be studied, including aerosols and droplets. These will be generated using a range of methods mimicking different atmospheric processes, such as smog chambers, flow tubes, plunging jets, atomisers etc. and studied *in situ* in a beam of free flying particles or droplets akin to the liquid jet. The combination of XPS and *in situ* generated aerosols will open new, world-unique possibilities to directly probe aerosol surfaces. Furthermore, we will develop predictive models for surface composition as a function of the bulk composition in

terms of molecular structure and environmentally relevant parameters. Together with atmospheric scientists, we will also create parameterised descriptions of aerosol surface phenomena needed to properly include them in climate models.

For the nanoconfinement studies to mimic the thermodynamic conditions on Mars (*challenge 3*), several inorganic mesoporous materials will be considered as host matrices for water and salts mentioned above. Besides nanoporous silica as model material, more geo-relevant and chemically active compositions as perovskites (e.g. $SrTiO_3$-based systems) [2.84, 2.85], metal silicates (e.g. forsterite, fayalite), aluminophosphates and silicates [2.86-2.88] will be employed. Pore size and morphology will be tuned by means of templating strategies, pseudomorphic transformation or a combination of both. Aside from laboratory scale methods (e.g. Raman spectroscopy, NMR, DSC, XRD), the confinement of water and salts in such soil-like pore networks and their phase changes will be investigated at large scale facilities (PETRA III/IV) via small-angle scattering of X-rays and neutrons (SAXS/SANS). This technique covers a fundamental role in the characterisation of confined matter as it addresses structural and morphological changes in quantitative and direct fashion [2.89-2.92]. Taking advantage of contrast variation techniques [2.93], SAXS/SANS will be used to monitor the processes involving density variation of the confined salts and their solutions (e.g. phase change equilibria, deliquescence, and hydration). In this respect, the employment of the new P62 anomalous SAXS beamline of PETRA III will be particularly relevant. Modelling of such phase equilibria will be based on electrolyte solution models (e.g. Pitzer type models) extended to low temperature and considering interfacial energy effects.

The stability of hydrous mineral phases and incorporation of H_2O in mineral phases at conditions of the Earth interior (*challenge 4*) will be investigated using high-pressure high-temperature experiments with large-volume presses and diamond anvil cells (DAC) installed at the PETRA III facility and in future at PETRA IV as well as the European XFEL. X-ray diffraction will serve as the tool for phase identification, structure determination, and texture characterisation. Vibrational

spectroscopy (IR and Raman spectroscopy) will serve as additional tool for pinpointing the structural incorporation of H_2O. In many compositional spaces, the stable phases and phase assemblies in response to a given pressure and temperature may not be quenchable and thus have to be analysed *in situ* at these extreme conditions. Time-dependent *in situ* experiments also allow for assessing reaction kinetics. A new field of experimental techniques that will make excellent use of the increased high-energy coherence of PETRA IV are hard X-ray imaging techniques that are currently under development at PETRA III. Techniques such as phase-contrast X-ray imaging applied to samples in pressure and temperature generating devices such as large volume press and the DAC will be part of the new methods developed in the framework of the CMWS. At P61B, LVP studies on the acoustic emissions from embrittlement caused by dehydration and deformation in candidate hydrous mantle minerals such as phase Shy-B will be performed.

Mineral solubility and metal complexation in aqueous fluids will be determined by *in situ* X-ray absorption spectroscopic techniques (*challenge 4*). Samples will be equilibrated in hydrothermal autoclaves [2.94] or hydrothermal DACs dedicated to X-ray spectroscopic techniques [2.95-2.97]. These apparatuses allow for equilibration of minerals with fluids of various compositions to determine reaction rates and equilibrium metal contents. Furthermore, the metal complexes present in these fluids at any given pressure and temperature will be determined by X-ray absorption spectroscopy. A particular focus will be on the effect of potential ligands such as Cl and F on the metal concentration and metal species. Further insight to the microscopic structure of these fluids will be acquired by in-situ Raman and in-situ X-ray Raman spectroscopy that can be performed in hydrothermal DACs. In addition to the investigations at the structural level, quantitative electron density distributions can be obtained by using quantum crystallography methods such as multipole refinement and/or Hirshfeld atom refinement to get accurate and precise positions of hydrogen atoms and reliable estimations of their thermal motion, energy of interactions and aspherical character in crystal lattices [2.98-2.100].

Methods for developing a deeper theoretical understanding of mesoscopic and large-scale systems will be based mostly on *ab initio* simulations with a quantum-mechanical treatment of the electrons using density functional theory [2.101]. Such simulations will give access to the electronic properties, ionic structure and chemical bonding on a scale of a few 100 molecules and for times of up to 100 ps. Experimental observables like structure factors [2.101] and electromagnetic scattering or absorption spectra for various wavelengths can be calculated, so that these theoretical methods form an indispensable part for understanding and interpreting experimental data. Relations for thermophysical quantities (e.g. [2.102,2.103] like the EoS, phase boundaries and transport properties (conductivity, viscosity, particle diffusion coefficients) (e.g. [2.104-2.106]) can be calculated as well. Such properties are necessary to describe mesoscopic and larger-scale processes in experiments and applications, e.g. by finite-element or hydrodynamic modelling.

III.2.5 References

[2.1] E. F. van Dishoeck, E. Herbst, D. A. Neufeld, Interstellar Water Chemistry: From Laboratory to Observations. Chem. Rev. 113, 9043–9085 (2013).

[2.2] Cologne database for molecular spectroscopy (CDMS) https://cdms.astro.uni-koeln.de (Accessed: 22.03.2021).

[2.3] E. F. van Dishoeck, Astrochemistry of dust, ice and gas: introduction and overview. Faraday Discuss. 168, 9–47 (2014).

[2.4] D. J. Burke, W. A. Brown, Ice in space: surface science investigations of the thermal desorption of model interstellar ices on dust grain analogue surfaces. Phys. Chem. Chem. Phys. 12, 5947–5969 (2010).

[2.5] H. Linnartz, S. Ioppolo, G. Fedoseev, Atom addition reactions in interstellar ice analogues. Int. Rev. Phys. Chem. 34, 205–237 (2015).

[2.6] K. I. Öberg, Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules. Chem. Rev. 116, 9631–9663 (2016).

[2.7] P. de Marcellus, C. Meinert, I. Myrgorodska, L. Nahon, T. Buhse, L. L. S. d'Hendecourt, U. J. Meierhenrich, Aldehydes and sugars from evolved precometary ice analogs: Importance of ices in astrochemical and prebiotic evolution. Proc. Natl. Acad. Sci. 112, 965–970 (2015).

[2.8] F. Du, B. Parise, P. Bergman, Production of interstellar hydrogen peroxide (H_2O_2) on the surface of dust grains. Astron. Astrophys. 538, A91 (2012).

[2.9] D. A. Horke, Y.-P. Chang, K. Długołęcki, J. Küpper, Separating para and ortho water. Angew. Chem. Int. Ed Engl. 53, 11965–11968 (2014).

[2.10] T. Loerting, N. Giovambattista, Amorphous ices: experiments and numerical simulations. J. Phys. Condens. Matter. 18, R919–R977 (2006).

[2.11] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, M. Parrinello, Superionic and metallic states of water and ammonia at giant planet conditions. Science. 283, 44–46 (1999).

[2.12] M. Millot, F. Coppari, J. R. Rygg, A. Correa Barrios, S. Hamel, D. C. Swift, J. H. Eggert, Nanosecond X-ray diffraction of shock-compressed superionic water ice. Nature 569, 251–255 (2019).

[2.13] M. Bethkenhagen, D. Cebulla, R. Redmer, S. Hamel, Superionic Phases of the 1:1 Water–Ammonia Mixture. J. Phys. Chem. A. 119, 10582–10588 (2015).

[2.14] B. A. Baum, P. Yang, S. Nasiri, A. K. Heidinger, A. Heymsfield, J. Li, Bulk Scattering Properties for the Remote Sensing of Ice Clouds. Part III: High-Resolution Spectral Models from 100 to 3250 cm−1. J. Appl. Meteorol. Climatol. 46, 423–434 (2007).

[2.15] IPCC (2007) Climate Change 2007: The physical science basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate Change. Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.), Cambridge University Press, Cambridge

[2.16] S. Bony, B. Stevens, D. M. W. Frierson, C. Jakob, M. Kageyama, R. Pincus, T. G. Shepherd, S. C. Sherwood, A. P. Siebesma, A. H. Sobel, M. Watanabe, M. J. Webb, Clouds, circulation and climate sensitivity. Nat. Geosci. 8, 261–268 (2015).

[2.17] K. G. Libbrecht, The physics of snow crystals. Rep. Prog. Phys. 68, 855 (2005). K. G. Libbrecht, A Quantitative Physical Model of the Snow Crystal Morphology Diagram. ArXiv191009067 Cond-Mat Physicsphysics (2019) (available at http://arxiv.org/abs/1910.09067).

[2.18] B. J. Finlayson-Pitts, Reactions at surfaces in the atmosphere: integration of experiments and theory as necessary (but not necessarily sufficient) for predicting the physical chemistry of aerosols. Phys. Chem. Chem. Phys. 11, 7760–7779 (2009).

[2.19] J. F. Davies, R. E. H. Miles, A. E. Haddrell, J. P. Reid, Influence of organic films on the evaporation and condensation of water in aerosol. Proc. Natl. Acad. Sci. 110, 8807–8812 (2013).

[2.20] W. C. Feldman, Global distribution of near-surface hydrogen on Mars. J. Geophys. Res. 109, E09006 (2004).

[2.21] D. T. Vaniman, D. L. Bish, S. J. Chipera, C. I. Fialips, J. William Carey, W. C. Feldman, Magnesium sulphate salts and the history of water on Mars. Nature. 431, 663–665 (2004).

[2.22] M. M. Osterloo, V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldridge, P. R. Christensen, L. L. Tornabene, F. S. Anderson, Chloride-Bearing Materials in the Southern Highlands of Mars. Science. 319, 1651–1654 (2008).

[2.23] S. C. Cull, R. E. Arvidson, J. G. Catalano, D. W. Ming, R. V. Morris, M. T. Mellon, M. Lemmon, Concentrated perchlorate at the Mars Phoenix landing site: Evidence for thin film liquid water on Mars. Geophys. Res. Lett. 37 (2010).

[2.24] M. C. Malin, K. S. Edgett, L. V. Posiolova, S. M. McColley, E. Z. N. Dobrea, Present-day impact cratering rate and contemporary gully activity on Mars. Science. 314, 1573–1577 (2006).

[2.25] R. V. Gough, V. F. Chevrier, M. A. Tolbert, Formation of aqueous solutions on Mars via deliquescence of chloride–perchlorate binary mixtures. Earth Planet. Sci. Lett. 393, 73–82 (2014).

[2.26] G. H. Findenegg, S. Jähnert, D. Akcakayiran, A. Schreiber, Freezing and Melting of Water Confined in Silica Nanopores. ChemPhysChem. 9, 2651–2659 (2008).

[2.27] J. Meissner, A. Prause, G. H. Findenegg, Secondary Confinement of Water Observed in Eutectic Melting of Aqueous Salt Systems in Nanopores. J. Phys. Chem. Lett. 7, 1816–1820 (2016).

[2.28] J. G. Dash, A. W. Rempel, J. S. Wettlaufer, The physics of premelted ice and its geophysical consequences. Rev. Mod. Phys. 78, 695–741 (2006).

[2.29] H. Hansen-Goos, E. S. Thomson, J. S. Wettlaufer, On the edge of habitability and the extremes of liquidity. Planet. Space Sci. 98, 169–181 (2014).

[2.30] H. Ni, Y.-F. Zheng, Z. Mao, Q. Wang, R.-X. Chen, L. Zhang, Distribution, cycling and impact of water in the Earth's interior. Natl. Sci. Rev. 4, 879–891 (2017).

[2.31] Y. Tatsumi, S. Eggins, Subduction Zone Magmatism, Blackwell Science, Cambridge, Mass., USA, 1. Edition., (1995).

[2.32] M. W. Schmidt, S. Poli, Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth Planet. Sci. Lett. 163, 361–379 (1998).

[2.33] H. Hwang, D. Seoung, Y. Lee, Z. Liu, H. P. Liermann, H. Cynn, T. Vogt, C. C. Kao, H. K. Mao, A role for subducted super-hydrated kaolinite in Earth's deep water cycle. Nat. Geosci. 10, 947–953 (2017).

[2.34] T. L. Grove, N. Chatterjee, S. W. Parman, E. Médard, The influence of H2O on mantle wedge melting. Earth Planet. Sci. Lett. 249, 74–89 (2006).

[2.35] J. Wang, D. Zhao, Z. Yao, Seismic anisotropy evidence for dehydration embrittlement triggering intermediate-depth earthquakes. Sci. Rep. 7, 1–9 (2017).

[2.36] M. Mookherjee, S. Speziale, H. Marquardt, S. Jahn, B. Wunder, M. Koch-Müller, H. P. Liermann, Equation of state and elasticity of the 3.65 Å phase: Implications for the X-discontinuity. Am. Mineral. 100, 2199–2208 (2015).

[2.37] M. Nishi, T. Irifune, J. Tsuchiya, Y. Tange, Y. Nishihara, K. Fujino, Y. Higo, Stability of hydrous silicate at high pressures and water transport to the deep lower mantle. Nat. Geosci. 7, 224–227 (2014).

[2.38] W. R. Panero, R. Caracas, Stability of phase H in the MgSiO4H2–AlOOH–SiO2 system. Earth Planet. Sci. Lett. 463, 171–177 (2017).

[2.39] J. Tsuchiya, M. Mookherjee, Crystal structure, equation of state, and elasticity of phase H (MgSiO4H2) at Earth's lower mantle pressures. Sci. Rep. 5, 1–8 (2015).

[2.40] P. Weis, T. Driesner, C. A. Heinrich, Porphyry-copper ore shells form at stable pressure-temperature fronts within dynamic fluid plumes. Science 338, 1613–1616 (2012).

[2.41] G. S. Pokrovski, A. Y. Borisova, A. Y. Bychkov, in Thermodynamics of Geothermal Fluids (De Gruyter Mouton, 2018), vol. 76, pp. 165–218. C. J. Sahle, C. Sternemann, C. Schmidt, S. Lehtola, S. Jahn, L. Simonelli, S. Huotari, M. Hakala, T. Pylkkänen, A. Nyrow, K. Mende, M. Tolan, K. Hämäläinen, M. Wilke, Microscopic structure of water at elevated pressures and temperatures. Proc. Natl. Acad. Sci. U. S. A. 110, 6301–6306 (2013).

[2.42] B. Noziere, Don't forget the surface. Science 351, 1396–1397 (2016).

[2.43] O. Björneholm, M. H. Hansen, A. Hodgson, L. M. Liu, D. T. Limmer, A. Michaelides, P. Pedevilla, J. Rossmeisl, H. Shen, G. Tocci, E. Tyrode, M. M. Walz, J. Werner, H. Bluhm, Water at Interfaces. Chem. Rev. 116, 7698–7726, (2016).

[2.44] R. Lu, T. Nagel, H. Shao, O. Kolditz, H. Shao, Modeling of Dissolution-Induced Permeability Evolution of a Granite Fracture Under Crustal Conditions. J. Geophys. Res. Solid Earth. 123, 5609–5627 (2018).

[2.45] B. Zhu, Z. Ye, L. Wang, D. Kong, W. Xu, O. Kolditz, T. Nagel, Y. Chen, Hydro-mechanical behavior of unsaturated soil surrounding a heated pipeline considering moisture evaporation and condensation. Comput. Geotech. 119, 103377 (2020).

[2.46] J. N. Stern, M. Seidl-Nigsch, T. Loerting, Evidence for high-density liquid water between 0.1 and 0.3 GPa near 150 K. Proc. Natl. Acad. Sci. U. S. A. 116, 9191–9196 (2019).

[2.47] L. J. Plaga, A. Raidt, V. Fuentes Landete, K. Amann-Winkel, B. Massani, T. M. Gasser, C. Gainaru, T. Loerting, R. Böhmer, Amorphous and crystalline ices studied by dielectric spectroscopy. J. Chem. Phys. 150, 234503 (2019).

[2.48] S. R. Domingos, K. Martin, N. Avarvari, M. Schnell, Angew. Chemie, in press, doi:10.1002/ange.201902889.

[2.49] B. Winter, M. Faubel, Photoemission from liquid aqueous solutions. Chem. Rev. 106, 1176–1211 (2006).

[2.50] I. Unger, R. Seidel, S. Thürmer, M. N. Pohl, E. F. Aziz, L. S. Cederbaum, E. Muchová, P. Slavíček, B. Winter, N. V. Kryzhevoi, Observation of electron-transfer-mediated decay in aqueous solution. Nat. Chem. 9, 708–714 (2017). M. N. Pohl, E. Muchová, R. Seidel, H. Ali, Š. Sršeň, I. Wilkinson, B. Winter, P. Slavíček, Do water's electrons care about electrolytes? Chem. Sci. 10, 848–865 (2019).

[2.51] J. Werner, I. Persson, O. Björneholm, D. Kawecki, C. M. Saak, M. M. Walz, V. Ekholm, I. Unger, C. Valtl, C. Caleman, G. Öhrwall, N. L. Prisle, Shifted equilibria of organic acids and bases in the aqueous surface region. Phys. Chem. Chem. Phys. 20, 23281–23293 (2018).

[2.52] N. L. Prisle, N. Ottosson, G. Öhrwall, J. Söderström, M. Dal Maso, O. Björneholm, Surface/bulk partitioning and acid/base speciation of aqueous decanoate: Direct observations and atmospheric implications. Atmos. Chem. Phys. 12, 12227–12242 (2012).

[2.53] M. M. Walz, C. Caleman, J. Werner, V. Ekholm, D. Lundberg, N. L. Prisle, G. Öhrwall, O. Björneholm, Surface behavior of amphiphiles in aqueous solution: A comparison between different pentanol isomers. Phys. Chem. Chem. Phys. 17, 14036–14044 (2015).

[2.54] L. Hautala, K. Jänkälä, M. H. Mikkelä, P. Turunen, N. L. Prisle, M. Patanen, M. Tchaplyguine, M. Huttula, Probing RbBr solvation in freestanding sub-2 nm water clusters. Phys. Chem. Chem. Phys. 19, 25158–25167 (2017).

[2.55] C. Pérez, M. T. Muckle, D. P. Zaleski, N. A. Seifert, B. Temelso, G. C. Shields, Z. Kisiel, B. H. Pate, Structures of cage, prism, and book isomers of water hexamer from broadband rotational spectroscopy. Science 336, 897–901 (2012).

[2.56] J. O. Richardson, C. Pérez, S. Lobsiger, A. A. Reid, B. Temelso, G. C. Shields, Z. Kisiel, D. J. Wales, B. H. Pate, S. C. Althorpe, Concerted hydrogen-bond breaking by quantum tunneling in the water hexamer prism. Science 351, 1310–1313 (2016).

[2.57] C. Pérez, D. P. Zaleski, N. A. Seifert, B. Temelso, G. C. Shields, Z. Kisiel, B. H. Pate, Hydrogen Bond Cooperativity and the Three-Dimensional Structures of Water Nonamers and Decamers. Angew. Chemie Int. Ed. 53, 14368–14372 (2014).

[2.58] C. Pérez, A. Krin, A. L. Steber, J. C. López, Z. Kisiel, M. Schnell, Wetting Camphor: Multi-Isotopic Substitution Identifies the Complementary Roles of Hydrogen Bonding and Dispersive Forces. J. Phys. Chem. Lett. 7, 154–160 (2016).

[2.59] A. L. Steber, C. Pérez, B. Temelso, G. C. Shields, A. M. Rijs, B. H. Pate, Z. Kisiel, M. Schnell, Capturing the Elusive Water Trimer from the Stepwise Growth of Water on the Surface of the Polycyclic Aromatic Hydrocarbon Acenaphthene. J. Phys. Chem. Lett. 8, 5744–5750 (2017).

[2.60] A. Yachmenev, S. N. Yurchenko, Automatic differentiation method for numerical construction of the rotational-vibrational Hamiltonian as a power series in the curvilinear internal coordinates using the Eckart frame. J. Chem. Phys. 143, 14105 (2015).

[2.61] A. Owens, A. Yachmenev, RichMol: A general variational approach for rovibrational molecular dynamics in external electric fields. J. Chem. Phys. 148, 124102 (2018).

[2.62] A. Yachmenev, J. Küpper, Communication: General variational approach to nuclear-quadrupole coupling in rovibrational spectra of polyatomic molecules. J. Chem. Phys. 147, 141101 (2017).

[2.63] G. W. Fuchs, D. Witsch, D. Herberth, M. Kempkes, B. Stanclik, J. Chantzos, H. Linnartz, K. Menten, T. F. Giesen, Deep search for hydrogen peroxide toward pre- and protostellar objects: Testing the pathway of grain surface water formation. Astron. Astrophys. 636, A114 (2020).

[2.64] M. Bilo, Y. J. Lee, M. Fröba, Millimeter-sized micellar-templated silica beads and phenylene-bridged mesoporous organosilica beads. Microporous Mesoporous Mater. 284, 327–335 (2019).

[2.65] A. C. Juhl, C. P. Elverfeldt, F. Hoffmann, M. Fröba, Porous carbon monoliths with pore sizes adjustable between 10 nm and 2 Mm prepared by phase separation – New insights in the relation between synthesis composition and resulting structure. Microporous Mesoporous Mater. 255, 271–280 (2018).

[2.66] J. B. Mietner, F. J. Brieler, Y. J. Lee, M. Fröba, Properties of Water Confined in Periodic Mesoporous Organosilicas: Nanoimprinting the Local Structure. Angew. Chemie Int. Ed. 56, 12348–12351 (2017).

[2.67] N. Lindström, T. Talreja, K. Linnow, A. Stahlbuhk, M. Steiger, Crystallization behavior of Na2SO4-MgSO4 salt mixtures in sandstone and comparison to single salt behavior. Appl. Geochemistry. 69, 50–70 (2016).

[2.68] F. Hoffmann, M. Fröba, Vitalising porous inorganic silica networks with organic functions—PMOs and related hybrid materials. Chem. Soc. Rev. 40, 608–620 (2011).

[2.69] B. R. Bzdek, J. P. Reid, J. Malila, N. L. Prisle, The surface tension of surfactant-containing, finite volume droplets. Proc. Natl. Acad. Sci. U. S. A. 117, 8335–8343 (2020).

[2.70] O. Mankinen, V. V. Zhivonitko, A. Selent, S. Mailhiot, S. Komulainen, N. L. Prisle, S. Ahola, V. V. Telkki, Ultrafast diffusion exchange nuclear magnetic resonance. Nat. Commun. 11, 1–8 (2020).

[2.71] V. Cerantola, E. Bykova, I. Kupenko, M. Merlini, L. Ismailova, C. McCammon, M. Bykov, A. I. Chumakov, S. Petitgirard, I. Kantor, V. Svitlyk, J. Jacobs, M. Hanfland, M. Mezouar, C. Prescher, R. Rüffer, V. B. Prakapenka, L. Dubrovinsky, Stability of iron-bearing carbonates in the deep Earth's interior. Nat. Commun. 8, 1–9 (2017).

[2.72] M. Mrosko, M. Koch-Müller, C. McCammon, D. Rhede, J.R. Smyth, R. Wirth, Water, iron, redox environment: effects on the wadsleyite-ringwoodite phase transition, Contributions to Mineralogy and Petrology 170, 9 (2015)

[2.73] B. Wunder, R. Wirth, M. Koch-Müller, The 3.65 Å phase in the system MgO-SiO2-H2O: Synthesis, composition, and structure, American Mineragolgist 96, 8-9, 1207 – 1214 (2011).

[2.74] S. Speziale, T.S. Duffy, R.J. Angel, Single-crystal elasticity of fayalite to 12 GPa, Journal of Geophysical Research 109, B12202 (2004).

[2.75] H. Marquardt, S. Speziale, H.J. Reichmann, D.J. Frost, F.R. Schilling, E.J. Garnero, Elastic Shear Anisotropy of Ferropericlase in Earth´s Lower Mantel, Science 324, Issue 5924, 224-226 (2009).

[2.76] S. Speziale, H. Marquardt, T.S. Dyffy, Brillouin Scattering and ist Application in Geosciences, Rev. Mineral. Geochem., 78, 543-603 (2014).

[2.77] J. Buchen, H. Marquardt, S. Speziale, T. Kawazoe, T. Boffa Ballaran, A. Kurnosov, High-pressure single-crystal elasticity of wadsleyite and the seismic signature of water in the shallow transition zone, Earth and Planetary Science Latters 498, 77-87 (2018).

[2.78] K. Schulze, H. Marquardt, T. Kawazoe, T. Boffa Ballaran, C. Mccammon, M. Koch-Müller, A. Kurnosov, K. Marquardt, Seismically Invisible Water in Earth's Transition Zone? Earth and Planetary Science Letters 498, 9-16 (2018).

[2.79] M.G. Pamato, A. Kurnosov, T. Boffa Ballaran, D.J. Frost, L. Ziberna, M. Giannini, S. Speziale, S.N. Tkahcev, K.K. Zhuravlev, V.B. Prakapenka, Single crystal elasticity of majoritic garnets: Stagnant slabs and thermal anomalies at the base of the transition zone, Earth and Planetary Science Letters 451, 114-124 (2016).

[2.80] A.S.J. Méndez, H. Marquardt, R.J. Husband, I. Schwark, J. Mainberger, K. Glazyrin, A. Kurnosov, C. Otzen, N. Satta, J. Bednarcik, H.-P. Liermann, A resistively heated dynamic diamond anvil cell (RHdDAC) for fast compression x-ray diffraction experiments at high temperatures, Review of Scientific Instrumrtnes 91, 073906 (2020).

[2.81] C.J. Sahle, J. Niskanen, C. Schmidt, J. Stefanski, K. Gilmore, Y. Forov, S. Jahn, M. Wilke, C. Sternemann, Cation Hydration in Supercritical NaOH and HCl Aqueous Solutions, J. Phys. Chem. B 121, 50 11383-11389 (2017).

[2.82] G. Spiekermann, I. Kupenko, S. Petitgirard, M. Harder, A. Nyrow, C. Weis, C. Albers, N. Biedermann, L. Libon, C. J. Sahle, V. Cerantola, K. Glazyrin, Z. Konopkova, R. Sinmyo, W. Morgenroth, I. Sergueev, H. Yavas, L. Dubrovinsky, M. Tolan, C. Sternemann, M. Wilke, A portable on-axis laser heating system for near-90° X-ray spectroscopy: Application to ferropericlase and iron silicide. Journal of Synchrotron Radiation, 27, 414-424 (2020).

[2.83] M. Elbers., C. Schmidt, C. Sternemann, C.J. Sahle, S. Jahn, C. Albers, R. Sakrowski, H. Gretarsson, M. Sundermann, M. Tolan, M. Wilke, Ion association in hydrothermal aqueous NaCl solu- tions: Implications for the microscopic structure of supercritical water. Physical Chemistry Chemical Physics (in review).

[2.84] B.E. Kayaalp, Y.J. Lee, A. Kornowski, S. Gross, M. D'Arienzo, S. Mascotto, Cooperative assembly synthesis of mesoporous $SrTiO_3$ with enhanced photocatalytic properties, RSC Adv. 6, 90401–90409 (2016).

[2.85] B. Kayaalp, S. Lee, K. Klauke, S. Jongsu, L. Nodari, A. Kornowski, W. Jung, S. Mascotto, Template-free mesoporous $La_{0.3}Sr_{0.7}Ti_{1-x}Fe_xO_{3+/-\delta}$ for CH_4 and CO oxidation catalysis, Appl. Catal. B 245, 536–545 (2019).

[2.86] M. Fröba, R. Köhn, G. Bouffaud, O. Richard, G. vanTendeloo, Fe2O3 Nanoparticles within Mesoporous MCM-48 Silica: In Situ Formation and Characterization, Chem. Mater. 11, 2858–2865 (1999).

[2.87] U. Ciesla, M. Fröba, G.D. Stucky, F. Schüth, Highly Ordered Porous Zirconias from Surfactant-Controlled Syntheses: Zirconium Oxide−Sulfate and Zirconium Oxo Phosphate, Chem. Mater. 11, 227–234 (1999).

[2.88] M. Tiemann, M. Schulz, C. Jäger, M. Fröba, Mesoporous Aluminophosphate Molecular Sieves Synthesized under Nonaqueous Conditions, Chem. Mater. 13, 2885–2891 (2001).

[2.89] M. Erko, D. Wallacher, G.H. Findenegg, O. Paris, Repeated sorption of water in SBA-15 investigated by means of in situ small-angle x-ray scattering, J. Phys. Condens Matter 24, 284112 (2012).

[2.90] Erko, M., Wallacher, D., Hoell, A., Hauß, T., Zizak, I., Paris O., Density minimum of confined water at low temperatures: a combined study by small-angle scattering of X-rays and neutrons, Phys. Chem. Chem. Phys. 14, 3852–3858 (2012).

[2.91] A. Petzold, A. Juhl, J, Scholz, B. Ufer, G. Goerigk, M. Fröba, M. Ballauff, S. Mascotto, Distribution of Sulfur in Carbon/Sulfur Nanocomposites Analyzed by Small-Angle X-ray Scattering, Langmuir 32, 2780–2786 (2016).

[2.92] J. Scholz, B. Kayaalp, A. Juhl, D. Clemens, M. Fröba, S. Mascotto, Severe Loss of Confined Sulfur in Nanoporous Carbon for Li–S Batteries under Wetting Conditions, ACS Energy Letters 3, 387–392 (2018).

[2.93] S. Mascotto, D. Kuzmicz, D. Wallacher, M. Siebenbürger, D. Clemens, S. Risse, J. Yuan, M. Antonietti, M. Ballauff, Poly(ionic liquid)-derived nanoporous carbon analyzed by combination of gas physisorption and small-angle neutron scattering, Carbon 82, 425–435 (2015).

[2.94] D. Testemale, R. Argoud, O. Geaymond, J.L. Hazemann, High pressure/high temperature cell for x-ray absorption and scattering techniques, Rev. of Scientific Instr. 76, 043905 (2005).

[2.95] C. Schmidt C. and K. Rickers, In-situ determination of mineral solubilities in fluids using a hydrothermal diamond-anvil cell and SR-XRF: Solubility of AgCl in water, Am. Mineral 88, 288-292 (2003).

[2.96] C. Schmidt, K. Rickers, D.H. Bilderback, R. Huang, In situ synchrotron-radiation XRF study of REE phosphate dissolution in aqueous fluids to 800 degrees C, Lithos 95, 87-102 (2007).

[2.97] M. Wilke, C. Schmidt, F. Farges, V. Malavergne, L. Gautron, A. Simionovici, M. Hahn, P.E. Petit, Structural environment of iron in hydrous aluminosilicate glass and melt-evidence from X-ray absorption spectroscopy, Chem. Geol., 229, 144-161 (2006).

[2.98] M. Woińska, S. Grabowsky, P.M. Dominiak, K. Woźniak, D. Jayatilaka, Hydrogen atoms can be located accurately and precisely by x-ray crystallography, Science Advances, Vol. 2 no. 5, e1600192 (2016).

[2.99] M. Stachowicz, M. Malińska, J. Parafiniuk, K. Woźniak, Experimental observation of charge-shift bond in fluorite CaF2, Acta Crystallographica B73, 643-653 (2017).

[2.100] R. Gajda, M. Stachowicz, A. Makal, S. Sutuła, J. Parafiniuk, P. Fertay, K. Woźniak, Experimental Charge Density of Grossular Under Pressure - a Feasibility Study IUCR J, 7(3) 383-392 (2020).

[2.101] D. Marx, J. Hutter, Ab Initio Molecular Dynamics, Cambridge University Press, Cambridge (2009).

[2.102] S. Jahn, J. Dubrail, M. Wilke, Complexation of Zr and Hf monomers in supercritical aqueous solutions: Insights from ab initio molecular dynamics simulations, Chem. Geol., 418, 30-39 (2015).

[2.103] French M., Desjarlais M. P., Redmer R., Ab initio calculation of thermodynamic potentials and entropies for superionic water, Phys. Rev. E 93, 022140 (2016).

[2.104] B.B.L. Witte, M. Shihab, S.H. Glenzer, R. Redmer, Ab initio simulations of the dynamic ion structure factor of warm dense lithium, Phys. Rev. B 95, 144105 (2017).

[2.105] M. Bethkenhagen, E.R. Meyer, S. Hamel, N. Nettelmann, M. French, L. Scheibe, C. Ticknor, L.A. Collins, J.D. Kress, J.J. Fortney, R. Redmer, Planetary Ices and the Linear Mixing Approximation, Astrophys. J. 848, 67 (2017).

[2.106] M. French, Thermal conductivity of dissociating water—an ab initio study, New J. Phys. 21, 023007 (2019).

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Water in Energy Research and Technology

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III.3 Water in Energy Research and Technology

III.3.1 Scientific Challenges and State of the Art

Water does not only play a role as a solvent, but also directly as a chemical or reactant in hydrolysis, olation and oxolation. It even potentially acts as template when nanostructures and nanopores are formed. The characterisations how water – especially under defined spatial and temporal conditions – conducts a chemical reaction, activates processes like corrosion, or influences catalysis and its role in confined chemistry (of pharmaceutical application) are two scientific challenges on which pillar 3 focuses. Further challenges to be mentioned include the study of water in electrochemistry and electrocatalysis: we want to determine the physical and chemical properties of water at the molecular level in the context of energy conversion technology and understand its contributions to the reaction mechanisms underlying these technologies. How the transport properties of water change through spatial confinement or at interfaces and their experimental determination as well as theoretical description is another challenge. Due to the vicinity to applications, the challenges are all quite complex and the goal of understanding and realistically describing the suggested systems can only be reached stepwise.

Challenge 1: Understanding Localised Corrosion

Wet electrochemical corrosion involving water as active transport medium is a major threat to the stability of most metallic materials, often causing catastrophic failure and immense costs to society. The benefits of detailed knowledge of corrosion mechanisms and control are therefore significant in many industrial applications from corrosion-resistant passive metals, steels, or new high-strength alloys, needed for many modern applications from electromobility to wind power and heterogeneous catalysis. Advances in surface science have revealed detailed insights in the homogeneous modes of corrosion on well-defined, flat surfaces. Mostly averaging over larger areas, the surface-science approach has provided understanding of the development and stability of rather smooth layers, passive films, and the structural characterisation of interfaces involved in corrosion, by successfully addressing simplified model systems [3.1].

Despite of this, corrosion engineering of typically complex, heterogeneous commercial materials is very challenging and the modern design of corrosion resistant alloys and steels is based on a huge portfolio of material tests. Today's understanding of wet corrosion has severe limitations because of heterogeneities in truly three-dimensional nano-architectured materials such as precipitations, elemental variations (eventually caused by oxide or hydroxide scale growth itself), which are often the origin of detrimental localised corrosion and treacherous pitting [3.2]. *In situ* characterisation with high spatial resolution is in the context of wet corrosion of particular importance because of the often only a few nanometres thick passive films and lateral heterogeneities in the sub-micrometre/nanometre range [3.3]. Localised corrosion events occur stochastically, preventing systematic and predictable observation. In addition, mechanical stress can promote wet chemical corrosion along grain boundaries leading to stress corrosion cracking, leading to mechanical failure of materials [3.4]. One challenge is here to identify the grain boundary structure responsible for this combined failure mechanism. Apart from the destructive effects of wet chemical corrosion it can also constructively be utilised for a tailored fabrication of materials with novel properties. Controlled corrosive dealloying may lead to 3D nanoporous materials with variable architecture and hierarchical levels for novel applications, i.e. in biomaterials [3.5, 3.6] or 2D nanoporous arrays, which can be used as templates for nanoscale electrochemical deposition [3.7]. The challenge consists here in tailoring independently nanopore size, morphology as well as surface composition and hierarchy by the wet chemical dealloying process.
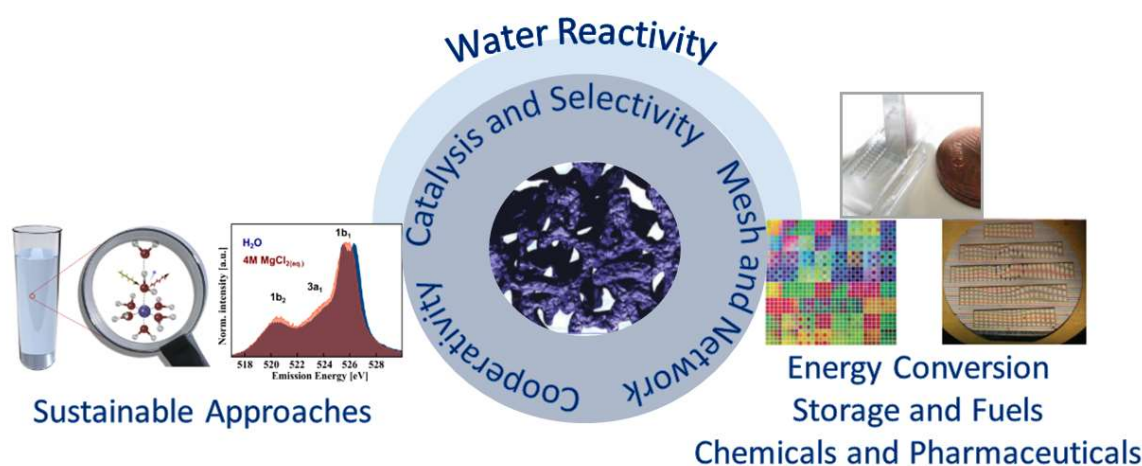
Figure III.3.1: Challenge 2 "Understanding water reactivity": Studying electronic water properties in relation to its structure (left side) in complex meshes and networks (like in hydrogels, middle) will allow improving sustainable approaches in chemistry, energy conversion and storage (right side) [3.16, 3.17].

Challenge 2: Understanding the Role of Reactive Water in Chemical Selectivity, Energy Conversion and Catalysis

Resource-saving, ecological as well as environmentally friendly approaches now play a significant role in chemistry and in technical processes; together they are called "green chemistry" and include topics like low chemical consumption through nanostructured functionalisation and materials [3.8], the use of biomimetic approaches [3.9] or recyclable synthesis routes (in materials research [3.10] and in pharmaceuticals [3.11]). In these sustainable approaches, water is no longer used only as a solvent, but also as a reactive species, so that the water reactions involved can be classified as "water-in-water", "water-on-water" or water-in-water-as-solvent chemistry [3.8-3.15] (Figure III.3.1):

(i) On one hand, "on-water" chemistry includes and describes water as a molecularly reactive and catalytic species. One difficulty of "on-water" chemistry for materials research but also for pharmacy is mainly due to the high complexity of "on-water" reactions and their typical multi-reactant chemical conditions. It is a challenge to determine and statistically describe precisely their multidimensional reaction space [3.16, 3.17]. It is furthermore a challenge to determine experimentally, and to describe theoretically the kinetics of water-catalytic reactions, which may either follow the so-called "Onsager's star triangle" type of or the so-called "Eigen's (and Schuster's) hypercycle" type of reactions.

(ii) On the other hand, the properties of surface water are fundamentally different from those of water in the bulk. A specific challenge in this complex "water chemistry" research relevant for energy conversion (excluding here electrochemistry which is *challenge 4*) is to unravel the mechanistic role of molecular water as a reactive molecule, from the role of solvent water [3.18, 3.19]: When does water block active sites of (surface) catalysts, how does it influence steric hindrances in complex formation or how does it modulate surface reactivities by influencing reaction time scales and steps under multiple conditions?

Challenge 3: Understanding Water as a Tunable Solvent in Energy Conversion and Catalysis

Water is the sustainable solvent of excellence with the caveat that its high polarity limits the solubility of non-polar compounds. Fortunately, confinement of water in hydrophobic pores alters its hydrogen bonding structure, the partition of molecules between pores and an external aqueous phase, and related properties (such as local dielectric constant). It provides an avenue for tuning the water properties towards non-polarity, and increases its solvation power. The potential of rendering of water into a tunable solvent by confinement ("water into a tunable solvent by confinement" is in the following abbreviated as "WATUSO") [3.20] essentially impacts the operation of (water splitting) catalysts, chemical sensors, membranes, and adsorbents in sustain-

able chemical synthesis, membrane water transport or separating electrode compartments [3.21]. Whether WATUSO systems can be turned into practical applications is hitherto underexplored. The WATUSO-challenge therefore includes multiple fields where aqueous behaviour is a key ingredient:

(i) Energy-efficient trapping of water from ambient air.

(ii) Pharmaceutical formulation of poorly soluble drug molecules with limited bioavailability.

(iii) *In situ* study of aqueous phase catalysis using porous catalysts is gaining importance because of the growing use of renewable feedstock (biomass) to replace fossil carbon.

(iv) Water intrusion/extrusion in hydrophobic pores can be used to develop molecular springs or bumpers [3.22] and for storing fuel molecules like methane in clathrates [3.23] and for modifying the water solvent properties (Figure III.3.2) [3.20].

Challenge 4: Clarifying Water Interactions with Electrode Surfaces in Electrocatalytic Energy Conversion

Electrochemical or photoelectrochemical processes that involve water are central for the development of sustainable, CO_2-free energy storage and usage [3.24, 3.25]. Key examples are hydrogen production via (photo) water splitting in electrolysers [3.26-3.28] and the reverse conversion back to electrical power using fuel cells [3.29, 3.30], which hold great promise but still require substantial development for economically viable applications. This challenge can therefore be divided into:

(i) Specifically, efficient, stable, and cost-competitive catalysts for the electrode reactions in these systems need to be found. This requires understanding how on the molecular scale electrolyte water interacts and reacts with the electrode material under realistic reaction conditions [3.31-3.33]. These include strong interfacial electric fields, highly oxidising or reducing conditions and pronounced gas evolution. Connecting *challenge 4* with *challenge 5*, this understanding is also necessary for using processes more efficiently at electrodes of electrochemical sensors, e.g. pH sensors or other ion sensitive electrodes to detect the respective species.

(ii) With recent improvements of *in situ* and *operando* experiments and *ab initio* calculations, a full understanding of the dynamic water structure at electrochemical interfaces comes within reach. However, even for the simplest systems a true atomistic picture is still missing. Current studies either attempt to identify the influence of electrode potential and electrolyte composition on the geometric and electronic structure, describe the electrode reaction without taking the precise water structure into account, or focus on the ultrafast dynamics of interfacial water in the absence of reactions. Evolving from these limited approaches to a molecular-scale understanding of the water-electrode interactions under the conditions of water splitting or fuel cell reactions is one of the future challenges, which needs to be addressed for a knowledge-based development of new catalyst materials [3.34].
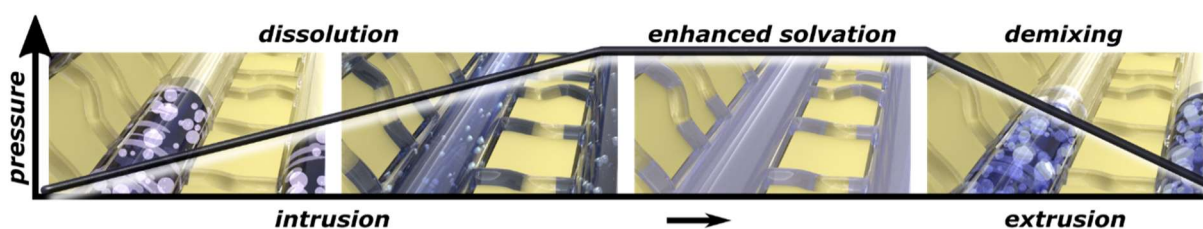
Figure III.3.2: WATUSO (WAter TUnable SOlvent) concept in challenge 3: a heterogeneous mixture of non-polar compounds and water is forced into the nanoporous host material. The mixture becomes a single phase suitable for storage or catalysis. Implemented in a pressure swing cycle, depressurization causes extrusion; water regains its bulk properties and non-polar compounds segregate again. Figure reproduced from [3.20] with permission from the Royal Society of Chemistry.

Challenge 5: Modifying Functional and Transport Properties of Water and Solution by Confinement in Nanomaterials and Catalysis

The particular properties of water, such as soft elastic properties with strong (hydrogen-bridged) adhesions to surfaces, enable particular applications when water covers surfaces or when water is buried in nanocavities [3.35, 3.36]. The technological and material science developments towards ever smaller length scales and ever larger-scale applications must not, however, hide the dilemma that the functionalities of membranes, whether for use in catalysis, (medical) water filtration, water remediation (decontamination of toxic water residues), water analysis (detection of macromolecules) or desalination for the production of drinking water, have not been predictable to date [3.37]. There are no solid mathematical descriptions based on physical models that make it possible to increase membrane performance on the smallest scale. This can ultimately be attributed to the fact that the water-membrane interactions underlying these applications are not sufficiently understood, resulting in the following three sub-items and steps in this pillar 3 challenge:

(i) Especially in nanofluidics and membrane technology, electrochemical interfaces reach their fundamental force and interaction limits under nanoconfinement conditions, which are determined by molecular sizes. Neither their fundamental interactions (which forces are responsible for the separation of which ions and water molecules under different membrane conditions?) nor their membrane-water chemistry are understood so far, especially since recent work indicates that the dielectric property of water is strongly altered when it is confined in nanopores and nanochannels (*challenge 4*). Thus, it is difficult to simulate, predict or study membrane properties (with and without pressure, under tension, under enrichment of biopolymers or DNA etc.) [3.38-3.40]. In addition, nano-water research lacks large-scale standards for the description of membrane efficiencies [3.41]: a detailed atomistic understanding of the interface structure of water on solids is usually only accessible through simulation. Increasing the complexity by approximating the environmental conditions reduces the accuracy of predicting the interfacial water interaction.

(ii) Beyond the unpredictable heat supply and removal mechanisms during osmosis, the considerations become even more complicated if one wants to control electro-repulsion, sorption and absorption and if electrostatic potentials are applied to the membranes or if they are electrically conductive [3.42]. For example, how do the water layers at electrochemical interfaces and interfacial hydration layers change in porous materials?

(iii) Another subtopic of the challenge nanoconfinement in and with water includes the investigation and characterisation of confined water layers and clusters at surfaces, buried solid-water interfaces, or detangling the role of their local interface structure during chemistry [3.43-3.46], i.e. by analysing their chemical role for specific binding conditions or their influence of their heterogeneities onto segregation.

(iv) Water in nanoporous materials plays an important role in energy systems for the storage of heat by means of reversible water vapor adsorption or water-based chemical reactions. Optimisation of these systems requires a better understanding of various and partially interacting rate-limiting effects in the transport of heat and mass through hierarchical pore spaces. In particular, the interaction of sorption, hydration and deliquescence in the meso- and micropores of hierarchical nanoporous media remains a challenge.

III.3.2 Preliminary Work and Competences

Within the pillar we have collected world-leading expertise in the materials research field of energy research and technology and a unique experimental method's portfolio. Our expertise ranges from photon-research (ultrafast optical and X-ray diffraction/spectroscopy/imaging to *in situ* and *operando* X-ray diffraction/ spectroscopy/ imaging) to highest-resolution NMR spectroscopy or surface-sensitive techniques like *in situ* STM or environmental TEM.

During the last years we have developed various X-ray based *in situ* techniques, relevant for studying corrosion *(challenge 1)*. One important goal of our previous work was the *in-situ* investigation of the onset of corrosion in sulphuric acid solution on

an alloy surface by surface sensitive X-ray diffraction [3.47, 3.48]. The experiments on a stoichiometric $Cu_3Au(111)$ surface revealed that in the initial stage of corrosion a Cu rich, single crystalline passivation layer forms, which prevents further corrosion. At the critical potential, Cu bulk dissolution sets in, accompanied by the formation of nanopores. Furthermore, we could demonstrate that the addition of chlorine to the sulfuric acid solution leads to accelerated formation of a passivation layer at lower electrochemical potentials [3.49]. To characterise local corrosion processes of construction materials, we have furthermore developed a novel strategy employing Pt markers and hard X-ray photoelectron microscopy (HAXPEEM). The one-to-one correlation allowing combining local structural and phase information was obtained by electron backscatter detection and local changes of the chemical composition measured by HAXPEEM [3.50]. *In situ* tomography has been applied studying corrosion in biomimetic materials [3.51]. Today's applications in hydrolysis require very stable electrode materials for the hydrogen evolution reaction (HER). We have tested the stability of an epitaxial RuO_2 model electrode under harsh HER conditions and found that it is transformed into hydrous RuO_2 and metallic Ru at room temperature. The onset of hydrous RuO_2 formation can be detected by a swelling of the film [3.52].

Severe corrosion processes occur also during the oxygen evolution reaction at the anode. Beyond RuO_2, IrO_2 has been identified as most suitable material with high stability and activity. We have also employed *in situ* surface sensitive X-ray diffraction to investigate the stability of an epitaxial IrO_2 electrode, which turns out to be stable in aqueous sulfuric acid solution at high positive potentials [3.53]. Pitting corrosion was observed to set in at IrO_2 surface grain boundaries. The interaction of water with magnetite surfaces plays an important role for the water gas shift reaction and Fischer Tropsch synthesis of hydrocarbons. Surface X-ray diffraction revealed that water adsorption at room temperature leads to a Fe cation redistribution and an atomic scale surface roughening, both important for the magnetite surface redox chemistry under reaction conditions [3.54].

Our investigations of complex water chemistry systems ("on-water chemistry") (*challenge 2*) representatively include the real-time structural dynamics studies of aqueous ions chemistry and, more complex, of hydrogels of biological and technological relevance [3.19]. With time-resolved X-ray scattering and X-ray spectroscopy we determined the kinetics and dynamics of the structural changes and the time-dependent electron redistribution of the underlying water-networks. Applying novel analysis formalisms, we could determine the role of entropy and structural entropy-transformation pathways in these hydrogen networks [3.55]. At the interface of electrochemistry to biotechnology is electro-biotechnology, another activity utilising the "on-water" approach. We have built-up an electro-biotechnology system which uses primarily regenerative electricity to drive biosynthesis and developed more efficient and biocompatible water hydrolysis process based on the *in situ* generation of H_2 and O_2 in a bio-mimicking reactor [3.56].

Our *WATUSO* systems (*challenge 2,* mainly *challenge 3* and *challenge 5*), have been optimally studied with our novel experimental setups with *in situ* diagnostics (NMR, EIS, DRS, X-ray scattering, microvolumetry), probing solute, solvent, host material and their interactions [3.20]. Related multidiagnostic methods are currently developed by our team [3.57]. We have characterised the dielectric properties and hydrogen bonding network of nano-confined water by using electrochemical impedance spectroscopy (*EIS*), dielectric relaxation spectroscopy (*DRS*) and ^1H NMR during water vapor adsorption, liquid water intrusion-extrusion cycling and in nafion membranes. Our measurement of the impedance (EIS) provides us with a simple broadband detection of any relevant changes to the (dielectric) properties of the confined system [3.58]. DRS completes our information to study comprehensively the evolution of the complex dielectric properties of water and its dielectric relaxation constants. Furthermore, we probe solvation properties using gas adsorption *(challenge 3* and *5)*. Although gas adsorption isotherms are a good starting point to investigate and characterise these processes, classical adsorption isotherm measurements generally determine only the volume or weight of
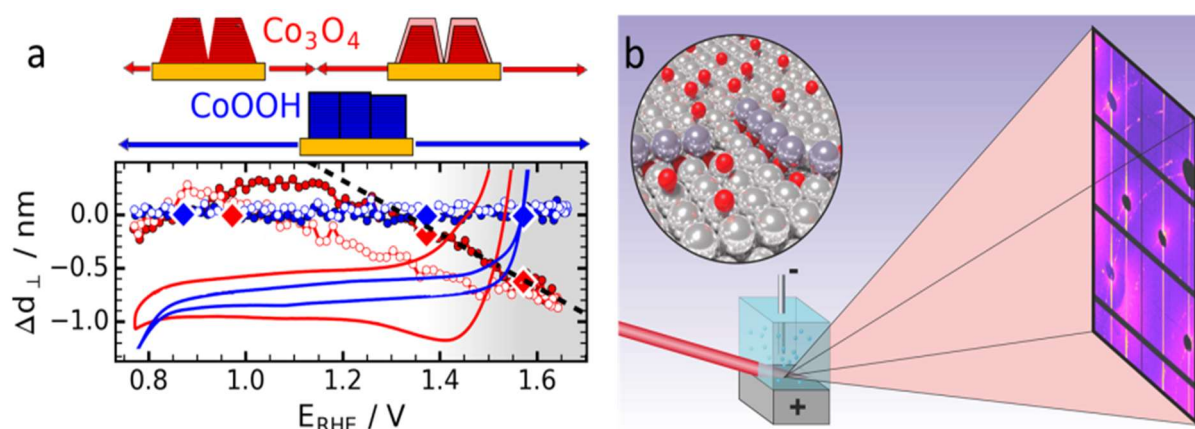
Figure III.3.3: Studying water–electrode interactions: (a) Formation of a nanoscale skin layer on Co_3O_4(111) electrodes during OER (0.1 KOH, potential sweep; symbols = layer thickness, lines = electrochemical current). The CoOOH(001) electrode does structurally not change. Reprinted with permission from [3.67]. Copyright 2019 American Chemical Society. (b) Studying atomic-scale mechanisms with high-energy surface X-ray diffraction of Pt surface oxidation with their structural arrangements (upper left).

the gas dosed [3.20, 3.59]. Gases are expected to adsorb by a combination of mechanisms: (i) dissolution of gas in the confined liquid, (ii) adsorption of gas at the interphase between liquid and pore walls and (iii) preferential adsorption of gas in the smallest pores devoid of liquid. High pressure X-ray and NMR cells have already been developed in-house for more detailed studies [3.57]. Our NMR scheme quantifies solutes with observable nuclear spins, e.g. H_2, CH_4, CO_2 and Xe, correlates them with micro-volumetric data, determines the evolution of water hydrogen bonding network, and observes the formation of water pools with different properties or in different environments. For solutes with NMR observable nuclei, we have also revealed changes in their local chemical environment [3.60-3.64]. Via the speciation of dissolved CO_2, we could specify information on the *in-situ* pH conditions of confined and CO_2-containing aqueous solvent.

In the context of *challenge* 4, we have investigated interface properties between solid electrodes and aqueous liquids by novel developed *in situ* surface X-ray scattering and scanning tunnelling microscopy (STM) techniques (relevant also for *challenge 1* and *challenge 3*). We have pioneered *in situ* video-rate STM, which allows observing the dynamic behaviour of single adsorbed atoms and molecules at electrochemical interfaces [3.65, 3.66] and reactions of these species with the solid electrode. Complementary, our novel developments in synchrotron-based X-ray scattering methods make *operando* studies of

the atomic-scale details of electrochemical reactions with unprecedented detail possible (Figure III.3.3). We have recently applied these methods to Co oxide electrocatalysts for investigating the oxygen evolution reaction in electrocatalytic water splitting. The studies allowed us observing a structural transformation of the topmost nanometre of the electrode at reaction rates that equaled those used in commercial alkaline electrolysers [3.67]. Similar studies of electrochemical Pt oxidation enabled us to determine the precise motion of the surface atoms during the ingress of oxygen atoms into the metal as well as the resulting nanoscale surface restructuring [3.68, 3.69]. For these studies, dramatically improved precision and time resolution could be obtained by *operando* high-energy surface X-ray diffraction *(challenge 4)*. We have even monitored irreversible interface processes, which require single shot studies on the millisecond timescale by X-ray surface diffracttion [3.70].

The chemical single bond of water, between the oxygen and the hydrogen, is one of the strongest single bonds known in chemistry. Storing energy in water-bond-making or water-bond-breaking, or utilising the water's bond for chemical transformations, is the chemical reaction which consumes and delivers most energy per atom unit (*challenge 2, challenge 3* and *challenge 4*). Novel materials such as perovskites catalysts are intensively developed and studied for oxygen evolution reaction (OER) from water since they are built from highly abundant elements on Earth;

we could demonstrate that perovskites show highest photo-conversion efficiencies – and one of the highest catalytic efficiency in the presence of water [3.71-3.75]. For disentangling the catalytic mechanisms of photo-energy conversion and photovoltaic water-splitting on perovskite surfaces, we have developed ultrafast optical methods [3.72], and highest-resolution ultrafast high flux X-ray imaging/scattering and X-ray spectroscopy techniques based on the "molecular movie" schemes at synchrotrons and FELs [3.76]. These studies paved us the way for the first time to resolve the mechanistic origins of OER on the time-scale of atomic movements (femtoseconds). Technically in particular challenging is the combination of *in situ* and time-resolved ultrafast X-ray scattering techniques [3.77] with multidimensional X-ray spectroscopy techniques (X-ray absorption (XAS), X-ray emission (XES), and resonant inelastic X-ray spectroscopy (RIXS)). With (for the first time) femtosecond RIXS we demonstrated that for homoleptic iron carbonyls (Mond process) solvent-complexation plays a major role for catalysis [3.78]. We furthermore found that for the perovskites water actively stabilies short-living intermediates during OER and that the micro-solvation dictates perovskite's reactivity [3.79].

Confined water (*challenge 5*) plays also an important role in chemical industry or desalination since membrane separations are considered among the most (cost) efficient methods [3.80]. As a prerequisite for the role of confined water in applications, and as one example, surface-water-confinement and the interaction of water with graphene supported on Ir(111) surfaces was investigated by Fourier Transform Infrared reflection absorption spectroscopy (FT-IRRAS). The 2.5 pitch of the Moire superstructure of graphene on Ir(111) represents a perfect template for the investigation of water clusters at low temperatures. The IRRAS results [3.81] gave evidence that the clusters exist in the form of amorphous solid water with an increased degree of order and oxygen atoms pointing towards the p doped graphene layer. Upon adsorption of higher water doses the formation of an amorphous solid water film was observed, together with the formation of dangling H-bonds at the interface. Our groups' current studies concentrate on the development of highly selective materials, forming large and defect-free films of minimal thickness to maximize permeability and minimize membrane pumping energy (together with pillar 1), best be realised using aromatic triacid and diamine yield in thin polyamide membranes [3.82]. We utilised molecular dynamics models for studying the impact of water surface tensions to nanoconfinement [3.83]. We have developed self-assembled membrane materials with tailored porosity, pore morphology and pore size distributions for tuning self-diffusion, hydraulic permeabilities and capillarity-driven flows. Our studies are based on X-ray and neutron scattering and imaging as well as opto-interferometric methods. Controlling externally and electrically the water's capillarity at the nanoscale (electrowetting, electrically switchable capillary rise), we could deduce the origin of the nanoporous material's transformation to mechanisms driven by adsorption energies and mechanical deformations influenced by capillary forces [3.40, 3.42]. These properties are very similar to many biological systems where the biological systems harvest mechanical energy from vapour condensation and evaporation energies [3.84. 3.85]. Water-nanoconfinement in swelling thin films composites of functional bio- and organic thin film materials (enzymatic cellulose, peptides), we call them "therapeutic nanopaper" bear the potential for being used as optimal matrices for drug delivery in the context of personalised medicine during pandemic situations (with pillar 5) [3.86]. Based on our time-resolved and *in situ* surface-sensitive X-ray (AFM and STM) characterisations we have developed a novel technique for low-dose drug delivery based on layer formation of enzymatic cellulose hydrogel and peptide hydrogel by airbrush spray coating [3.87]. Our studies confirm a drug-sensitive built-in into the different nanofilm layers and phases of distinct sizes and crystallinity emphasising the importance of tailoring the cellulose nanofibrils.

Water-confinement in surface reactions has been studied for the Pt/Si system. For Pt/Si chemically-propelled motors ("swimmers") we have identified two chemomechanical mechanisms: 1) the photo-activated electroosmosis, 2) water/Pt interfacial, light-insensitive diffusioosmosis [3.88]. The long-range solute-free regions of nafion nanofilms are formed in water [3.89]. Applying optical contrast

methods, we have imaged the formation of this exclusion zone with optical markers, which allow for visualising transport processes in confined space. We found that in this zone the solutes are subjected to multiionic diffusiophoresis near the nafion / water interface, so that the electrophoretic contribution in multiionic diffusiophoresis becomes dominant behind the formation of the zone [3.90]. Furthermore, we have studied nano-porous materials and water-based chemical reactions in the context of heat storage by means of reversible water vapour adsorption or water-based chemical reactions [3.91, 3.92].

III.3.3 Objectives

The performance of the systems presented in the various challenges heavily relates, e.g. on the robustness of the materials, their stability and their efficiency when interacting with water and when water guides the systems performances. This requires a whole set of characterisation tools structurally as well as dynamically and *in situ* and *in operando*. Since we deal with the scientific challenges how the water's properties shape or influences matter relevant for technology, not only near-equilibrium und static properties are important, but also their out-of-equilibrium conditions as well as their dynamic response functions. Therefore, some of the following listed objectives are very much the same for even differently formulated challenges, so that we will present them together.

In one common objective we want to determine the real-time dynamics of the pillar 3 water-confined materials and detangling its relation to water dynamics. This requires the study of metastable and nano-structured intermediates at selected (when diffusion controlled) or at various time scales (from the diffusion limit (millisecond time regime) to atom time scales (femtosecond time regime)). We want to understand the role of hydrogen network, local dielectric properties, their length-scale-dependent irregularities and the role of the O-H bond and its specific interaction with various chemical elements and functional groups in energy research and technological relevant materials. Our technologies will be capable detecting transient (structural, energetically and element specific) features guiding water reactions in confinement: during corrosion (*challenge 1*)

and catalysis (*challenge 2*), in "on-water" chemistry (*challenge 3*), at electrodes (challenge 4) or in cavities and interfaces during chemical separation processes (*challenge 5*). For resolving the reaction-specific chemical site, structure and dynamics of the transient features at atomic scales, we will continue our recently started efforts in developing highest-resolution surface-sensitive, ultrafast, and *in situ* and *operando* X-ray scattering/spectroscopy (XAS to RIXS)/ imaging methods. Investigating structurally and in real-time irreversible water reactions and their impact on catalysis (*challenges 2–4*), will require a combination of the methods as well as an extension to *operando* studies also at laboratory sources like STM or NMR.

Furthermore, common objectives of all challenges include the development of performance and efficiencies optimisation strategies (either of the model or in technological systems) by tuning the structure and time-dependent water properties (i.e. in corrosion or water-splitting reactions at electrodes, in storage materials), its chemical reactivity (i.e. in selective chemical or pharmaceutical reactions), or its selectivity (i.e. desalination). In pillar 3 we will therefore uniquely combine X-ray, optical and NMR methods (*challenges 2–5*) providing us tools to study electrocatalysis and gas–solid interfaces (*challenge 3*) and water at nanoparticle model electrodes (*challenge 4*) to novel levels of precision allowing to derive atomistic models of the energy storage mechanisms.

Specific objectives for *challenge 1* include the determination of typical changes of water's physical and chemical properties during corrosion such as the creation of holes or atoms migration, surface micro-solvation and the network stabilising the surface solvation. We will continue to develop novel state of the art X-ray spectroscopy and diffraction tools, among them high-resolution HAXPES or X-ray surface scattering at highest sensitivity.

For catalytic water and "on-water" reactions, as described in *challenge 2* (and partially in *challenge 5*), we will determine its specific hydrogen networks, the dynamics of the networks and study their impact in pharmaceutical approaches, i.e. during pandemic crisis (together with pillar 5). The

big overall objective however includes quantitatively determining the kinetics and dynamics of catalytic water. We will study different water catalytic model system and determine whether catalytic water follows Onsager's star triangle, or Eigen's and Schuster's hypercycle approaches and whether the mechanism can be influenced by the statistically relevant multiple conditions (diffusion-control versus non-linear concentration changes, chemical site selectivity versus stochastic distributions etc.). Besides the pure observation of on-water reaction systems, we will also detangle the structural (steric hindrance, active site blocking) and energetic (complex formation, modulation of surface reactivities) mechanisms driving such type of reactions.

Specifically, for *challenge 3* we will design a novel NMR-dielectric coupled cell allowing to analyse the water-network and its influence on the breakdown of macroscopic properties (like dielectric constant) in nanoconfinement. We plan to demonstrate an NMR coil as a non-contact sensor for dielectric permittivity measurements in samples with a low ionic conductivity (such as water confined into a WATUSO host matrix) and to exploit the NMR probes both as permittivity meter and NMR detector to provide a unique multi-diagnostic tool for characterisation of macro- and microscopic parameters. Another substantial objective of the WATUSO *challenge 3* includes systematic studies of energy-efficient water trapping under systematically tuned conditions, like the hydrophobicity of the studied nanopores which bury water, or the determination of equilibrium and rate constants for the storage of methane in clathrates and their deviations under *in situ* conditions. The suggested space and time investigations of water–solvent-tuning principles with dielectric relaxation spectroscopy (DRS) and ^{1}H NMR will allow for novel multi-diagnostic characterisation tools, creating new approaches for solvent-based chemical manufacturing and gas storage in a greener and more sustainable chemical context.

In *challenge 4* for detangling the atomistic mechanism of OER for energy storage and the role of water for stabilising catalytic surface features, voltage sweep capabilities or light-induction will be implemented for the various surface X-ray scattering and X-ray spectroscopy methods, enabling (ultrafast) *operando* and *in situ*

characterisation of the solid– liquid interfaces like electrode–electrolyte interfaces. In a next step of objectives, the characterisation schemes will be expanded to novel OER systems of relevance for energy storage, electrochemistry and electrocatalysis. Besides the systems described in the challenges, prototypes of fuel cell reactions will be studied. Specifically, we plan full ab-initio theoretical description of interfacial water at surfaces under electrochemical conditions at defined potentials.

The big objective of *challenge 5* includes a precise, atomistic and physical description of nano-defined and nano-confined processes where water is buried into nanocavities, and chemical and transport phenomena that are dictated by this spacial confinement. Besides membranes, also low-dose drug carriers or bio-mimicking materials are influenced by this soft-matter nanoconfinement. Chemically we will vary the hydrophobicity of the materials, the degree of water-confinement, solutes and host material. We will determine their equilibrium and out-of-equilibrium conditions, their rate constants, or mechanistic features such as hydrogen network and their changes, local permeability as well as osmose properties. Based on the findings, models will be developed. Specifically addressing the objectives in *challenges 3 and 5*, nano-confined water also offers a potential alternative to compression, for storing CH_4 and H_2 gas, and opens new opportunities for sustainable approaches in green chemistry, such as aqueous phase hydrogenation reactions, which benefit from enhanced hydrogen solubility. Materials designs of hierarchical nanoporous media for the storage of heat designed, screened or selected from an application perspective will be investigated more closely in CMWS.

III.3.4 Methodologies

Phasing the objectives of *challenge 1,* advanced X-ray scattering methods using very high photon energies will provide capabilities for time-resolved, *in situ* and *operando* studies of complex interface and corrosion processes. Novel specialised sample preparation techniques will allow preparation under defined nano-confined conditions, including micro-capillaries, nano-capillaries, patterned surfaces and materials sectioning with

providing further specialised sample preparation units. These techniques will also be accessible for *challenge 5* (and other challenges) researches if required. DESY NanoLab expertise will provide marker technology, scanning Auger microscope, and an electrochemistry laboratory which is jointly operated together with CAU Kiel (see *challenge 4*).

Challenge 2 phases the precise description of the kinetics of multi-component chemical reactions where water acts as catalyst. Besides the synthesis of tailored model-molecules (together with pillar 5 and *challenge 5*), novel concepts of flat jet and micro-jet technologies need to be developed for deriving out-of-equilibrium conditions of the systems studied. For investigating deterministic reactions and reaction cycles within stochastic noise the experiments require highest sensitivity and chemical selectivity. With atomic-motion resolving ultrafast time-resolved X-ray diffraction and scattering studies, and time-resolved X-ray diffraction and scattering studies within the diffusion limit (millisecond time resolution) we will determine structural changes and electron density changes from the first femtoseconds of the reactions up to the diffusion limit utilising the first principles of direct Fourier-transformation of Pink Laue diffraction and extended approaches of small and wide angle X-ray scattering analysis. Monitoring structural changes as a function of time will allow us directly deriving information about in a chemical and structural sense ordering and disordering processes as a function of time, which can directly be feed-in into the models described in *challenge 2* – for determining the impact of water catalytic features. Ultrafast and time-resolved soft X-ray spectroscopy, in particular ultrafast RIXS, introduces the chemical sensitivity needed for separating catalytically active water from bulk water (see also *challenge 4*).

For solving the objectives of *challenge 3* our laboratory-based adsorption/intrusion micro-volumetric setups will be combined with *in situ* ^{1}H NMR, EIS and DRS spectroscopy. Sum frequency generated and Fourier-transform infra-red spectroscopy will be added, in collaboration with pillar 2. Together with the efforts described in pillar 1, coherent X-ray diffraction methods (like XPCS) will be involved and adapted to higher spatial and temporal resolution. The combination of X-ray and neutron scattering will provide direct access to the evolution of the water density from small angle X-ray and neutron scattering, or the formation of structured water clusters or ice-like periodicity via the radial distribution functions (RDFs). Analysing the total X-ray scattering data with full pattern fitting using Pair Distance distribution Function (PDF) analysis and Rietveld refinement of the X-ray powder diffraction will lead to a global approach when combined with NMR crystallography. Via the CMWS high-field NMR-facility "NMRCoRe", four mixed solid/liquid high-resolution NMR machines and two high-throughput high-resolution NMR machines, are accessible. Various combinations of complementary techniques are foreseen. They include a combination of vibration free / temperature-stabilised *in situ* NMR and EIS/DRS techniques for following chemical processes. Furthermore, it is envisioned to combine X-ray scattering with infrared to NIR; and XUV/VUV with infrared to NIR excitation and sample characterisation techniques.

In *challenge 4* we aim for studying complex chemical aqueous reactions relevant for energy conversion and electrocatalysis, so that the experimental, surface-sensitive methods also cover other challenges (*challenges 1-4*). In particular, the LISA liquid interface diffractometer designed by CAU Kiel at PETRA III as well as high-energy surface scattering methods for investigating electrocatalysis will be further developed. With LISA during *in situ* conditions RDFs and PDFs can be derived. Soft X-ray spectroscopy gains element-selective information about local elements (redox states, 1st solvation shell formation, association complexes) and their electronic structures in real-time during chemical conversion. Photon-in/photon-out techniques like ultrafast multidimensional soft X-ray spectroscopy (XES and RIXS) will allow for studying reactive water and to distinguish it from water in aqueous solutions (also together with *challenge 2*). Corresponding experiments have been developed at the Liquid-Jet endstation (@HZB/LCLS), the ChemRIXS endstation (@PETRA/FLASH/DESY) and they are currently continued to fundamental resolution limits at the HeisenbergRIXS endstation of the hRIXS consortium (located at

European XFEL). Very recently we have extended our real-time X-ray spectroscopy techniques including *in situ* and electrochemical conditions. The experiments will, e.g. allow determining ultrafast surface spin state changes during catalytic water splitting or during water electrochemistry. Additionally, at PETRA III high-flux X-ray diffraction methods (like X-ray reflectometry, surface and grazing incidence X-ray diffraction) and X-ray fluorescence in scanning modes have been developed and will be applied. The equilibrium studies will be complemented by electrokinetics studies such as electrochemical microscopy, streaming potential measurements, local EMK determination, differential electrochemical mass spectrometry, mass spectrometry of electrolytes under nano-confined conditions or electrochemical AFM combined with laser-induced fluorescence, and environmental SEM and TEM. *In situ* environmental transmission electron microscopy (TEM) and Atom Probe Tomography (in combination with electrochemical units) will allow an additional atomically resolved characterisation of, e.g. electrocatalysis. Additional video-rate scanning tunneling microscopy and electrochemical methods will also be utilised. Comparison to *ab initio* predictions is anticipated. For energy research on technical relevant materials, fuel cell testing station, Faraday cages and basic equipment for battery research compatible with synchrotron and FEL beamlines will be accessible.

Challenge 5 also heavily requires the nano-specialised sample preparation techniques described in *challenge 1*. For monitoring surface and surface sensitive hydrogen networks in confined media but also, e.g. during desalination, for the optical studies advanced infrared characterisation and non-linear optical spectroscopy will be utilised. Optical studies will also include dynamic light scattering, interferometric and quartz-crystal microscopy. Auger spectroscopy will allow for surface characterisation. Dielectric characterisation of surfaces will also be accessible. Thermodynamic studies for determining equilibrium constant will be possible utilising calorimeters, thermogravimetry, surface tension characterisation techniques (tensiometers etc.), thermal desorption spectroscopy and *in situ* UV-photoelectron spectroscopy. Rheology will be added for fluidity studies. To determine hydrogen network and its formation in detail, on the X-ray side surface-sensitive small and wide-angle X-ray scattering (GISAXS and GIWAXS @PETRA III) will be combined with *in situ* techniques for the real-time monitoring of the network formation and interactions in nano-films, nano-cavities and pharmaceutical relevant matrices and under *operando* conditions. Their analysis will provide information about gyration radii, nanocrystal properties, and PDFs. The experimental results will be compared to state-of-the-art simulations, based on novel developments of theoretical methods for the robust prediction of the structure and dynamics of confined water structures.

III.3.5 References

[3.1]   V. Maurice, P. Marcus, Progress in Corrosion Science at Atomic and Nanometric Scales, Progress in Materials Science 95, 132 (2018).

[3.2]   G. S. Frankel, Pitting Corrosion of Metals - A Review of the Critical Factors, J. Electrochem. Soc. 145, 2186 (1998).

[3.3]   M. J. Duarte, J. Klemm, S. O. Klemm, K. J. J. Mayrhofer, M. Stratmann, S. Borodin, A. H. Romero, M. Madinehei, D. Crespo, J. Serrano, S. S. A. Gerstl, P. P. Choi, D. Raabe, F. U. Renner, Element-Resolved Corrosion Analysis of Stainless-Type Glass-Forming Steels, Science 341, 372 (2013).

[3.4]   A. King, G. Johnson, D. Engelberg, W. Ludwig, J. Marrow, Observations of Intergranular Stress Corrosion Cracking in a Grain-Mapped Polycrystal, Science 321, 382 (2008).

[3.5]   J. Biener, A. Wittstock, L. A. Zepeda-Ruiz, M. M. Biener, V. Zielasek, D. Kramer, R. N. Viswanath, J. Weissmüller, M. Bäumer, A. V. Hamza., Surface-chemistry-driven Actuation in Nanoporous Gold, Nat. Mat. 8, 47 (2009).

[3.6]   B. Luthringer, F. Feyerabend, R. Willumeit-Römer, Magnesium-based Implants: a Mini Review, Magnes. Res. 27 (4), 142-154 (2014).

[3.7]   W. Lee, K. Schwirn, Martin Steinhart, Eckhard Pippel, Roland Scholz, Ulrich Gösele, Structural Engineering of Nanoporous Anodic Aluminium Oxide by Pulse Anodization of Aluminium, Nat. Nanotech. 3, 234 (2008).

[3.8] S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb, K. B. Sharpless, Unique Reactivity of Organic Compounds in Aqueous Suspension, Angew. Chem. Int. Ed. 21, 3157 (2005).

[3.9] A. Chanda, V. Fokin, Organic Synthesis "On Water", Chem. Rev. 109 (2), 725-748 (2009).

[3.10] Y. Jung, R. A. Marcus, On the Theory of Organic Catalysis "on Water", J. Am. Chem. Soc. 129, 5492-5502 (2007).

[3.11] I. Nam, J. K. Lee, H. G. Nam, R. N. Zare, Abiotic Production of Sugar Phosphates and Uridine Ribonucleoside in Aqueous Microdroplets, Proc. Nat. Am. Soc. 114 (47) 12396-12400 (2017).

[3.12] P. Dolcet, S. Diodati, F. Zorzi, P. Voepel, C. Seitz, B. M. Smarsly, S. Mascotto, F. Nestolad, S. Gross, Very Fast Crystallisation of MFe2O4 Spinel Ferrites (M=Co, Mn, Ni, Zn) under Low Temperature Hydrothermal Conditions: a Time-resolved Structural Investigation, Green Chem. 26, 2257–2268 (2018).

[3.13] J. Holladay, J. Hu, D.L. King, Y. Wang, An Overview of Hydrogen Production Technologies, Catal. Tod. 139, 244–260 (2009).

[3.14] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, The Mechanism of Water Oxidation: from Electrolysis via Homogeneous to Biological Catalysis, Chem. Cat. Chem. 2 (7), 724-761 (2010).

[3.15] H. Wang, I. Choi, T. Rogge, N. Kaplaneris, L. Ackermann, Versatile and Robust C–C Activation by Chelation Assisted Manganese Catalysis in Water, Nat. Catal. 1, 993-1001 (2018).

[3.16] Z. Yin, L. Inhester, S. Thekku Veedu, W. Quevedo, A. Pietzsch, P. Wernet, G. Groenhof, A. Föhlisch, H. Grubmüller, S. Techert, Cationic and Anionic Impact on the Electronic Structure of Liquid Water, J. Phys. Chem. Lett. 8, 3759-3764 (2017).

[3.17] M. Petri, S. Frey, A. Menzel, D. Görlich, S. Techert, Structural Characterization of Nanoscale Meshworks within a Nucleoporin FG Hydrogel, Biomacromolec. 13 (6), 1882-1889 (2012).

[3.18] F. Keutsch, R. Saykally, Water Clusters: Untangling the Mysteries of the Liquid, one Molecule at a Time, Proc. Nat. Acad. Sci. 98 (19), 10533-10540 (2001).

[3.19] P. Petersen, R. Saykally, On the Nature of Ions at the Liquid Water Surface, Annu. Rev. Phys. Chem. 57, 333-364 (2006).

[3.20] E. Breynaert, M. Houlleberghs, S. Radhakrishnan, G. Grübel, F. Taulelle, J. A. Martens, Water as a Tuneable Solvent: A Perspective. Chem. Soc. Rev. 49, 2557-2569 (2020).

[3.21] J. Rongé, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordigac, J. A. Martens, Monolithic Cells for Solar Fuels, Chem. Soc. Rev. 43 (23), 7963–81 (2014).

[3.22] V. Eroshenko, R. Regis, M. Soulard, J. Patarin, Energetics: A New Field of Applications for Hydrophobic Zeolites, J. Am. Chem. Soc. 123 (33), 8129–30 (2001).

[3.23] M. Casco, J. Silvestre-Albero, A. J. Ramírez-Cuesta, F. Rey, J. L. Jordá, A. Bansode, A. Urakawa, I. Peral, M. Martínez-Escandell, K. Kaneko, F. Rodríguez-Reinoso, Methane Hydrate Formation in Confined Nanospace Can Surpass Nature, Nat. Comm. 6, 6432 (2015).

[3.24] V. R. Stamenkovic, D. Strmcnik, P. P. Lopes, N. M. Markovic, Energy and Fuels from Electrochemical Interfaces, Nat. Mater. 16, 57-69 (2017).

[3.25] R. Schlögl, The Role of Chemistry in the Energy Challenge, ChemSusChem, 3, 209 (2010).

[3.26] N. S. Lewis, D. G. Nocera, Powering the Planet: Chemical Challenges in Solar Energy Utilization, Proc. Nat. Acad. Sci. 103, 15729–15735 (2006).

[3.27] M. Carmo, D. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, Int. J. Hydr. Ener. 38 (12), 4901-4934 (2013).

[3.28] J. M. Andujar, F. Segura, Fuel Cells: History and Updating. A Walk along Two Centuries, Renew. Sust. Energ. Rev. 13, 2309–2322 (2009).

[3.29] M. K. Debe, Electrocatalyst Approaches and Challenges for Automotive Fuel Cells, Nature 486, 43–51 (2012).

[3.30] N. M. Marković, P.N. Ross, Surface Science Studies of Model Fuel Cell Electrocatalysts, Surf. Sci. Rep., 45, 117–229 (2002).

[3.31] O. M. Magnussen; A. Gross, Towards an Atomic-scale Understanding of Electrochemical Interface Structure and Dynamics, J. Am. Chem. Soc. 141, 4777−4790 (2019).

[3.32] L. Jacobse, Y. Huang, M. T. M. Koper, M. J. Rost, Correlation of Surface Site Formation to Nanoisland Growth in the Electrochemical Roughening of Pt(111), Nat. Mat. 17, 277 (2018).

[3.33] H. Mistry, A. Valera, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. Roldan Cuenya, Highly Selective Plasma-activated Copper Catalysts for Carbon Dioxide Reduction to Ethylene, Nat. Comm. 7, 12123 (2016).

[3.34] W. Hong, M. Risch, K. A. Stoerzinger, A. Grimaud, J. Suntivich, Y. Shao-Horn, Toward the Rational Design of non-precious Transition Metal Oxides for Oxygen Electrocatalysis. Energy Environ. Sci. 8, 1404-1427 (2015).

[3.35] D. Li, H. Wang, Recent Developments in Reverse Osmosis Desalination Membranes, Desalination 434, 121-160 (2018).

[3.36] A. Boretti, S. Al-Zubaidy, M. Vaclavikova, M. Al-Abri, S. Castelletto, S. Mikhalovsky, Outlook for Graphene-based Desalination Membranes, Nat. Clean Water 1, 5 (2018).

[3.37] T. S. Y. Choong, T. G. Chuah, Y. Robiah, F. L. Gregory Koay, I. Azni, Arsenic Toxicity, Health Hazards and Removal Techniques from Water: an Overview, Desalination 217, 139 (2007).

[3.38] A. Fumagalli, A. Esfandiar, R. Fabregas, S. Hu, P. Ares, A. Janardanan, Q. Yang, B. Radha, T. Taniguchi, K. Watanabe, G. Gomila, K. S. Novoselov, A. K. Geim, Anomalously Low Dielectric Constant of Confined Water, Science 360, 1339 (2018).

[3.39] T. Mantel, P. Benne, S. Parsin, M. Ernst, Electro-Conductive Composite Gold-Polyethersulfone-Ultrafiltration-Membrane: Characterization of Membrane and Natural Organic Matter (NOM) Filtration Performance at Different In-Situ Applied Surface Potentials, Membranes 8, E64 (2018).

[3.40] S. Gruener, D. Wallacher, S. Greulich, M. Busch, P. Huber, Hydraulic Transport across Hydrophilic and Hydrophobic Nanopores: Experiments with Water and n-Hexane, Phys. Rev. E 93, 013102 (2016).

[3.41] A. Szymczyk, V. Freger, Membrane Characterization, in A. Schaefer, A. Fane (eds.) Nanofiltration: Principles and Applications, Elsevier (2005).

[3.42] Z. Wang, Z. Wang, S. Lin, H. Jin, S. Gao, Y. Zhu, J. Jin, Nanoparticle-templated Nanofiltration Membranes for Ultrahigh Performance Desalination, Nat. Comm. 9, 2004 (2018).

[3.43] R. Devanathan, A. Venkatnathan, M. Dupuis, Atomistic Simulation of Nafion Membrane. 1. Effect of Hydration on Membrane Nanostructure, Phys. Chem. B 111 (28), 8069-8079 (2007).

[3.44] R. Devanathan, A. Venkatnathan, M. Dupuis, Atomistic Simulation of Nafion Membrane. 2. Dynamics of Water Molecules and Hydronium Ions, J. Phys. Chem. B 111 (45), 13006-13013 (2007).

[3.45] P. Sudarsanam, E. Peeters, E. V. Makshina, V. I. Parvulescu, B. F. Sels, Advances in Porous and Nanoscale Catalysts for Viable Biomass Conversion, Chem. Soc. Rev. 48. 2366-2421 (2019).

[3.46] J. Pan, H. Dou, Z. Xiong, C. Xu, J. Ma, X. Zhao, Porous Photo Catalysts for Advanced Water Purifications, J. Mater. Chem. 20, 4512-4528 (2010).

[3.47] F. Renner, A. Stierle, H. Dosch, D. M. Kolb, T.-L. Lee, J. Zegenhagen, Initial Corrosion of a Noble Metal Alloy Studied by In situ X-ray Diffraction, Nature 439, 707 (2006).

[3.48] F. Renner, A. Stierle, H. Dosch, D. M. Kolb, T. L. Lee, J. Zegenhagen, Initial Dealloying and Passivation of $Cu_3Au(111)$ during Electro-corrosion: an In situ X-ray Diffraction Study, Phys. Rev. B 77, 5433 (2008).

[3.49] F. Renner, A. Stierle, H. Dosch, D. M. Kolb, J. Zegenhagen, The Influence of Chloride on the Initial Anodic Dissolution of Cu3Au, Electrochem. Comm. 9, 1639 (2007).

[3.50] M. Långberg, C. Örnek, F. Zhang, J. Cheng, M. Liu, E. Grånäs, C. Wiemann, A. Gloskovskii, Y. Matveyev, S. Kulkarni, H. Noei, T. F. Keller, D. Lindell, U. Kivisäkk, E. Lundgren, A. Stierle, J. Pan, Characterization of Native Oxide and Passive Film on Austenite/Ferrite Phases of Duplex Stainless Steel Using Synchrotron HAXPEEM, J. Electrochem. Soc. 166, C3336 - C3340 (2019).

[3.51]   J. Moosmann, D. Wieland, B. Zeller-Plumhoff, S. Galli, D. Krüger, A. Ershov, S. Lautner, J. Sartori, M. Dean, S. Köhring, H. Burmester, T. Dose, N. Peruzzi, A. Wennerberg, R. Willumeit-Römer, F. Wilde, P. Heuser, J. U. Hammel, F. Beckmann, A Load Frame for In situ Tomography at PETRA III. Proc. SPIE 11113, Develop. in X-Ray Tomography XII, 1111318 (2019).

[3.52]   T. Weber, M. Abb, O. Khalid, J. Pfrommer, F. Carla, R. Znaiguia, V. Vonk, A. Stierle, H. Over, In situ Studies of the Electrochemical Reduction of a Supported Ultrathin Single-Crystalline RuO2(110) Layer in an Acidic Environment, J. Phys. Chem. C 123, 3979 (2019).

[3.53]   T. Weber, J. Pfrommer, M. J. S. Abb, B. Herd, O. Khalid, M. Rohnke, P. H. Lakner, J. Evertsson, S. Volkov, F. Bertram, R. Znaiguia, F. Carla, V. Vonk, E. Lundgren, A. Stierle, H. Over, Potential-Induced Pitting Corrosion of an $IrO_2(110)$-$RuO_2(110)/Ru(0001)$ Model Electrode under Oxygen Evolution Reaction Conditions, ACS Catal. 97, 6530 (2019).

[3.54]   B. Arndt, M. Creutzburg, E. Grånäs, S. Volkov, K. Krausert, A. Vlad, H. Noei, A. Stierle, Water and Atomic Hydrogen Adsorption on Magnetite (001), J. Phys. Chem. C, 123, 26662-26672 (2019).

[3.55]   S. Techert, S. Thekku Veedu, S. Bari, Development of Ultrafast X-ray Free Electron Laser Tools in (Bio)Chemical Research, Springer Series in "Physical Chemistry and Biophysics" (2019).

[3.56]   T. Utesch, A.-P. Zeng, A Novel "All in One" Electrolysis Electrode and Bioreactor Enable Better Study of Electrochemical Effects and Electricity-Aided Bioprocesses, Eng. Life Sci. 18, 600-610 (2018).

[3.57]   M. Castro, P. Losch, W. Park, M. Haouas, F. Taulelle, C. Loerbroks, G. Brabants, E. Breynaert, C. E. A. Kirschhock, R. Ryoo, W. Schmidt, Unraveling Direct Formation of Hierarchical Zeolite Beta by Dynamic Light Scattering, Small Angle X-ray Scattering, and Liquid and Solid-State NMR: Insights at the Supramolecular Level, Chem. Mater. 30 (8), 2676 (2018).

[3.58]   G. Brabants, S. Lieben, E. Breynaert, E. K. Reichel, F. Taulelle, J. A. Martens, B. Jakoby, C. E. A. Kirschhock, Monitoring Early Zeolite Formation via In situ Electrochemical Impedance Spectroscopy, Chem. Commun. 52 (31), 5478–5481 (2016).

[3.59]   B. Vallaey, S. Radhakrishnan, S. Heylen, C. Vinod Chandran, F Taulelle, E. Breynaert, J. A. Martensa, Reversible Room Temperature Ammonia Gas Absorption in Pore Water of Microporous Silica-Alumina for Sensing Applications, Phys. Chem. Chem. Phys. 20, 13528-13536 (2018).

[3.60]   S. Smet, P. Verlooy, S. Pulinthanathu, C. E. A. Kirschhock, F. Taulelle, E. Breynaert, J. A. Martens, A Porous POSiSil Suited for Pressure Driven Reversible Confinement of Solutions: PSS-2, Chem. Eur. J. 25, 12957-12965 (2019).

[3.61]   A. Kubarev, E. Breynaert, J. Van Loon, A. Layek, G. Fleury, S. Radhakrishnan, J. A. Martens, M. B. J. Roeffaers, Solvent Polarity-Induced Pore Selectivity in H ZSM-5, ACS Catal. 7(7), 4248–4252 (2017).

[3.62]   P. Goossens, C. Martineau-Corcos, F. Saidi, J. Martens, F. Taulelle, Unlocking the Observation of Different Proton Populations in Fluorinated Polymers by Solid-State ^{1}H and ^{19}F Double Resonance NMR Spectroscopy. Phys. Chem. Chem. Phys. 18 (41), 28726–28731 (2016).

[3.63]   E. Breynaert, M. Houlleberghs, S. Radhakrishnan, F. Taulelle, J. Martens, Replication Data for: Isothermal (22 °C) Evolution of the ^{1}H MAS NMR Spectrum and Dielectric Shift of Water in Posisil Foam with MAS Frequency. V1 ed. Harvard Dataverse (2020).

[3.64]   M. Houlleberghs, A. Hoffmann, D. Dom, C. E. A. Kirschhock, F. Taulelle, J. A. Martens, E. Breynaert, Absolute Quantification of Water in Microporous Solids with ^{1}H Magic Angle Spinning NMR and Standard Addition, Anal. Chem. 89 (13) 6940–6943 (2017).

[3.65]   B. Rahn, R. Wen, L. Deuchler, J. Stremme, A. Franke, E. Pehlke, O. M. Magnussen, Coadsorbate-Induced Reversal of Solid–Liquid Interface Dynamics, Angew. Chem. Int. Ed. 21, 6065-6068 (2018); Angew. Chem. 130, 6173-6176 (2018).

[3.66]   B. Rahn, O. M. Magnussen, Formation and Diffusion of Subsurface Adsorbates at Electrodes, J. Am. Chem. Soc. 140, 9066–9069 (2018).

[3.67]   F. Reikowski, F. Maroun, I. Pacheco, T. Wiegmann, P. Allongue, J. Stettner, O. M. Magnussen, Operando Surface X-ray Diffraction Studies of Structurally-defined Co_3O_4 and CoOOH Thin Films during Oxygen Evolution, ACS Catal. 9, 3811-3821 (2019).

[3.68] T. Fuchs, J. Drnec, F. Calle-Vallejo, N. Stubb, D.J.S. Sandbeck, M. Ruge, S. Cherevko, D.A. Harrington, O.M. Magnussen, Strucutre-dependence of the Atomic-Scale Mechanisms of Pt Electrooxidation and Dissolution, Nat. Catal. 3, 754-761 (2020).

[3.69] M. Ruge, J. Drnec, B. Rahn, F. Reikowski, D. A. Harrington, F. Carlà, R. Felici, J. Stettner, O. M. Magnussen, Structural Reorganisation of Pt(111) Electrodes by Electrochemical Oxidation and Reduction, J. Am. Chem. Soc., 139, 4532-4539 (2017).

[3.70] F. Golks, K. Krug, Y. Gründer, J. Zegenhagen, J. Stettner, O. M. Magnussen, High-speed In situ Surface X-ray Diffraction Studies of the Electrochemical Dissolution of Au(001), J. Am. Chem. Soc., 133, 3772-3775 (2011).

[3.71] G. Lole, V. Roddatis, U. Ross, M. Risch, T. Meyer, L. Rump, J. Geppert, G. Wartner, P. Blöchl and C. Jooss, Dynamic Observation of Mn-adatom Mobility at Perovskite Oxide Catalyst Interfaces to Water, Nat. Commun. Mat. 1, 68-74 (2020).

[3.72] D. Raiser, S. Mildner, M. Sotoudeh, P. Blöchl, S. Techert, Ch. Jooss, Evolution of Hot Polaron States with a Nanosecond Lifetime in a Manganite, Adv. Energy Mat. 1, 1-9 (2017).

[3.73] M. Risch, F. Ringleb, M. Kohlhoff, P. Bogdanoff, P. Chernev, I. Zaharievaa, H. Dau, Water Oxidation by Amorphous Cobalt-based Oxides: In-situ Tracking of Redox Transitions and Mode of Catalysis, Energy Environ. Sci. 8, 661-674 (2015).

[3.74] N. Hall, M. Stuckelberger, T. Nietzold, J. Hartman, J.-S. Park, J. Werner, B. Niesen, M. L. Cummings, V. Rose, C. Ballif, M. K. Chan, D. P. Fenning, M. I. Bertoni, The Role of Water in the Reversible Optoelectronic Degradation of Hybrid Perovskites at Low Pressure, Phys. Chem. C 121, 25659-25665 (2017).

[3.75] M. Kodur, R. E. Kumar, Y. Luo, D. N. Cakan, X. Li, M. Stuckelberger, D. P. Fenning, Weinheim Review: X-Ray Microscopy of Halide Perovskites: Techniques, Applications, and Prospects, Adv. Energ. Mat. 1, 1903170 (2020).

[3.76] I. Rajkovic, J. Hallmann, S. Grübel, R. More, W. Quevedo, M. Petri, S. Techert, Development of a Multipurpose Vacuum Chamber for Serial Optical and Diffraction/Scattering Experiments with Free Electron Laser Radiation, Rev. Sci. Instr. 81, 045105-1-6 (2010).

[3.77] R. Neutze, R. Wouts, S. Techert, J. Davidsson, M. Kocsis, A. Kirrander, F. Schotte, M. Wulff, Visualising Photo-Chemical Dynamics in Solution through Picosecond X-ray Scattering, Phys. Rev. Lett. 87, 195508-195512 (2001).

[3.78] Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, A. Föhlisch, Orbital-specific Mapping of the Ligand Exchange Dynamics of $Fe(CO)_5$ in Solution, Nature 520 (7545), 78-81 (2015).

[3.79] P. Busse, Z. Yin, D. Mierwaldt, J. Scholz, B. Kressdorf, L. Glaser, P. S. Miedema, A. Rothkirch, J. Viefhaus, C. Jooss, S. Techert, M. Risch, Probing the Surface of LSMO in Water Vapor by in-situ RIXS: Interpretation of the Fluorescence Yields, J. Phys. Chem. C 124, 7893-7902 (2020).

[3.80] V. Kolev, V. Freger, Molecular Dynamics Investigation of Ion Sorption and Permeation in Desalination Membranes, J. Phys. Chem. B 119, 14168-14179 (2015).

[3.81] R. Gleissner, M. Creutzburg, H. Noei, A. Stierle, Interaction of Water with Graphene/Ir(111) Studied by Vibrational Spectroscopy, Langmuir 35(35), 11285 - 11290 (2019).

[3.82] V. Freger, Outperforming Nature's Membranes, Science 348 (6241), 1317-1318 (2015).

[3.83] J.-L. Barrat, L. Bocquet, Large Slip Effect at a Nonwetting Fluid-solid Interface, Phys. Rev. Lett. 82 (23), 4671-4674 (1999).

[3.84] P. Huber, Soft Matter in Hard Confinement: Structure, Texture, Diffusion and Flow in Nanoporous Media, J. Phys. Cond. Mat. 103102 (2015).

[3.85] G. Gor, P. Huber, N. Bernstein, Adsorption-Induced Deformations of Nanoporous Materials – A Review, Appl. Phys. Rev. 4, 011303 (2017).

[3.86]   N. Biswas, E. Erbes, C. J. Brett, M. Schwartzkopf, K. Basuroy, Q. Chen, A. Chumakov, S. Frenzke, M. Gensch, K. Gordeyeva, P. Kielb, S. Kirchner, V. Körstgens, P. Müller-Buschbaum, H. Müller-Werkmeister, J. Rubeck, S. Thekku Veedu, J. J. Velazquez-Garcia, V. Waclawek, D. Söderberg, S. V. Roth, S. Techert, Therapeutic Nanopaper Allows for a Locally Defined, Small-dosing Drug-Release, in press (2020).

[3.87]   S. V. Roth, A Deep Look into the Spray Coating Process in Real-time—the Crucial Role of X-rays, J. Phys. Condens. Mat. 28, 403003 (2016).

[3.88]   M. Esplandiu, K. Zhang, J. Fraxedas. B. Sepulveda, D. Reguera, Unraveling the Operational Mechanisms of Chemically Propelled Motors with Micropumps – Self-powdered Nano- and Micromotors, Acc. Chem. Res. 51, 1921-1930 (2018).

[3.89]   J. Fraxedas, Water at Interfaces: a Molecular Approach, B. Raton: CRC Press (2014). ISBN 9781439861042.

[3.90]   M. Xu, M. Soliman, X. Sun, B. Pelaz, N. Feliu, W. J. Parak, S. Liu, How Entanglement of Different Physicochemical Properties Complicates the Prediction of in Vitro and in Vivo Interactions of Gold Nanoparticles, ACS Nano 12, 10104−10113 (2018).

[3.91]   T. Nagel, H. Shao, A. K. Singh, N. Watanabe, C. Roßkopf, M. Linder, A. Wörner, O. Kolditz, Non-equilibrium Thermochemical Heat Storage in Porous Media: Part 1 – Conceptual Model. Energy 60, 254-270 (2013), ISSN: 03605442.

[3.92]   W. Ranke and Y. Joseph, Determination of adsorption energies and kinetic parameters by isosteric methods; Phys. Chem. Chem. Phys. 4, 2483-2498 (2002).

CMWS Pillar 4: Real-Time Chemical Dynamics

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III.4 Real-Time Chemical Dynamics

III.4.1 Scientific Challenges and State of the Art

Many, if not most, of the important chemical reactions take place in liquid water. These processes occur on multiple time scales, ranging from femtoseconds to minutes. Therefore, a central objective of ultrafast science is to provide a real-time characterisation of the fundamental processes occurring in this ubiquitous solvent. Such a characterisation has to address the temporal evolution of both the electronic structure and the atomic positions. This is because the electronic structure determines the forces acting on the atoms, and the atomic positions in turn affect the properties of the electronic states. In the following, the main directions to be pursued in the CMWS in the area of real-time chemical dynamics will be discussed. We present below these pursuits as five key challenges in the field of aqueous-phase dynamics.

Challenge 1: Characterisation of the Energetics and Dynamics of the Transient Radicals Produced by Water Radiolysis

A primary challenge to be pursued within the CMWS is the investigation and understanding of ultrafast aqueous radiolysis, i.e. the "electron and hole-doping" dynamics of liquid water and aqueous solutions. These processes inevitably arise
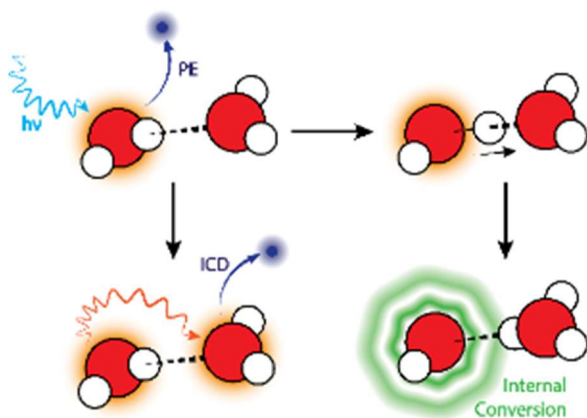
Figure III.4.1: Processes triggered by inner-valence photoionization of water: Electron emission by Intermolecular Coulombic Decay competes with relaxation by proton transfer. Observing these processes, and further conversions of their reaction products, in real time is part of *challenge 1.* Figure reproduced from [4.35].

following vacuum ultraviolet (VUV), extreme ultraviolet (XUV) or X-ray photoabsorption, energetic electron or ion irradiation, or via optical strong-field ionisation of aqueous systems (see, e.g. Figure III.4.1). Upon such irradiation, a highly-excited medium of transient radicals ($H_2O^{\bullet+}$, $H_2O^{\bullet-}$, $OH^\bullet$, $H^\bullet$ and hydrated electrons, $e^-_{(aq.)}$ [4.1, 4.2, 4.60, 4.61]) is formed [4.3–4.7, 4.62, 4.63]. The result is a complex cascade of light- or charged-particle-initiated ultrafast processes and an aggressive chemical environment that is further complicated by the addition of solutes or interfaces. The global importance of these processes motivates their characterisation on ultrashort time scales spanning diverse fields such as photon science [4.6–4.8], radiation chemistry and associated biological damage [4.4, 4.9–4.13], radiotherapy [4.14], water purification [4.15] and nuclear reactor operation/waste management [4.5]. A detailed molecular-level understanding of this dynamic medium is a prerequisite for tracking aqueous phenomena using newly available ultrashort pulse XUV, X-ray, electron and/or ion sources.

Challenge 2: Interrogation of Transient Electron, Proton, and Hydroxide Solvation Structures in Water, including their Generation, Propagation, and Reaction Dynamics

While chemical reactions in organic solvents are often well described as unimolecular reactions (reacting solute treated as a single species in a solvent continuum), at least bimolecular descriptions are necessary for an exact description of the reaction dynamics and kinetics of aqueous systems due to the nature of hydrogen bond networks. Furthermore, chemical reactions in water are often driven by charge-propagating hydrogen-bridge dynamics; with water rather actively behaving as a participant in the reaction as opposed to a passive spectator. Protons and hydroxyl anions are produced naturally and spontaneously in bulk water but also through solvation or excitation of aqueous solutions. Aqueous acid–base chemistry and the majority of biological redox processes are driven by proton [4.16–4.18] and hydroxyl anion [4.19, 4.20] migration processes. The anomalously high mobility of these species is commonly ascribed to the structural Grotthuss diffusion and hypercoordination-driven transport

mechanisms, respectively. Additionally, an understanding of the hydration, migration, and reaction dynamics of aqueous electrons – injected *ex situ* or *in situ* – are prerequisite to developing a microscopic view of radiolysis and aqueous redox processes in general [4.4, 4.21, 4.22]. The unusually high mobility of aqueous electrons is intrinsically linked to ultrafast solvent motions and is partly responsible for the high reactivity and activity of strongly reducing aqueous electrons. Addressing *challenge 2* is required to identify the ultrafast mechanisms of proton, hydroxyl anion, and (pre-)hydrated electron generation, migration, and reaction.

Challenge 3: Real Time Probing of Transient Electronic and Nuclear Structure in Solvated Complexes in Bulk Aqueous Solution, including "Rare Events"

Chemical reactions in liquids, particularly in aqueous media, are fundamentally different than those occurring in isolation, i.e. under low-pressure or gas-phase conditions. When solute molecules are imbedded in polar (strongly-interacting) solvents such as water, the energetics of their states and associated reaction coordinates are perturbed, leading to potential variations in reaction probabilities, time scales, and mechanisms. Furthermore, at the typical densities of aqueous systems, solute molecules interact with

the solvent on few hundred femtosecond timescales [4.23]. The diffusive approach of reagents, solvent caging, solvent reorganisation dynamics, buffeting of reactive species by solvent molecules, stabilisation of charged species and associated reactive pathways, and ultrafast equilibration of formed products or frustrated reactants must all be considered when following and interpreting the chemical dynamics. Accordingly, *challenge 3* necessitates the adoption of highly differential and selective experimental techniques for the disentanglement and understanding of such processes.

Challenge 4: Real Time Probing of Solvation Dynamics in Aqueous Solutions

Theoretical and simulation methods can decompose solvation dynamics and energetics into distinct short- and long-range interactions, but complementary experimental probes that robustly sample the complex many-body dynamics of solute–solvent interactions with atomic resolution are needed to develop reliable models for dynamic solvation processes. Here, experimental approaches investigating well-defined gas-phase systems involving microsolvated molecules bridge the gap from theory to condensed-phase liquids. Gaining a microscopic understanding of chemical reactivity in aqueous solution motivates these developments. For example, charge transfer, radical activity, and many biological processes
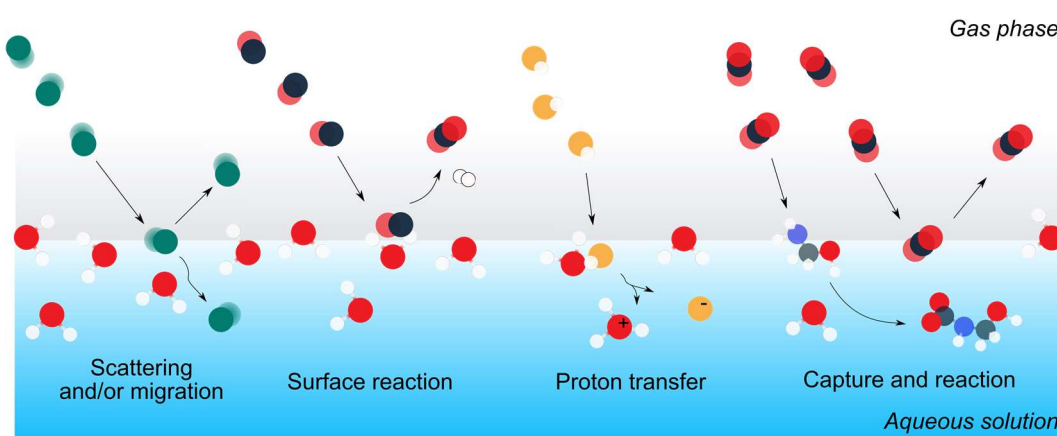
Figure III.4.2: Several possible interaction processes occurring between gas-phase molecules and an aqueous solution. Primary research questions include how chemical reactivity evolves from the gas phase through the interface, the role played by the liquid surface structure, and how these processes depend on conditions such as temperature, velocity, molecular orientation during the collision, and the nature of the chemical species.

depend on and are driven by the interplay between the energetics of the solutes and their neighboring water shells [4.24, 4.25]. Despite extensive studies [4.26, 4.27, 4.28] of aqueous solutions over the last decades, a complete understanding of associated solvation structures has yet to be achieved and is prerequisite for an understanding of dynamical aspects. As dynamical molecular structure – fluxional hydrogen-bond environments evolving on few-fs time scales – is a defining characteristic of liquid water/aqueous solution (*challenge 4*), ultrafast probes of solvation dynamics are an essential ingredient in developing a microscopic understanding of these systems. This pillar focuses on identifying fundamental mechanisms, whereas the application of these findings to biomolecular function is central to pillar 5.

Challenge 5: Application of Time-Resolved Probes to develop an Understanding of Reactions at Aqueous Interfaces

Chemical reactions involving liquid water and aqueous solutions at interfaces are important in numerous fields that are relevant to life on Earth, e.g. atmospheric science, energy research, and geochemistry [4.29, 4.30]. Solution–vacuum, solution–gas, solution–solid (both macroscopic surfaces and nanoparticles) and solution–solution interfaces are all important in this regard. Following the processes and reactions that occur at these interfaces (Figure III.4.2) on their natural time scale will lead to a detailed understanding of the underlying mechanisms of the associated phenomena. Such studies require the development of new methods that can, for example, selectively probe the composition of the interface of the liquid on the time scales of the chemical transformations. Elucidating the chemical state of the respective species at the interfacial water layer is necessary to draw conclusions on the actual reactions that took place. As an example, thus far, there is very little experimental insight into how chemical reactions involving gas-phase reactive species occur when they impinge on aqueous solutions [4.64]. Even the reaction of gaseous CO_2 with a liquid water surface is not understood [4.65], despite the importance of this reaction for the terrestrial climate and biology. With this in mind, the development of highly-

selective, time-resolved spectroscopies and their application to such problems is a major aim of pillar 4 of the CMWS.

Reactions at aqueous interfaces represent an over-arching topic of the CMWS, with cross-pillar links in particular to activities in pillar 2 on gas-phase reactions at the surface of ice grains and atmospheric aerosols and in pillar 1 on temporally resolved, structural studies of water interfaces.

III.4.2 Preliminary Work and Competences

The groups contributing to this effort are collectively in command of a unique repertoire of methods for probing ultrafast phenomena in water targets and solutions.

Over the last two decades, we have developed and extensively applied the liquid jet photoelectron spectroscopy (PES) technique [4.31], allowing electronic structure in bulk aqueous solution and at aqueous interfaces to be directly probed on an absolute energy scale [4.32, 4.66]. Ultrafast electronic and nuclear relaxation processes have been studied using core-hole clock spectra [4.33]. We have additional experience in the production of clusters and aerosol particle beams for experiments on water ensembles [4.34]. For example, by combination of energy domain measurements and theory we estimated the intermolecular-Coulombic-decay (ICD) lifetime in small water clusters (12–52 fs) [4.35].

For time-resolved experiments on such targets, we have created several unique setups using ultrashort photon pulses. The FXE instrument at the European XFEL permits to study global structural changes (via wide-angle X-ray scattering) together with local intramolecular changes (via X-ray spectroscopies) on the atomic level and with femtosecond time resolution [4.67]. It aims to offer new possibilities to study solvation shell dynamics with new observables. We employed ultrafast laser and X-ray technology to get a glimpse of the response of an aqueous solvation shell to intramolecular dynamics [4.36, 4.37]. Other new opportunities for investigating real-time chemical dynamics arise from our expertise in tuning coherence, particularly in connection with free-electron lasers (FELs). Our recent transfer of a powerful optical method towards short-wavelength FEL technology [4.38] paves the way

towards utilisation of advanced nonlinear methodologies in water-related research. Furthermore, we have developed and commissioned a sample-delivery setup for the interrogation of controlled, species-specific molecules at the European XFEL: COMO. This enables us to investigate ultrafast dynamics of microsolvated molecules in combination with the aforementioned photon tools, which was demonstrated in a first beamtime on microsolvated pyrrole.

We have developed advanced table-top sources providing extreme time resolution (from few femtoseconds down to few hundreds attoseconds) in a broad spectral range (from the visible to the extreme ultraviolet). In Ref. [4.39], we demonstrated the generation of high-energy isolated attosecond pulses, which are crucial tools for the investigation of complex targets [4.40] with extremely high temporal resolution. For fs time-resolved PES, we have developed the required infrastructure (laser systems, non-linear optical IR to soft X-ray beam lines, sample sources, photoelectron spectrometers, detection architectures) and applied it to gas- and liquid-phase samples in the perturbative and non-perturbative regimes [4.43, 4.44]. To follow electron dynamics of chemical reactions in water on an atto- to femtosecond time scale, we are developing a high-flux isolated attosecond pulse source starting from our initial results where we reached the water window up to 450 eV [4.41]. We are performing transient absorption experiments, triggering chemical reactions in properly prepared mixtures of gases and liquids. The construction of relativistic, 2–4 MeV, THz driven electron guns for ultrafast electron diffraction in water, synchronised with all the above tools, is also on the horizon [4.42].

Over the last years we have developed a versatile photon spectroscopy setup. It is specifically designed for multi target systems, including water clusters and liquid water jets [4.45]. In Ref. [4.46], we showed that fundamentally different processes occur in the surface and bulk regions of liquid water. In terms of measurements at THz frequencies we have a range of instrumentation including broadband (up to 10 THz) linear and non-linear THz spectrometers, THz quantum cascade lasers and on-chip THz spectrometers specifically designed to measure spectral

properties of small volumes of liquid [4.47, 4.48]. We have also developed a combined setup for X-ray emission (XES) and X-ray Raman scattering for the study of melts at extreme conditions that can be used for the investigation of a solvent's and solute's electronic and local atomic structure in parallel under the same excitation conditions [4.49]. This portable setup can be implemented at synchrotron sources and XFEL end stations.

In the realm of theory, we have experience with the development and application of diverse theoretical and computational tools suitable for investigating the dynamics of water. In Ref. [4.50], we summarised our work on water using FEL sources, in particular the structure of water in supercooled liquid droplets as well as measurements of XES down into "No-man's land" (see also pillar 1). Molecular dynamics is an essential tool in many simulations of water dynamics. In Ref. [4.51], we developed an efficient and accurate coupled-cluster-based path-integral molecular dynamics method, which we used to demonstrate the impact of nuclear quantum effects on the low-temperature protonated water dimer. We developed in Ref. [4.52] a novel *ab initio* path-integral method, explicitly including nuclear quantum effects without any additional
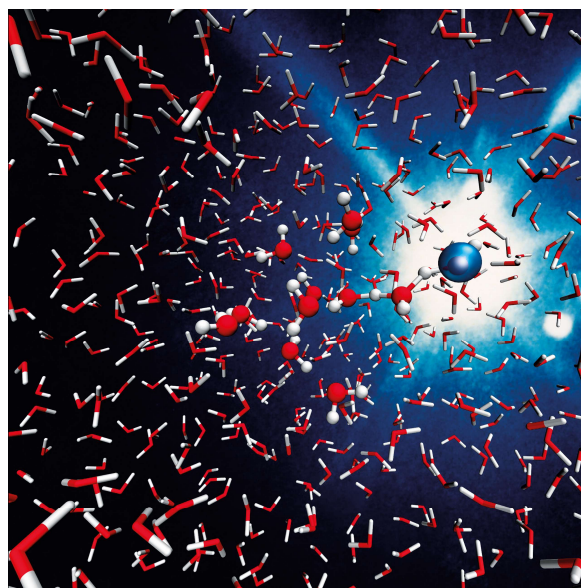
Figure III.4.3: Femtosecond X-ray pulses capture the ultrafast proton transfer reaction in ionised liquid water, forming a hydroxyl radical and a hydronium ion [4.62]. Extensive molecular-dynamics simulations made it possible to understand the connection between the experimentally observed resonant X-ray absorption signal and the proton-transfer reaction.

computational costs, and applied it to liquid water at ambient conditions. In Ref. [4.53], we performed on-the-fly *ab initio* and force-field molecular dynamics simulations of liquid water pumped with suitable high-intensity THz pulses. Our simulations revealed the possibility of ultrafast temperature-jumps over a wide range of pump frequencies. The use of PES to investigate the transient state of such THz-pumped water was investigated in Ref. [4.54].

Relevant theoretical tools for describing non-equilibrium quantum solvation dynamics include numerically exact path integral simulations of time dependent dielectric solvents, and Langevin and master equation approaches. Using such approaches, we studied the relaxation dynamics of photoexcited Fe-II complexes dissolved in water and identified the relaxation pathway that the molecular complex follows in the presence of a hydration shell of bound water at the interface between the complex and the solvent [4.57].

In connection with *challenge 1* from section III.4.1, we theoretically investigated nonadiabatic dynamics in water clusters following ultrafast electron removal ("hole doping") [4.55]. In the Zundel cation, the formation of a strongly (anti)correlated proton–electron hole pair within only 3 fs was observed. In this case, a quantum-dynamical treatment of the nuclear degrees of freedom was still possible. A promising direction to include quantum effects in simulations of the dynamics of nuclei is the ring polymer molecular dynamics (RPMD) approach. Ref. [4.56] shows that RPMD can be employed in settings with non-equilibrium initial conditions, e.g. following photoexcitation, and thus enables the simulation of pump-probe experiments. Important studies on light-induced vibrational and electronic dynamics of molecules in water, conducted spectroscopically and by modelling the experiments, are reported in Refs. [4.58, 4.59]. There, the electronic dynamics of nucleobases in water were investigated, providing new microscopic insights into solvation dynamics and related chemical processes. Furthermore, our computational methodology played an important role in connection with the observation of the fastest chemical processes in the radiolysis of water [4.62] (see Figure III.4.3).

Combining the competences of the participating groups in one coherent environment will enable strong intra-pillar synergies, as it will become possible to combine several unique, leading techniques brought in by their inventors into new experiments that push the limits of what is scientifically accessible. This includes the combination of experimental techniques, e.g. light sources with tailored liquid targets, and the collaboration of experimentalists with leading groups in theory and modeling.

III.4.3 Objectives

A characteristic of liquid water is its dynamical structure, which is reflected in order/high disorder descriptions. The intrinsic time scales of the dynamics of water/aqueous solutions span the attosecond to millisecond regime. This pillar of the CMWS will directly address the five challenges listed in section III.4.1 in the time-domain, with a primary focus on ultrafast dynamics, but also addressing the reaction kinetics that emerge on longer timescales, in connection with the time-resolved activities described in the other research pillars. Here we will make use of the unique, highly-differential and selective probe techniques vailable within the consortium of participating groups.

Besides following the evolution of electron solvation upon light-induced electron and hole doping, one objective of the CMWS with respect to *challenge 1* is to unravel the electron hole dynamics in water. There is indeed some evidence that quantum coherences and complex couplings between electronic and nuclear degrees of freedom play a key role in hole migration, redistribution and localisation. After sudden ionisation, the charge is expected to migrate rapidly (sub-femtosecond time scale) between the water molecules and the solute molecule (see Figure III.4.4). Questions related to electronic quantum coherence and decoherence times, and the impact on nuclear quantum effects, will play a central role. This work will also provide information that is of relevance in connection with radiation-induced astrochemical processes studied in pillar 2. The electron-hole-excited states encountered in radiolysis require a nonstandard theoretical treatment. This treatment must not only be able to capture the dense bands of electronic eigenstates in electron-hole-excited
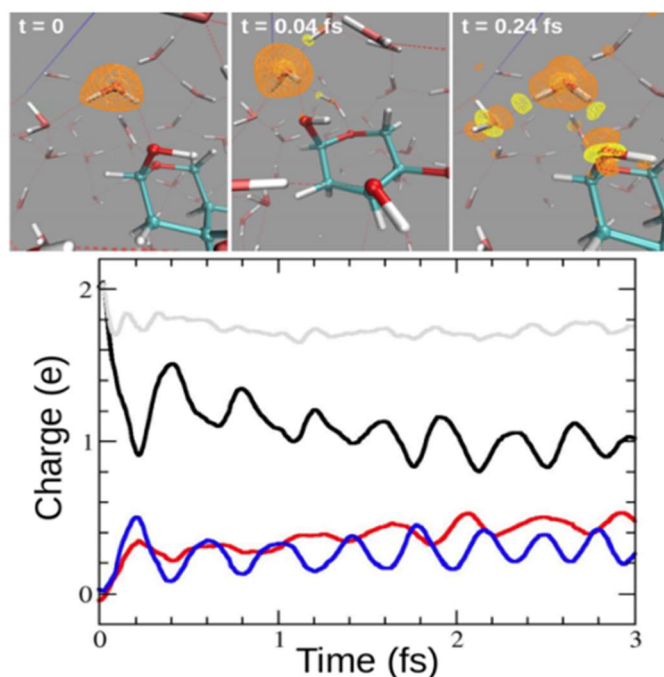
Figure III.4.4: Simulated sub-femtosecond charge migration from water to water and water to 2-deoxy-D-ribose (DR). Top panel shows the calculated charge density variation and bottom panel shows the integrated charge around the water molecule (black line), the water molecule attached to the DR (blue line) and the DR (red line). Figure reproduced from M. A. Hervé du Penhoat et al., J. Phys. Chem. A 122, 5311−5320 (2018).

water, but it must also be able to quantitatively describe non-Born-Oppenheimer effects associated with nonadiabatic transitions among the states in these electronic bands. Another challenge in this context arises from standard molecular dynamics that are based on the assumption of classical nuclei. In view of the strong vibrational quantum effects characterising, for instance, the heat capacity of water, the inclusion of nuclear quantum effects in the theoretical description of radiolytic processes is of importance. Therefore, a key objective of pillar 4 is addressing these theoretical challenges by developing a corresponding first-principles simulation framework. Congruent to these theoretical developments, associated experiments – newly enabled by the infrastructure available within the consortium – will investigate ionisation-initiated aqueous electron-hole dynamics on ultrafast time scales. A more specific goal is the combined experimental and theoretical mapping of the photon excitation energy dependence of such dynamics. This will include the precise determination of the formation and reactive time-scales, as well as the absolute energetics of the transient radicals formed in neat water – as well as select aqueous solutions – following XUV and soft X-ray irradiation. Thus, benchmark experimental and theoretical data will be garnered in tandem, bringing perspicacity to the ultrafast radiation chemistry of aqueous systems.

In order to address *challenge 2* – and in the process of addressing *challenges 1, 3* and *5* – we will selectively and directly monitor the real-time behaviours of protons, hydroxyl anions and (pre)hydrated electrons in water, as well as their effects on surrounding solvent and solute molecules. Interactions of these species with increasingly complex solutes ranging from atomic radicals to biomolecules will be studied. Potential experiments include ultrafast time-resolution and element-/functional-group-resolved studies of dissociative electron attachment and proton-bridge driven/catalysed rearrangement reactions. In both cases, following optical pump electron/proton production, multidimensional IR and X-ray spectroscopic probe techniques will be utilised to elucidate the ensuing dynamics.

Due to the ultrashort time window over which dynamical signatures of chemical transformations in aqueous solution (*challenge 3*) have to be probed, ultrafast techniques are essential to gain the deepest insights into these processes. We will adopt such methods within this pillar of the CMWS, allowing unimolecular, bimolecular and multimolecular reaction dynamics of solutes to be investigated on attosecond to microsecond time scales. Studied solutes are expected to span hydrated electrons and simple ions all the way up to macromolecular species such as proteins suspended in aqueous solution. Exemplary studies within *challenge 3* include site-selective

investigations of UV and XUV photorelaxation mechanisms of aqueous UV chromophores, bases, nucleotides, and nucleosides of DNA. The unique combination of infrastructures within the consortium would allow such experiments to be performed with increasing degrees of hydration. Here, our ultrafast time-resolution and site-specific X-ray and IR spectroscopic probes, as well as modern *ab initio* electronic structure and simulation methods, are expected to provide hitherto unavailable understanding of the photo-protection behaviours of these complex, bio-logically relevant aqueous solutes.

We will address *challenge 4* using ultrashort pulse radiation sources and time-resolved spectroscopies/diffractometries to trigger and interrogate evolving solvation structures in real time. Ultrafast time-resolution, highly-differential, and selective approaches will be required to extract solvation-sensitive signals from this inhomogeneous, fluxional environment. The im-pact of the solvent on the time evolution of the spectral response of the solute will be investigated in different spectral regions spanning the THz to hard X-ray range. Additionally, local and non-local solvent structural dynamics will be probed directly using soft X-ray/IR and THz spectroscopies to specifically monitor the solvating water molecules and their collective behaviours. Furthermore, single-shot X-ray and charged particle diffraction techniques will be adapted to record time-stamped snapshots of the 'frozen' solvent nuclear structure as it evolves. Accordingly, unprece-dented insights into the ultrafast dynamics of solvation will be garnered.

In connection with *challenge 5*, we will focus on the following pertinent questions: (a) How many layers of solvent molecules constitute "the reac-tive surface"? (b) What is the effect of interfacial surface roughness? (c) How does reactivity evolve across phases and potentially through interfaces? (d) How do these processes and their evolution depend on conditions such as tempera-ture, reactant velocity, reactant orientation, and the nature of the reactive chemical species? We aim to address these questions with the aid of spatially- and temporally-resolved spectrosco-pies. For example, we intend to address some of these far-reaching goals and photoelectrochemi-cal water splitting mechanisms using aqueous

inorganic oxide nanoparticle – for example TiO_2 – suspension jets, ultrashort UV-VIS pulse initiated interfacial charge transfer, and aqueous-solid interface selective and sensitive time-resolved, XPS techniques. In view of the overarching importance of interfacial water in all pillars of CMWS, we expect our research addressing *challenge 5* to provide numerous opportunities for inter-pillar exchange and collaboration.

III.4.4 Methodologies

Real-time investigation of chemical – i.e. electro-nic and geometric structural – dynamics requires time-resolved techniques, primarily based on the pump-probe approach. To address the above listed challenges, it will be necessary to exploit a broad range of advanced light sources (table-top laser based, synchrotrons and FELs) with differ-ent photon energies (covering the THz to hard X-ray ranges) and different pulse durations (from attoseconds to nanoseconds).

On the route towards a molecular description of biological function, gas-phase studies of micro-solvated species allow the gradual introduction of perturbations associated with the local environ-ment. To this end, biologically relevant molecules will be studied embedded in water clusters (with variable numbers of water molecules), water droplets, and bulk aqueous solutions. We will compare results obtained from gas-phase complexes of increasing size with those from bulk aqueous solutions. Accordingly, the gap from gas-phase water complexes to bulk aqueous solutions will be bridged, allowing the effects of solvation on solute-water interaction dynamics to be isolated and understood.

The following list summarises the specific meth-odologies that will be used within pillar 4.

(a) Real-time monitoring of light-activated electron dynamics and combined electron as well as nuclear dynamics in biological systems embed-ded in water clusters or droplets will be investigated with extremely high time resolution. Attosecond light sources with relatively high repetition rates (tens of kHz) and with photon energies spanning the XUV to the soft X-ray range will be used in combination with sub-2 fs UV-VIS pulses for time-resolved measurements. Elec-tronic dynamics initiated in biomolecules solvated in water will be investigated by time-resolved
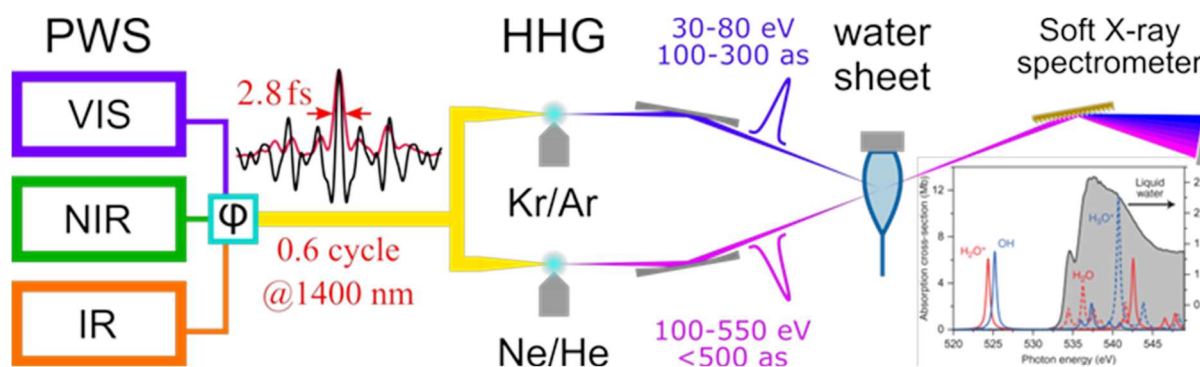
Figure III.4.5: Schematic of the transient-absorption attosecond-pump/attosecond-probe experiment on ultrathin water sheet, driven by our Parametric Waveform Synthesizer (PWS).

photo-electron and photo-ion spectroscopy as well as transient absorption spectroscopy (see Figure III.4.5) in the water window.

(b) Alternatively, direct strong-field ionisation photoelectron imaging experiments allow for few- and sub-femtosecond imaging of electronic wave-packet dynamics through resonance-enhanced photoionisation momentum features and of atomic structural dynamics through laser-induced electron diffraction. Precision measurements of these dynamics in well-defined microsolvated clusters are enabled by novel experimental approaches for the preparation and purification of these systems [4.68]. These techniques were recently also implemented in the COMO setup at European XFEL and enable further ultrafast dynamics experiments utilising soft X-ray radiation as a site-specific probe. By exploiting novel efficient and temperature-controlled sample preparation methodology for aerosol particles [4.69], one can envision to extend these precision experiments to chemical reactions in and on aerosols.

(c) To interrogate ultrafast chemical transformations in bulk aqueous environments, time-resolved XUV and soft X-ray PES will be applied. Novel, synchronised laser sources (few-fs pulse duration, sub-eV-bandwidths, 10^9–10^{15} photon s^{-1} fluxes, at hundred kHz repetition rates) will be utilised. In combination with liquid jet targets and high-collection efficiency spectrometers, it is planned to explore aqueous-phase reactive processes and biological system damage mechanisms on femtosecond to nanosecond time scales. Global understandings of the associated dynamic electronic structure will be garnered through a combination of valence- and core-state-sensitive experiments.

(d) Interfacial dynamics will similarly be studied by combining such laser infrastructure with more modern aqueous jet technologies – gas-dynamic virtual nozzles (gas–liquid), colliding/variable thickness flat jets (liquid–liquid) and aqueous nanoparticle suspension jets (solid-liquid). The combination of resonant optical excitation of interfacial reactive precursors with interfacially sensitive and -selective ultrafast time resolution XPS and XAS probes, will permit aqueous interfacial dynamics to be studied with nanometre, femtosecond spatio-temporal resolution.

(e) Electron and nuclear dynamics will also be traced by coherent nonlinear X-ray spectroscopy schemes making use of intense femtosecond FEL pulses. High photon energies will allow for site-specific excitation, to address processes in an element and state-selective way. Charge, energy and information transfer will all be monitored, with unprecedented spatial and temporal resolution, by electron, ion and photon spectroscopies and by different coincidence techniques (used for identifying individual processes among the typically large manifolds of possible processes at these high excitation energies).

(f) To efficiently study bimolecular reaction dynamics in the aqueous bulk and at aqueous interfaces, it is anticipated to make use of variable polarisation XUV and soft X-ray synchrotron beam lines (for example, P04 at PETRA III), synchronised MHz-repetition rate laser sources, and a state-of-the-art liquid jet X-ray PES setup (recently developed by FHI, see Figure III.4.6). Experiments will be initiated in bespoke liquid jet environments to produce reactive radicals from
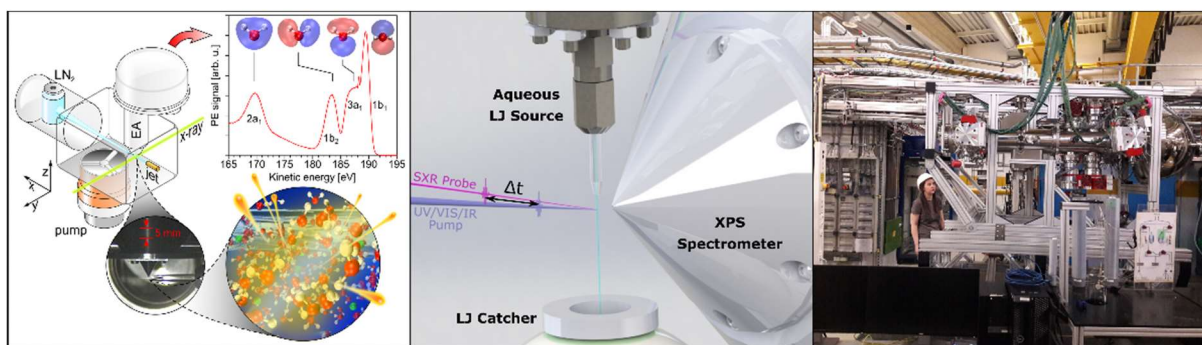
Figure III.4.6: (left) isometric schematic of a liquid jet (LJ) X-ray photoelectron spectrometer setup [4.72]. (middle) Optical-pump-X-ray-probe liquid jet time-resolved PES scheme. (right) Photograph of a fourth generation LJ photoelectron spectrometer (Electronic structure from Aqueous Solutions & Interfaces, EASI, Instrument, FHI Berlin) being commissioned at the P04 beam line at PETRA III.

photoactive precursors. The combined infrastructure will allow diffusion, geminate-recombination, reactive, and product relaxation kinetics in dilute aqueous solutions to be element-, state- and site-specifically probed on picosecond to microsecond time scales with picosecond time-resolution. Complementary insights can be obtained through similar experiments on the corresponding micro-solvated molecules [4.70, 4.71].

(g) Chemical dynamics in wet metal clusters will be addressed using few-fs and intense SXR pulses delivered by the European XFEL in combination with high-resolution and angle-resolved electron, ion (also in coincidence) and fluorescence spectroscopies (all available at the SQS instrument). The possibility of two-color SXR pump-probe experiments with independent adjustment of the wavelength, pulse duration, intensity and arrival time of each pulse will allow the internal dynamics of these systems – such as electronic and nuclear rearrangement, charge transfer processes, fragmentation and general energy dissipation – to be studied. Such experiments will take particular advantage of the high repetition rate of the European XFEL, which is a prerequisite for coincidence measurements.

(h) Structural dynamics in water will also be investigated using electron diffraction as a probe. To this end, strong THz fields will produce sub-50 fs relativistic electron bunches with energies in the 2–4 MeV range. In combination with synchronised ultrashort pulse excitation sources and the described liquid target infrastructure, ultrafast electron diffraction studies of aqueous systems will be enabled.

(i) In order to simulate ultrafast radiolytic processes in water, simulation frameworks that can handle bands of excited electronic states, non-Born-Oppenheimer effects, and nuclear quantum effects will be developed. We will base the electronic-structure part of this framework on the method of configuration interaction singles (CIS). CIS is size-consistent and is practically the only wave-function-based method that scales sufficiently favorably with system size. From CIS, we will compute, on the fly, gradients and non-adiabatic coupling matrix elements, which serve as input to a surface-hopping molecular-dynamics calculation. Nuclear quantum effects we plan to incorporate via concepts connected to ring-polymer molecular dynamics and ring-polymer contraction. Furthermore, we will explore embedding strategies of the QM/MM type, where the QM region will be based on CIS.

III.4.5 References

[4.1]   J. M. Herbert and M. P. Coons, The hydrated electron, Ann. Rev. Phys. Chem. 68, 447-472 (2017).

[4.2]   F. Uhlig, O. Marsalek, and P. Jungwirth, Unraveling the complex nature of the hydrated electron, J. Phys. Chem. Lett. 3, 3071–3075 (2012).

[4.3]   J. Ma, F. Wang, and M. Mostafavi, Ultrafast Chemistry of Water Radical Cation, $H2O^{\bullet+}$, in Aqueous Solutions, Molecules 23, 244 (2018).

[4.4] B. C. Garrett, D. A. Dixon, D. M. Camaioni, D. M. Chipman, M. A. Johnson, C. D. Jonah, G. A. Kimmel, J. H. Miller, T. N. Rescigno, P. J. Rossky, S. S. Xantheas, S. D. Colson, A. H. Laufer, D. Ray, P. F. Barbara, D. M. Bartels, K. H. Becker, K. H. Bowen, Jr., S. E. Bradforth, I. Carmichael, J. V. Coe, L. R. Corrales, J. P. Cowin, M. Dupuis, K. B. Eisenthal, J. A. Franz, M. S. Gutowski, K. D. Jordan, B. D. Kay, J. A. LaVerne, S. V. Lymar, T. E. Madey, C. W. McCurdy, D. Meisel, S. Mukamel, A. R. Nilsson, T. M. Orlando, N. G. Petrik, S. M. Pimblott, J. R. Rustad, G. K. Schenter, S. J. Singer, A. Tokmakoff, L.-S. Wang, C. Wittig, and T. S. Zwier, Role of Water in Electron-Initiated Processes and Radical Chemistry: Issues and Scientific Advances, Chem. Rev. 105, 355-390 (2005).

[4.5] H. Christensen and S. Sunder, Current State of Knowledge of Water Radiolysis Effects on Spent Nuclear Fuel Corrosion, Nucl. Technol. 131, 102-123 (2000).

[4.6] M. G. Gonzalez, E. Oliveros, M. Wörner, and A. M. Braun, Vacuum-ultraviolet photolysis of aqueous reaction systems, J. Photoch. Photobio. C 5, 225-246 (2004).

[4.7] O. Marsalek, C. G. Elles, P. A. Pieniazek, E. Pluhařová, J. VandeVondele, S. E. Bradforth, and P. Jungwirth, Chasing charge localization and chemical reactivity following photoionization in liquid water, J. Chem. Phys. 135, 224510 (2011).

[4.8] G. Heit, A. Neuner, P.-Y. Saugy, and A. M. Braun, Vacuum-UV (172 nm) Actinometry. The Quantum Yield of the Photolysis of Water, J. Phys. Chem. 102, 5551-5561 (1998).

[4.9] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons, Science 287, 1658-1660 (2000).

[4.10] J. Nguyen, Y. Ma, T. Luo, R. G. Bristow, D. A. Jaffray, and Q.-B. Lu, Direct observation of ultrafast-electron-transfer reactions unravels high effectiveness of reductive DNA damage, PNAS 108, 11778-11783 (2011).

[4.11] C.-R. Wang, J. Nguyen, and Q.-B Lu, Bond Breaks of Nucleotides by Dissociative Electron Transfer of Nonequilibrium Prehydrated Electrons: A New Molecular Mechanism for Reductive DNA Damage, J. Am. Chem. Soc. 131, 11320–11322 (2009).

[4.12] J. Simons, How Do Low-Energy (0.1−2 eV) Electrons Cause DNA-Strand Breaks?, Acc. Chem. Res. 39, 772–779 (2006).

[4.13] J. Ma, F. Wang, S. A. Denisov, A. Adhikary, and M. Mostafavi, Reactivity of prehydrated electrons toward nucleobases and nucleotides in aqueous solution, Science Adv. 3, e1701669 (2017).

[4.14] P. O'Neill and P. Wardman, Radiation chemistry comes before radiation biology, International Journal of Radiation Biology 85, 9-25 (2009).

[4.15] K. Zoschke, H. Börnick, and E. Worch, Vacuum-UV radiation at 185 nm in water treatment – A review, Water Res. 52, 131-145 (2014).

[4.16] A. Hassanali, F. Giberti, J. Cuny, T. D. Kühne, and M. Parrinello, Proton transfer through the water gossamer, PNAS 110, 13723-13728 (2013).

[4.17] M. Thämer, L. De Marco, K. Ramasesha, A. Mandal, and A. Tokmakoff, Ultrafast 2D IR spectroscopy of the excess proton in liquid water, Science 350, 78-82 (2015).

[4.18] F. Dahms, B. P. Fingerhut, E. T. J. Nibbering, E. Pines, and T. Elsaesser, Large-amplitude transfer motion of hydrated excess protons mapped by ultrafast 2D IR spectroscopy, Science 357, 491-495 (2017).

[4.19] M. E. Tuckerman, A. Chandra and D. Marx, Structure and Dynamics of OH-(aq), Acc. Chem. Res. 39, 151- 158 (2006).

[4.20] D. Marx, A. Chandra, and M. E. Tuckerman, Aqueous Basic Solutions: Hydroxide Solvation, Structural Diffusion, and Comparison to the Hydrated Proton, Chem. Rev. 110, 2174-2216 (2010).

[4.21] L. Turi and P. J. Rossky, Theoretical Studies of Spectroscopy and Dynamics of Hydrated Electrons, Chem. Rev. 112, 5641–5674 (2012).

[4.22] J. Savolainen, F. Uhlig, S. Ahmed, P. Hamm, and P. Jungwirth, Direct observation of the collapse of the delocalized excess electron in water, Nature Chem. 6, 697–701 (2014).

[4.23] A. Rosspeintner, B. Lang, and E. Vauthey, Ultrafast Photochemistry in Liquids, Annu. Rev Phys. Chem. 64, 247- 271 (2013).

[4.24] V.-T. Pham, T. J. Penfold, R. M. van der Veen, F. Lima, A. El Nahhas, S. L. Johnson, P. Beaud, R. Abela, C. Bressler, I. Tavernelli, C. J. Milne, and M. Chergui, Probing the Transition from Hydrophilic to Hydrophobic Solvation with Atomic Scale Resolution, J. Am. Chem. Soc. 133, 12740–12748 (2011).

[4.25] D. Laage, T. Elsaesser, and J. T. Hynes, Water Dynamics in the Hydration Shells of Biomolecules, Chem. Rev. 117, 10694–10725 (2017).

[4.26] M. Heyden, J. Sun, S. Funkner, G. Mathias, H. Forbert, M. Havenith, and D. Marx, Dissecting the THz spectrum of liquid water from first principles via correlations in time and space, PNAS 107, 12068-12073 (2010).

[4.27] T. Fransson, Y. Harada, N. Kosugi, N. A. Besley, B. Winter, J. J. Rehr, L. G. M. Pettersson, and A. Nilsson, X-ray and Electron Spectroscopy of Water, Chem. Rev. 116, 7551–7569 (2016).

[4.28] J. Niskanen, M. Fondell, C. J. Sahle, S. Eckert, R. M. Jay, K. Gilmore, A. Pietzsch, M. Dantz, X. Lu, D. E. McNally, T. Schmitt, V. Vaz da Cruz, V. Kimberg, F. Gel'mukhanov, and A. Föhlisch, Compatibility of quantitative X-ray spectroscopy with continuous distribution models of water at ambient conditions, PNAS 116, 4058-4063 (2019).

[4.29] P. Jungwirth and B. Winter, Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins, Annu. Rev. Phys. Chem. 59, 343-366 (2008).

[4.30] O. Björneholm, M. H. Hansen, A. Hodgson, L.-M. Liu, D. T. Limmer, A. Michaelides, P. Pedevilla, J. Rossmeisl, H. Shen, G. Tocci, E. Tyrode, M.-M. Walz, J. Werner, and H. Bluhm, Water at Interfaces, Chem. Rev. 116, 7698–7726 (2016).

[4.31] Bernd Winter, Liquid microjet for photoelectron spectroscopy, Nuclear Instruments and Methods in Physics Research A, 601, 139 (2009).

[4.32] Robert Seidel, Bernd Winter, and Stephen E Bradforth, Aqueous Solutions: Insights from Photoelectron Spectroscopy, Annu. Rev. Phys. Chem. 67, 283 (2016).

[4.33] Stephan Thürmer, Milan Ončák, Niklas Ottosson, Robert Seidel, Uwe Hergenhahn, Stephen E. Bradforth, Petr Slavíček, and Bernd Winter, On the nature and origin of dicationic, charge-separated species formed in liquid water on X-ray irradiation, Nature Chemistry 5, 590 (2013).

[4.34] R. Signorell, M. Goldmann, B.L. Yoder, A. Bodi, E. Chasovskikh, L. Lang, and D. Luckhaus, Nanofocusing, shadowing, and electron mean free path in the photoemission from aerosol droplets. Chem. Phys. Lett. 658, 1 (2016).

[4.35] C. Richter, D. Hollas, C.-M. Saak, M. Förstel, T. Miteva, M. Mucke, O. Björneholm, N. Sisourat, P. Slavicek, and U. Hergenhahn, Competition between proton transfer and intermolecular Coulombic decay in water, Nature Commun. 9, 4988 (2018).

[4.36] C. Bressler, W. Gawelda, A. Galler, M. M. Nielsen, V. Sundström, G. Doumy, A. M. March, S. H. Southworth, L. Young, and G. Vankó, Solvation Dynamics Monitored by Combined X-Ray Spectroscopies and Scattering: Photoinduced Spin Transition in aqueous [Fe(bpy)3]2+, Faraday Discussions 171, 169 (2014).

[4.37] K. Haldrup, W. Gawelda, R. Abela, R. Alonso-Mori, U. Bergmann, A. Bordage, M. Cammarata, S. Canton, A. O. Dohn, T. Brandt van Driel, D. M. Fritz, A. Galler, P. Glatzel, T. Harlang, K. S. Kjaer, H. T. Lemke, K. B. Moller, Z. Németh, M. Papai, N. Sas, J. Uhlig, D. Zhu, G. Vankó, V. Sundström, M. M. Nielsen, and C. Bressler, Observing Solvation Dynamics with Simultaneous Femtosecond X-Ray Emission Spectroscopy and X-ray Scattering, J. Phys. Chem. B120, 1158-1168 (2016).

[4.38] S. Usenko, A. Przystawik, M.A. Jakob, L.L. Lazzarino, G. Brenner, S. Toleikis, Ch. Haunhorst, D. Kip, and T. Laarmann, Attosecond interferometry with self-amplified spontaneous emission of a free-electron laser, Nature Commun. 8, 15626 (2017).

[4.39] F. Ferrari, F. Calegari, M. Lucchini, C. Vozzi, S. Stagira, G. Sansone, and M. Nisoli, High- energy isolated attosecond pulses generated by above-saturation few-cycle fields, Nature Photon. 4, 875-879 (2010).

[4.40] F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. B. Greenwood, F. Martín, and M. Nisoli, Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses, Science 346, 336 (2014).

[4.41] G. J. Stein, P. D. Keathley, P. Krogen, H. Liang, J. P. Siqueira, C.-L. Chang, C.-J. Lai, K.-H. Hong, G. M. Laurent, and F. X. Kärtner, Water-window soft X-ray high-harmonic generation up to the nitrogen K-edge driven by a kHz, 2.1 μm OPCPA source, J. Phys. B.: At. Mol. Opt. Phys. 49, 155601 (2016).

[4.42] D. Zhang, A. Fallahi, M. Hemmer, X. Wu, M. Fakhari, Y. Hua, H. Cankaya, A.-L. Calendron, L. Zapata, N. H. Matlis, and F. X. Kärtner, Segmented THz electron accelerator and manipulator (STEAM), Nature Photon. 12, 336 (2018).

[4.43] A. Ferré, A. E. Boguslavskiy, M. Dagan, V. Blanchet, B. D. Bruner, F. Burgy, A. Camper, D. Descamps, B. Fabre, N. Fedorov, J. Gaudin, G. Geoffroy, J. Mikosch, S. Patchkovskii, S. Petit, T. Ruchon, H. Soifer, D. Staedter, I. Wilkinson, A. Stolow, N. Dudovich, and Y. Mairesse, Multi-channel electronic and vibrational dynamics in polyatomic resonant high-order harmonic generation, Nature Commun. 6, 5952 (2015).

[4.44] R. Forbes, A. E. Boguslavskiy, I. Wilkinson, J. G. Underwood, and A. Stolow, Excited state wavepacket dynamics in NO2 probed by strong-field ionization, J. Chem. Phys., 147, 054305 (2017).

[4.45] A. Hans, Ph. Schmidt, C. Ozga, G. Hartmann, X. Holzapfel, A. Ehresmann, and A. Knie, Extreme Ultraviolet to Visible Dispersed Single Photon Detection for Highly Sensitive Sensing of Fundamental Processes in Diverse Samples, Materials 11, 869 (2018).

[4.46] A. Hans, C. Ozga, R. Seidel, P. Schmidt, T. Ueltzhöffer, X. Holzapfel, P. Wenzel, P. Reiß, M.N. Pohl, I. Unger, E.F. Aziz, A. Ehresmann, P. Slavíček, B. Winter, and A. Knie, Optical Fluorescence Detected from X-ray Irradiated Liquid Water, Journal of Physical Chemistry B 121, 2326-2330 (2017).

[4.47] M. Swithenbank, A. D. Burnett, C. Russell, L. H. Li, A. G. Davies, E. H. Linfield, J. E. Cunningham, and C. D. Wood, On-Chip Terahertz-Frequency Measurements of Liquids, Analytical Chemistry 89, 7981-7987 (2017).

[4.48] K. M. Tych, C. D. Wood, A. D. Burnett, A. R. Pearson, A. G. Davies, E. H. Linfield, and J. E. Cunningham, Probing temperature- and solvent-dependent protein dynamics using terahertz time-domain spectroscopy, J. Appl. Cryst. 47, 146-153 (2014).

[4.49] C. Weis, G. Spiekermann, C. Sternemann, M. Harder, G. Vanko, V. Cerantola, C.J. Sahle, Y. Forov, R. Sakrowski, I. Kupenko, S. Petitgirard, H. Yavaş, C. Bressler, W. Gawelda, M. Tolan, and M. Wilke, Combining X-ray Kβ1,3, valence-to-core, and X-ray Raman spectroscopy for studying Earth materials at high pressure and temperature: the case of siderite, Journal of Analytical Atomic Spectroscopy 34, 384 (2019).

[4.50] A. Nilsson, S. Schreck, F. Perakis, and L.G.M. Pettersson, Probing Water with X-ray Lasers, Advances in Physics X 1, 226-245 (2016).

[4.51] T. Spura, H. Elgabarty, and T. D. Kühne, "On-the-fly" Coupled Cluster Path-Integral Molecular Dynamics: Impact of Nuclear Quantum Effects on the Protonated Water Dimer, Phys. Chem. Chem. Phys. 17, 14355 (2015).

[4.52] C. John, T. Spura, S. Habershon, and T. D. Kühne, Quantum Ring-Polymer Contraction Method: Including nuclear quantum effects at no additional computational cost in comparison to ab-initio molecular dynamics, Phys. Rev. E 93, 043305 (2016).

[4.53] P. K. Mishra, V. Bettaque, O. Vendrell, R. Santra, and R. Welsch, On the prospects of using high-intensity THz pulses to induce ultrafast temperature-jumps in liquid water, J. Phys. Chem. B 122, 5211 (2018).

[4.54] C. Arnold, L. Inhester, S. Carbajo, R. Welsch, and R. Santra, Simulated XUV photoelectron spectroscopy of THz-pumped water, J. Chem. Phys 150, 044505 (2019).

[4.55] Z. Li, M. El-A. Madjet, O. Vendrell, and R. Santra: Correlated dynamics of the motion of proton-hole wave packets in a photoionized water cluster. Phys. Rev. Lett. 110, 038302 (2013).

[4.56] R. Welsch, K. Song, Q. Shi, S. C. Althorpe, and T. F. Miller III, Non-equilibrium quantum correlation functions from RPMD and CMD, J. Chem. Phys. 145, 204118 (2016).

[4.57] P. Nalbach, A.J.A. Achner, M. Frey, M. Grosser, C. Bressler, and M. Thorwart, Hydration shell effects in the relaxation dynamics of photoexcited Fe-II complexes in water, J. Chem. Phys. 141, 044304 (2014).

[4.58] V. I. Prokhorenko, A. Picchiotto, M. Pola, A. G. Dijkstra, and R. J. D. Miller, New Insights into the Photophysics of DNA Nucleobases, J. Phys. Chem. Lett. 7, 4445 (2016).

[4.59] A. G. Dijkstra and V. I. Prokhorenko, Simulation of photo-excited adenine in water with a hierarchy of equations of motion approach, J. Chem. Phys. 147, 064102 (2017).

[4.60] S. Karashima, Y. Yamamoto, and T. Suzuki, Ultrafast Internal Conversion and Solvation of Electrons in Water, Methanol, and Ethanol, J. Phys. Chem. Lett. 10, 4499-4504 (2019).

[4.61] M. Pizzochero, F. Ambrosio, and A. Pasquarello, Picture of the wet electron: a localized transient state in liquid water, Chem. Sci. 10, 7442-7448 (2019).

[4.62] Z.-H. Loh, G. Doumy, C. Arnold, L. Kjellsson, S. H. Southworth, A. Al Haddad, Y. Kumagai, M.-F. Tu, P. J. Ho, A. M. March, R. D. Schaller, M. S. Bin Mohd Yusof, T. Debnath, M. Simon, R. Welsch, L. Inhester, K. Khalili, K. Nanda, A. I. Krylov, S. Moeller, G. Coslovich, J. Koralek, M. P. Minitti, W. F. Schlotter, J.-E. Rubensson, R. Santra, and L. Young, Observation of the fastest chemical processes in the radiolysis of water, Science 367, 179–182 (2020).

[4.63] V. Svoboda, R. Michiels, A. C. LaForge, J. Med, F. Stienkemeier, P. Slavíček, and H. J. Wörner, Real-time observation of water radiolysis and hydrated electron formation induced by extreme-ultraviolet pulses, Science Advances 6, eaaz0385 (2020).

[4.64] L. Artiglia, J. Edebeli, F. Orlando, S. Chen, M.-T. Lee, P. C. Arroyo, A. Gilgen, T. Bartels-Rausch, A. Kleibert, M. Vazdar, M. A. Carignano, J. S. Francisco, P. B. Shepson, I. Gladich, and M. Ammann, A surface-stabilized ozonide triggers bromide oxidation at the aqueous solution-vapour interface, Nature Commun. 8, 700 (2017).

[4.65] R. K. Lam, J. W. Smith, A. M. Rizzuto, O. Karslıoğlu, H. Bluhm, and R. J. Saykally, Reversed interfacial fractionation of carbonate and bicarbonate evidenced by X-ray photoemission spectroscopy, J. Chem. Phys. 146, 094703 (2017).

[4.66] H. Ali, R. Seidel, M. N. Pohl, and B. Winter, Molecular species forming at the α-Fe2O3 nanoparticle–aqueous solution interface, Chem. Sci. 9, 4511-4523 (2018).

[4.67] A. Galler, W. Gawelda, M. Biednov, C. Bomer, A. Britz, S. Brockhauser, T.-K. Choi, M. Diez, P. Frankenberger, M. French, D. Görries, M. Hart, S. Hauf, D. Khakhulin, M. Knoll, T. Korsch, K. Kubicek, M. Kuster, P. Lang, F. Alves Lima, F. Otte, S. Schulz, P. Zaldena, and C. Bressler, Scientific instrument Femtosecond X-ray Experiments (FXE): instrumentation and baseline experimental capabilities, J. Synchr. Rad. 26, 1432-1447 (2019).

[4.68] S. Trippel, M. Johny, T. Kierspel, J. Onvlee, H. Bieker, H. Ye, T. Mullins, L. Gumprecht, K. Długołęcki, and J. Küpper, Note: Knife edge skimming for improved separation of molecular species by the deflector, Rev. Sci. Instrum. 89, 096110 (2018).

[4.69] A. K. Samanta, M. Amin, A. D. Estillore, N. Roth, L. Worbs, D. A. Horke, and J. Küpper, Controlled beams of shockfrozen, isolated, biological and artificial nanoparticles, Struct. Dyn. 7, 024304 (2020).

[4.70] H. Bieker, J. Onvlee, M. Johny, L. He, T. Kierspel, S. Trippel, D. Horke, and J. Küpper, Pure Molecular Beam of Water Dimer, J. Phys. Chem. A 123, 7486 (2019).

[4.71] M. Johny, J. Onvlee, T. Kierspel, H. Bieker, S. Trippel, and J. Küpper, Spatial separation of pyrrole and pyrrole-water clusters, Chem. Phys. Lett. 721, 149–152 (2019).

[4.72] R. Seidel, S. Thürmer, and B. Winter, Photoelectron Spectroscopy Meets Aqueous Solution: Studies from a Vacuum Liquid Microjet, J. Phys. Chem. Lett., 2 (6), pp 633–641 (2011).

CMWS Pillar 5: Water in the Molecular Life Science

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III.5 Water in the Molecular Life Sciences

III.5.1 Scientific Challenges and State of the Art

Water is the molecule of life, ubiquitous in biological environments and indispensable for biochemical reactions [5.1, 5.2]. Living cells contain about 60–70% water, and evolution has optimized the sophisticated biological processes that determine life to function in an aqueous environment.

Water's unique characteristics are fundamental to all known biological processes, spanning from simple biochemical reactions to the emergence of biological complexity. Yet deciphering the role of water as the universal solvent, in which all life is embedded, remains challenging. One of the most striking challenges is correlating water's intrinsic physical properties – hydrogen-bond networks, polarisability and collective vibrational states – with its spontaneous capacity to generate frustrated order out of apparent chaos [5.5]. To fully understand the structure and structural dynamics of biological systems it is of great importance to unravel the interplay between the bulk-water activity and the formation of the solvation shells, which envelope macromolecules. These are highly influenced by co-solutes,

pressure and temperature, and counterions – especially in the case of DNA and RNA. Non-covalent, in particular electrostatic interactions, between biomolecules, solvated ions, and water are crucial for the stabilisation and folding of large molecular structures [5.2, 5.7]. Similarly, water influences the transition from uncorrelated local dynamics to concerted harmonic motions of proteins (non-equilibrium mechanics) which accounts for biological activity of macromolecules. The influence of water on the association states of proteins, RNA, DNA, lipids and carbohydrates is also of the highest interest. The formation of higher-order assemblies consisting of multiple components are fundamental to all intracellular processes and are associated with a number of disease states. Understanding solvation potentials, water rearrangements and the exchange of water at the surface of, or within, bio-macromolecules underpin these large-scale interactions. Ultimately, these interactions act as the driving potential of cellular evolution across environments, from extremely hot to extremely cold; to extreme pressure and chemical environments and combinations thereof.

Therefore, the role of water in biomolecular structures, be it defined and ordered or intrinsically disordered, and the link that water provides between structure, bio-catalysis, regulation and molecular transport [5.4] will be the focal points of the research on water in the molecular life
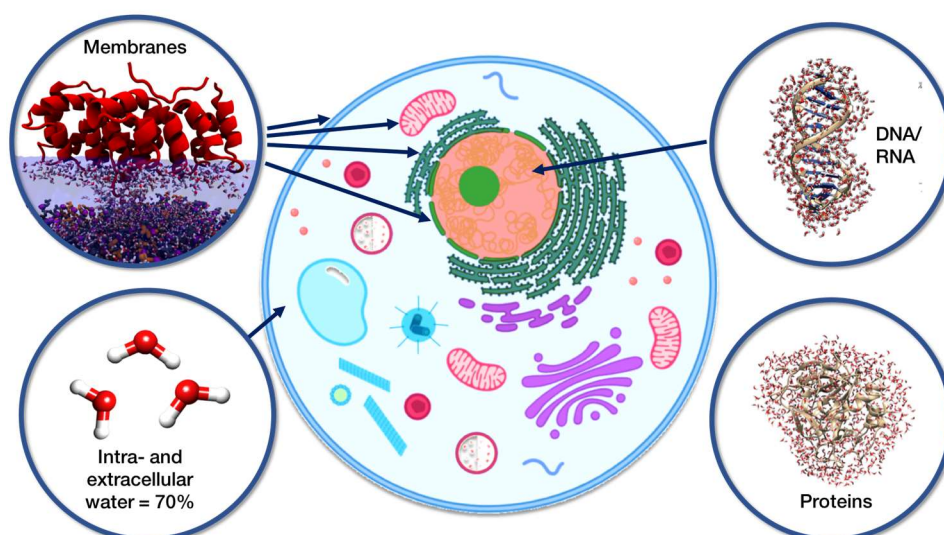
Figure III.5.1: Water in the cellular environment. Illustration using input from biorender.com, water at a simulated protein/membrane interface, figures of hydrated DNA & Protein adapted from [5.5].

sciences at the CMWS – covered by the following scientific challenges.

The focus of the research programme of pillar 5 is to deliver a fundamental understanding of the role of water in the molecular processes of life. This will empower the wider life science, biomedical and biotechnological communities to address the pressing societal challenges of ageing, emerging diseases, sustainability and the climate crisis.

Timely research topics addressed within pillar 5 include biomedical applications targeting neuro-degenerative diseases, translational research towards optimised drug delivery, i.e. for the pressing issue of treating infectious diseases like COVID 19, as well as molecular insight into the basis of water mediated biocatalysis with implycations for energy research.

Challenge 1: Water and Biological Disorder- How is Water Modulating Intrinsically Disordered Proteins and their Function?

How does disorder affect biology and how can we use it to our advantage? Water and biological disorder go hand in hand: Without water and without disorder, life could not exist. Somehow through the evolutionary process, islands of stability form and respond to disorder, using it to its advantage, even incorporating it. Indeed, many of the major challenges facing medicine – disruptions to gene regulation (cancer); protein-based pathologies (Alzheimer's, Parkinson's disease, etc.) [5.8, 5.9], viral infections [5.10], cardiovascular diseases [5.11] and even the

emergence of antibiotic resistance (bacterial responses to *being* disrupted) – are all based on the interplay between complex biological systems and disorder [5.12]. Water is the conduit through which these problems are addressed.

The classical paradigm of structural biology had been that proteins adopt well-defined three dimensional structures and that these structures essentially adhere to a 'key-and-lock' mode of interaction. However, a more and more dynamical picture, starting from the realisation that structural changes govern recognition (known as "induced fit") has emerged. Active research is ongoing to understand the complex protein dynamics and substrate interplay [5.13]. Moreover, 10–20% of all eukaryotic proteins are intrinsically disordered, i.e. remain natively unstructured while around 40% of otherwise-structured proteins incorporate significant disordered regions (over 50 amino acids) [5.14]. Consequently, intrinsic disorder is now recognised as a fundamental mechanism through which biological function, regulation and adaption to local environmental changes – on different time and length scales – can be established and maintained. This 'spectrum of (dis)order' is ultimately dictated by the spontaneous interactions of proteins and water, the universal solvent.

Understanding the balance between solvation potential and the formation of spontaneous (dis-) ordered macro-scale phases, especially within a crowded environment, paves the way for understanding the macromolecular foundation of
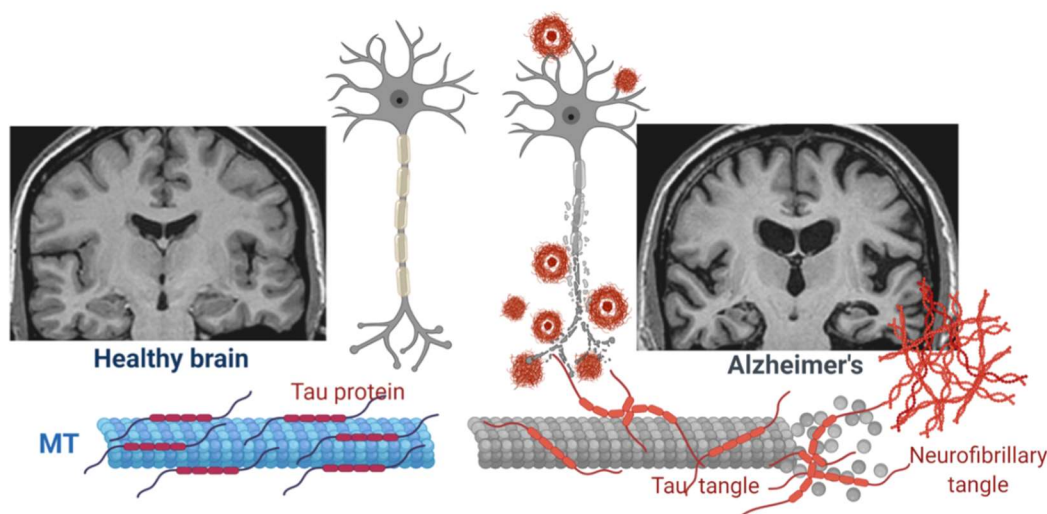
Figure III.5.2: Intrinsically disordered proteins cause neurodegenerative diseases (e.g. Alzheimer's disease).
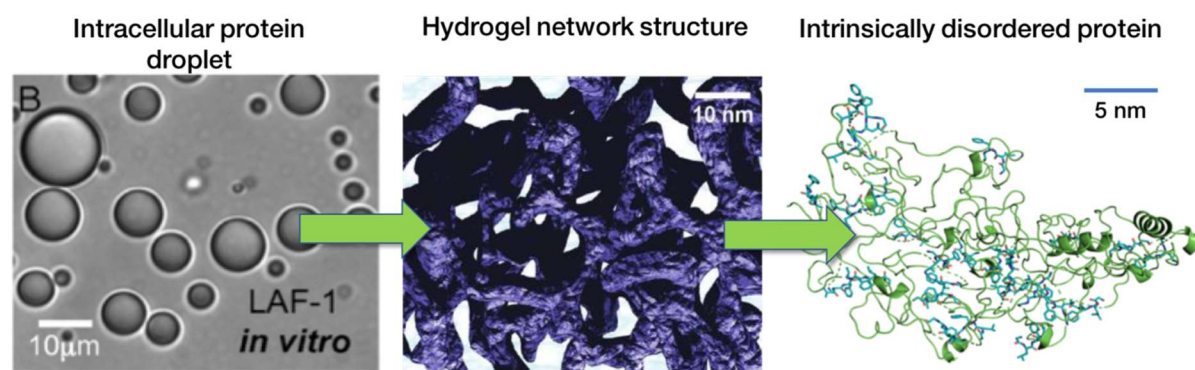
Figure III.5.3: Disorder results in hierarchical structures in organisms. Protein droplets are formed in cells by phase transitions. Within these droplets (or in similar mesoscale structure) native hydrogels can be found, which themselves are comprised of fully intrinsically disordered proteins or intrinsically disordered regions (IDPs/IDRs). References left [5.8], middle [5.15].

a number of disease states. What triggers the assembly of proteins into those intracellular phases is poorly understood, especially with respect to the activity of water and how this impacts the separation process or even promotes additional 'disorder-within-disorder', as for example in the case of protein amyloids.

Challenge 2: Why is Heavy Water Poisonous to Mammals and Plants but not to Bacteria?

Although the electron shells that determine chemical reactions are identical for hydrogen and its heavier isotope deuterium, heavy water (D_2O) was found to be poisonous to mammals and plants [5.16, 5.17]. These higher organisms die when their body water content approaches 50% D_2O. Bacteria, on the other hand, can grow in 100% D_2O. The reasons for this toxicity of heavy water on higher organisms are not at all understood. Eukaryotic cell division processes seem to be particularly vulnerable to D_2O, the underlying molecular basis for this is, however, still unknown. The deuterium atoms originating from heavy water incorporated in a variety of bio-macromolecules are involved in different (bio-) chemical reactions. Due to the kinetic isotope effect the rate determining step in a chemical reaction in which the bond to a deuterium is broken, can be up to 10 times slower compared to the case of hydrogen. Other parameters that contribute to the adverse effects of heavy water are differences in hydrogen bond strength (O-H vs. O-D and pH vs. pD) [5.18]. These differences in hydrogen bonds involving either H_2O/D_2O or exchangeable hydrogen/deuterium atoms are

responsible for the differences in protein stability in heavy water (D_2O) [5.19, 5.20]. Furthermore, the viscocity of D_2O is slightly higher than that of H_2O, which might have implications for the finely balanced timing of biochemical networks inside the cell. But what is the exact interplay between water and macromolecules? What is the role of water in modulating macromolecular material properties? Proteins have evolved to function in water. Many proteins have a well-defined three-dimensional structure while at the same time maintaining sufficient flexibility to perform their catalytic/mechanistic tasks. As natural selection can only randomly favour the best of available options, a better understanding of the basic principles of how water influences protein structure and stability (by comparison with D_2O) is highly desirable. This may allow the design of better proteins suitable for alternative solvents with huge implications for biotechnology.

Challenge 3: Water at Biological Interfaces

The first few layers of water around biomolecules (nucleic acids, proteins and lipids), biomolecular complexes and bio-membranes [5.21, 5.22] are critical for their structure and function. Recent years have witnessed a change in the perception of these water layers from a passive bystander, to an active player in determining structural stability and dynamics of biological entities ranging from the single biomolecules to even complex systems such as cell membranes [5.23]. The properties of this hydration water in biomolecular crowded environments appear to be different from those of bulk water [5.1, 5.5]. Insight into the spatial extent,
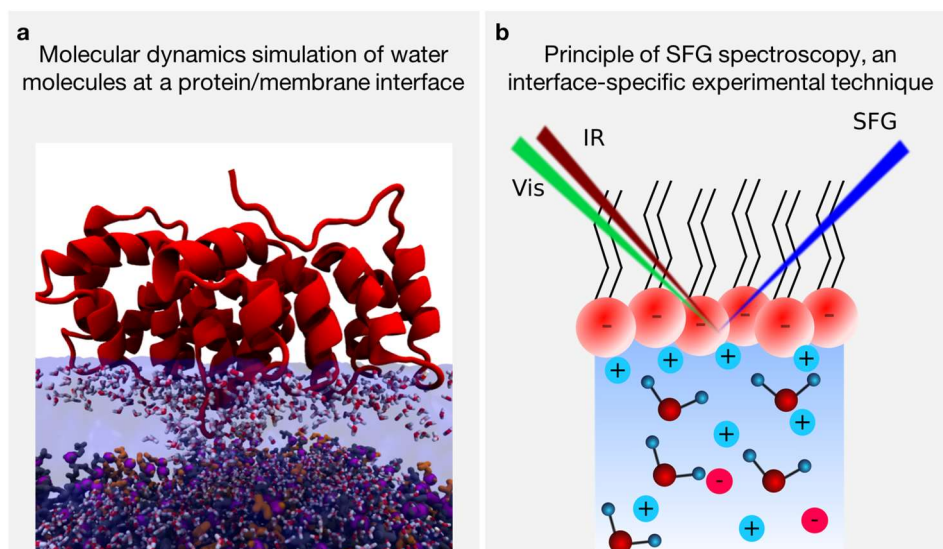
Figure III.5.4: Theoretical (a) and experimental (b) approaches allow to study water at biological interfaces.

dynamic nature and microscopic origins of the coupling of water with the biological partners thus provides the basis for a deeper understanding of macromolecular interactions mediated by interfaces and governed by the hydration/ dehydration forces. As an example, together with hydration water, the ion atmosphere forms a diffuse and highly mobile cloud around charged DNA/RNA that, because to its fluctuating nature, is challenging to access experimentally and, hence an understanding of its impact on protein-DNA/RNA dynamics is lacking [5.24]. Thus, an understanding of the central role of water in biomolecular aggregation processes like protein-DNA/RNA recognition, viral packing and functional assembly of the ribosome requires a deep understanding of the interplay of hydration and electrostatic interactions [5.2]. Similarly, in biomembranes, consisting of lipids and proteins, for a long time only electrostatic interactions have been considered to be responsible for processes such as permeability, enzyme activity and transport of ions and protons. While the impact of water on biological functions is starting to be acknowledged as important [5.1, 5.25, 5.26], a full picture that also considers water with its structural and (thermo)dynamic properties, while of paramount importance, is still missing.

Challenge 4: How does Water Modulate Reactivity and Conformational Dynamics?

Water acts as a lubricant for all biomacromolecular machines, in particular proteins, which fulfill functions from scaffolding to signaling and catalysis [5.7, 5.27]. All these fundamental biochemical functions (only) occur in the presence of liquid water. In recent years our understanding of protein function, enzymatic catalysis and the regulation of protein function through allostery has moved from a simple (static) picture of protein–protein or protein–ligand interactions to a dynamic picture. Water has leapt into view as the additional active key component rather than a simple passive solvent [5.28-5.30]. With this increased understanding, the dream of rationally designing a biomacromolecule or biological system to deliver a specific function is coming into reach. For example, green chemistry that minimises environmental impact or novel bio-based solutions for solar power and renewable energy generation becomes feasible, allowing for strong interaction of the research programme in pillar 5 with work planned in pillar 3.

The conformational flexibility of structurally well-defined proteins (in contrast to intrinsically disordered proteins (IPDs) in *challenge 1*) ranging from the picosecond to millisecond timescale is determinant for the accurate operation of these molecular machines. This flexibility is increased by water molecules bound to proteins, for instance
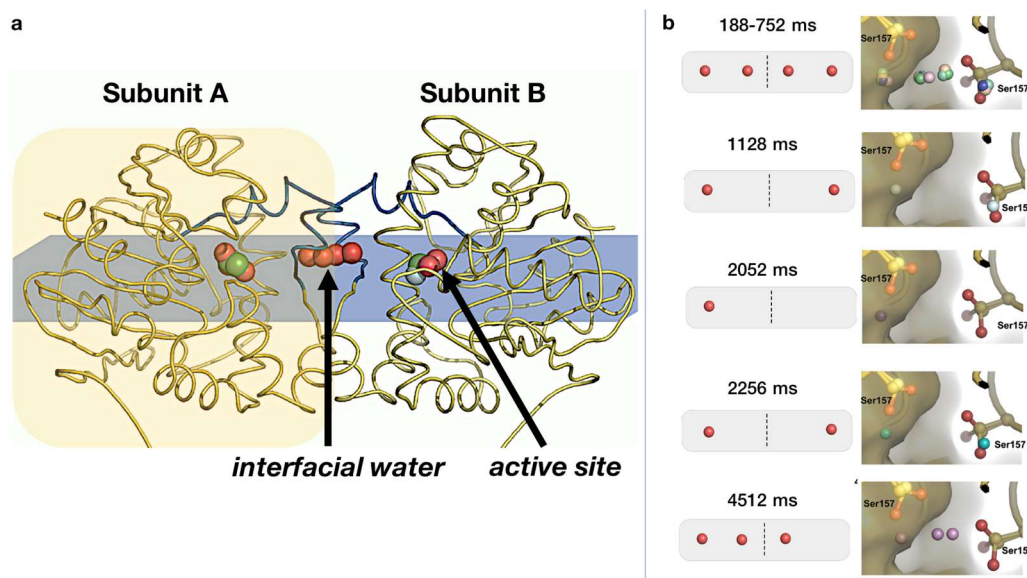
Figure III.5.5: Water is an active component in biochemical reactions and involved in modulating protein function as revealed in the enzyme defluorinase using time-resolved serial crystallography. In a) the protein consisting of two identical subunits is shown, a wire of four interfacial water molecules connects the two active sites and is modulating the allosteric communication during the enzymatic reaction (see time-resolved cartoon in b) for the modulation of this water wire) [5.31].

water molecules facilitating chemical reactions in active centres (*catalytic waters*), water molecules stabilising a desired protein conformation (*functional waters*), water molecules involved in ligand binding, *interfacial waters* between domains of a protein complex and surface bound waters mediating conformational dynamics and interactions with co-solutes (compared to *challenge 1* and *challenge 3*). Especially the role of functional and interfacial waters in the regulation of protein dynamics and the switching between an active and inactive conformation remains to be understood. The activity and accurate function of

proteins, not only enzymes, is further highly pH dependent. A detailed understanding of the underlying molecular mechanisms, how pH – aside from the pure electrostatic effect – mediates function, is not yet understood and points to the general concept in biology of compartmentalisation – either by lipid bilayer structures as the membranes surrounding cell organelles (*challenge 3*) with different pH and ion concentrations or in, i.e. protein droplets, through the mechanism of phase separation (*challenge 1*).
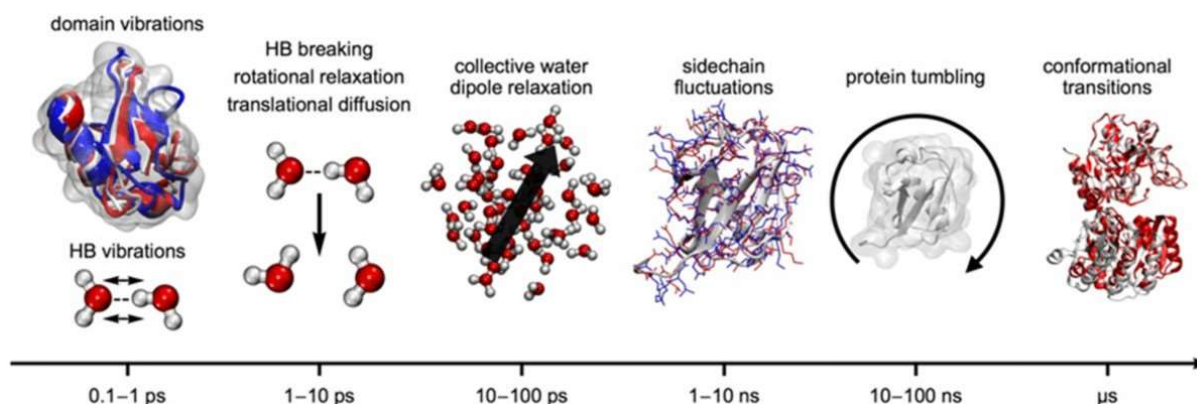
Figure III.5.6: Water dynamics relevant for biomolecular processes cover the timescale from 0.1 ps to µs and beyond, and have to be addressed both experimentally and by modelling approaches, figure adapted from [5.32].

Computer simulations play an essential role, as they can provide molecular interpretations of experimental observations and, in such synergistic combination, reveal structure–dynamics-function relationships in real biomolecular systems. However, specifically for water models there are lots of approximations and for most computational models, water molecules are approximated with the (fixed) same parameters, independent whether they are bulk, interfacial, surface or active water molecules. Improving these computational models will only become feasible with improved time and structurally resolved experimental data that directly report on these different types of functional water molecules. In turn, better models of water or aqueous solutions would highly benefit the experimental determination of molecular structures by widely-used methods such as cryo electron microscopy (cryo-EM) or crystallography. Despite tremendous progress in the field, and despite broad application of state-of-the-art molecular simulation methods in many areas, further improving computational models of water-biomolecular interaction and functional water molecules is of paramount importance – and a formidable challenge. High accuracy experimental data is key for this endeavour. The world-class facilities at DESY with the ability to collect time-resolved structural data – several structural snapshots forming a molecular movie – from femtoseconds to seconds in combination with ultrafast spectroscopies, are now providing the first experimental insight into different types of functional water molecules. There is a unique opportunity for the CMWS to systematically test and improve current computational models, from the atomic scale (force fields, polarisability) via the mesoscopic scale (continuum models) up to the organelle or cellular scale (systems biology). Overarching progress in each of these realms and combining the scales in a multi-scale manner will be essential for developing a quantitative and hence predictive model of a living cell, one of the grand challenges of our time.

III.5.2 Preliminary Work and Competences

The investigation of biochemical (*challenge 1, 3 and 4*) and biological (*challenge 2*) function from the inverted perspective of water requires a unique combination of experimental and theoretical approaches (*challenge 5*). Those include state-of-the art biophysical methods, existing technologies to be adapted for biochemical research and novel instrumentation to be developed.

The team of pillar 5 involves experts for X-ray techniques, ultrafast (vibrational) spectroscopy, MD simulations and further biophysical techniques, each of which are the only and still emerging tools to the study of molecular water in biological systems. Recent examples of unprecedent insights include, i.e. the observation of functional water wires relevant for enzymatic catalysis (see Figure III.5.5) by time-resolved crystallography or the local water structure caging Mg^{2+} ions and phosphate, relevant for stabilisation of proteins and DNA, as observed by 2D-IR in combination with MD simulations (see Figure III.5.7).

Our team includes researchers using synchrotron radiation and FEL sources (small-angle X-ray scattering (SAXS), X-ray diffraction and time-resolved serial crystallography) and researchers from complementary fields, namely vibrational spectroscopy (Raman, sum frequency generation (SFG), infrared (IR) and 2D-IR, THz) (*challenge 1, 2* and *3*), nuclear magnetic resonance (NMR) spectroscopy and neutron-based techniques. These experimental techniques are further supported with computational approaches (molecular dynamics (MD) simulation, quantum chemistry, etc. and data analysis).

We envision a strong integration of our research programme with ongoing activities on the Bahrenfeld Campus in the field of biophysics and structural biology (at EMBL, CSSB and others), for instance we anticipate to use and to connect to existing research and local infrastructure for, i.e. protein purification and characterisation. Specific techniques, like biomolecular NMR or ultrafast vibrational spectroscopies, not accessible in Hamburg are provided by partnering laboratories within the CMWS.

The availability of XFELs has revolutionised the research in structural biology [5.33, 5.34]. We have pioneered serial femtosecond crystallography (SFX) [5.35–5.37]. Knowledge and expertise in the areas of method development, sample delivery (liquid jets, fixed targets and hybrid approaches), sample preparation and data analysis as well as experimental setups at different XFEL sources is available in our team. Only recently we have performed the first structural biology experiments at the European XFEL, demonstrating the potential of rapid data collection with a megahertz XFEL source [5.38]. For time-resolved studies of protein structures we are experts in the field of time-resolved crystallography and have access to world-class facilities enabling studies from the femtosecond to nanosecond regime using SFX [5.35-5.38] (*challenge 4*).

We have established the same experimental concept of serial, room-temperature data for storage ring-based experiments [5.39] as serial synchrotron crystallography (SSX) with a time-resolution from milliseconds onwards [5.31, 5.40] using fixed targets for sample delivery in a hit-and-return (HARE) experiment. We have built an endstation dedicated to pump-probe time-resolved macromolecular crystallography, T-REXX on P14 at PETRA III, which, in combination with Hadamard-Transformation [5.41], will be able to reach a time-resolution down to the nanosecond regime (*challenge 1* to *4*).

These novel crystallography approaches enable dynamic X-ray crystallography, allowing the investigation of functional and reactive water molecules, previously not possible, as shown for the enzymatic reaction in defluorinase (Figure III.5.5, [5.31]). However, serial crystallography still can only access structured water molecules ordered in crystalline samples. Further experimental insights can be gained by small-angle X-ray and neutron scattering (SAXS and SANS) applied to bio-macromolecules in solution, such as intrinsically disordered proteins (IDPs) [5.42] (*challenge 1*) or osmolytes relevant for protein stability [5.43]. Moreover, we have demonstrated the application of these methods as rapid-mixing time-resolved SAXS to investigate dynamical processes like protein unfolding [5.44] with the perspective to expand studies on the role of water molecules by time-resolved SAXS and SANS.

Neutron based tools have the advantage of a very high sensitivity to hydrogen atoms and the ability to distinguish hydrogen and deuterium, which gives an opportunity to "label" samples and use contrast variation techniques [5.45], thereby being complementary to X-ray based studies.

The P12 beamline at PETRA III is ideally suited for methods development in SAXS and time-resolved SAXS, and integrate experiments with additional in-line spectroscopies (i.e. Raman), as they are part of the research proposed here (*challenge 4*). While X-ray sources provide unprecedented insight into biological structures, the associated radiation damage can distort objective results. We have worked on X-ray induced radiation damage and specifically solvent mitigated damage [5.46].

Complementary to scattering experiments, we employ X-ray spectroscopies as powerful tools to investigate the local electronic and nuclear structure of biochemical systems in liquid and gas phase (*challenge 2, 3* and *4*). We have extensive expertise on resonant inelastic X-ray scattering (RIXS) [5.47] and X-ray absorption spectroscopy [5.48-5.50] on hydrated systems used to study decay processes in water and aqueous solutions or access differences in the water–structure between surface and bulk. Furthermore, we have developed combined tools using mass spectrometry at advanced light sources to study local (electronic) structure, i.e. in combination with near-edge X-ray spectroscopy [5.51, 5.52].

Beyond X-ray techniques we use several advanced spectroscopies, which are essential and well-suited to investigate solvation dynamics, water structure and the influence of water on biomolecular functions. Namely vibrational spectroscopies allow detailed studies of water in solution (Raman, IR, 2D-IR) or at surfaces SFG, surface enhanced IR and Raman) and long-range effects (THz spectroscopy). We are experts in both experiment and theory in above mentioned spectroscopies, with specific focus on applications of ultrafast vibrational spectroscopies to water and biological molecules [5.23, 5.53-5.61].

We are actively developing and advancing ultrafast nonlinear spectroscopies, in particular new multidimensional spectroscopies, to specifically tackle biochemical questions and work further on
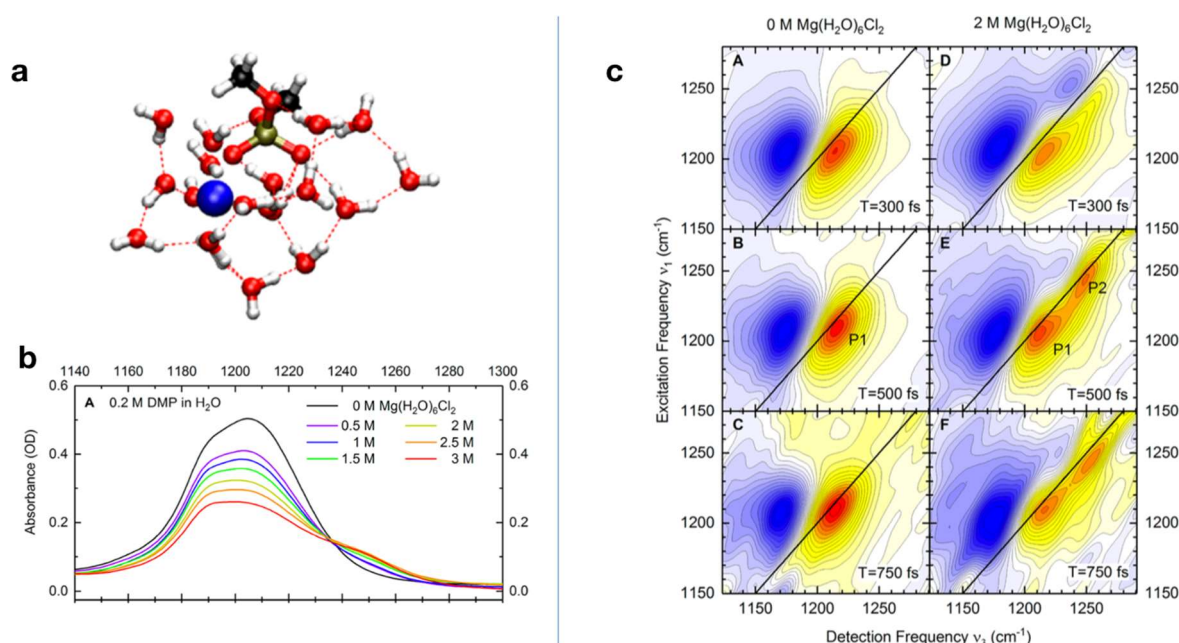
Figure III.5.7: Solvation dynamics and the influence of co-solutes can be accurately studied by a combination of MD simulation (a), linear IR spectroscopy (b) and 2D-IR spectroscopy (c) as shown here for the example of solvated dimethyl phosphate in H_2O with Mg^{2+} as co-solute. Figure adapted from [5.54].

improved approaches for simulation and modelling of spectra to assist data analysis, in particular in complex molecular environments [5.53-5.56]. One research focus is on interface specific spectroscopies, ideally matching the need to investigate water on the protein surface or within membranes or the interaction of biomolecules with soft surfaces [5.23, 5.57-5.58]. We have further demonstrated vibrational spectroscopy with local resolution to investigate changes in, i.e. electrostatics or hydration of biomolecules or during a biochemical reaction [5.59-5.61].

As vibrational spectroscopy can be applied to biomacromolecules in solution, it is suited to investigate non-structured proteins like IDPs, here we have pioneered first experiments [5.61]. The conformation-specific detection is ideally matched by further structure sensitive experiments using NMR spectroscopy. While nonlinear vibrational spectroscopy still needs further development to be applied to larger biomolecular complexes, NMR spectroscopy is able to not only study flexible proteins (IDPs, for instance in lipid interacting proteins) not suited for crystallography but also membrane proteins like transporters and ion channels. We have expertise in using solution and solid-state NMR to study lipid–protein and ligand(drug)–protein interactions, allostery and

protein dynamics [5.62, 5.63] and improved time-resolved exchange studies [5.64].

We have expertise using cryo-EM and SEM on self-assembly liquid phase to study the connection between the nature of molecules and the aggregates they form spontaneously [5.65], and the relation between the nanostructure of those assemblies to the macroscopic properties of the systems.

Beyond experimental and technological expertise, the ability to prepare samples and engineer proteins and simplified biomimetic artificial model systems to address the questions associated with our presented challenges is crucial. We have experts from different areas of structural biology, chemical biology and chemistry that focus on experimental techniques and specialise on these sample preparation techniques.

We addressed the role of water in enzymology, protein–protein and protein-DNA or protein–polysaccharide interactions, mainly interlinked with crystallographic techniques using X-rays and neutrons. Using advanced crystal preparation techniques, we study the diffusion of molecules into crystals and crystal solvent channels [5.66, 5.67].

Similarly, we have strong expertise in the preparation of membrane protein samples of i.e. ATPases, ABC transporters and membrane

Native H$_2$O channel:
membrane proteins,
e.g. aquaporin

Artifical H$_2$O channels:
left: carbon nanotubes, middle: self-assembled
macrocycles, right: single-molecule synthetic channel
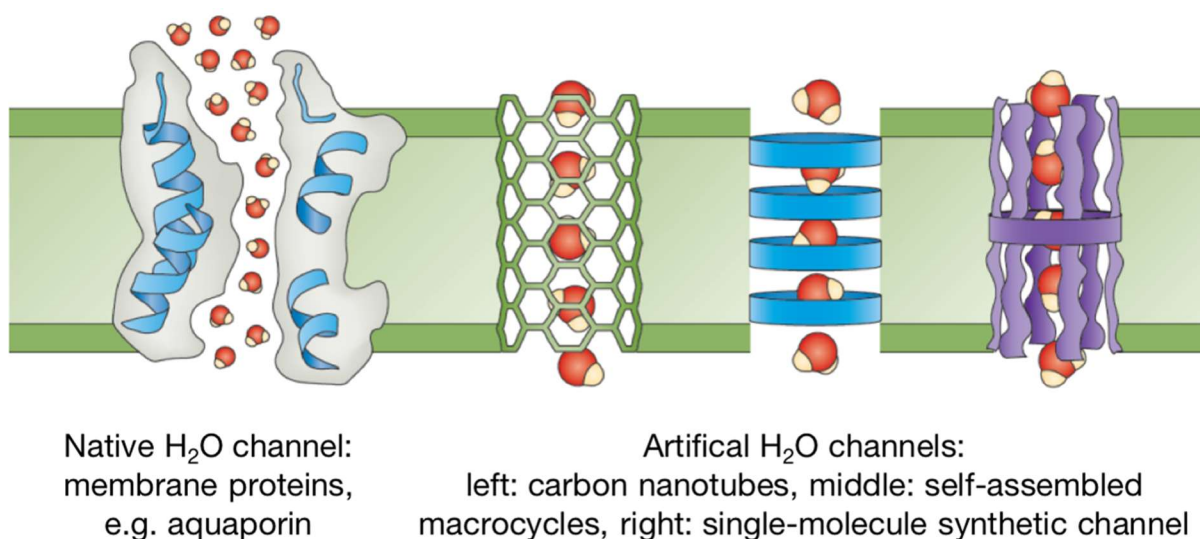
Figure III.5.8: Comparison of native and artificial H$_2$O channels in membranes. Figure adapted and modified from [5.77].

channels [5.68-5.71] and mutation studies, including the incorporation of unnatural amino acids for functional studies or the usage of stealth nanodiscs for further studies of membrane proteins using, i.e. neutron scattering [5.69]. Additionally, we have expertise in protein engineering for the study of the interaction of water with protein structures and the effect of water on conformational dynamics and how water compensates and is compensated by the presence of bound ligands on protein interfaces [5.72, 5.73].

Synthetic biomimetic artificial water-channels and pores are suited to study the function of protein channels in a model system. We have worked on nanoporous organic–inorganic hybrid materials with modified functionalities to prepare uniform or modulated surface polarity within the channel, which has a strong impact on the local structure and mobility of water [5.74-5.76].

All of the experimental work needs to be compared and validated by theoretical calculations (*challenge 5*). To this end, we develop and apply molecular dynamics simulation methods to investigate the hydration of biomolecules, and how it governs their structure, dynamics and thermodynamics [5.78-5.80]. Emphasis is on hydration-mediated collective dynamics of proteins and lipid membranes, and the link to entropy, hydration changes upon large-scale conformational changes of membrane proteins, such as ABC transporters [5.81]. Implications for drug binding, protein–water interactions, especially of

structurally conserved active site water molecules, and their role in enzymatic hydrolysis reactions and proton shuttling are derived.

III.5.3 Objectives

One of the principal overarching aims of the research in pillar 5 is to investigate the role of water and the aqueous environment (hydration water, bulk water, confined water, surface water) and to understand its impact on the structures and interactions of biological macromolecules, thereby yielding both fundamental science and generating platforms for developing technologies in the fields of structural biology, structural infection biology and molecular cell biology.

To understand the role of water as biological solvent for all challenges, we need to develop and improve the physical descriptions of water and other solvents in biomolecular systems. Objectives thereby are the structural and dynamic characterisation of solvation sites at the surface of biomolecules, ion binding sites and diffuse ion atmosphere (*challenge 3*) as well as of prototypical solvation sites at the surface of biomolecules and of (counter)ions (*challenge 1 and challenge 3 to challenge 5*). In addition, for all *challenges* long-range coupling of water dynamics and biological entities must also be taken into account. Beyond that, systematic, exemplary, studies of co-solutes and their effects on water structure subsequent alterations to intrinsically disordered proteins and

fully folded proteins will be performed (*challenge 1, challenge 4*).

To decipher reaction pathways and biological function modulated by water we need to quantify noncovalent, in particular electrostatic and van-der-Waals interactions between biomolecules, solvated ions, and water and their impact on stabilisation and folding (*challenge 1* to *challenge 3*) and allosteric regulation and catalytic activity (*challenge 2, challenge 5*). For this it is also necessary to understand the role of coordination and exciplex formation in catalytically active water in protein catalysis, i.e. metal coordination, source of protons etc. (*challenge 4*). For all *challenges* we will investigate the role of water in modulating macromolecular material properties by studying channels, cavities and voids often found in soluble as well as membrane proteins, and we will gain a full (molecular-level) picture on structure and (thermo)dynamics at biomembranes in order to understand how lipids, proteins and water interact with themselves and with each other (*challenge 3, challenge 5*).

The study of the effect of normal versus heavy water on the properties of different cellular organelles, focusing on physico-chemical properties as pH/pD, density and viscosity will help us to get an improved understanding of the effect of molecular crowding (*challenge 1, challenge 2, challenge 3, challenge 5*). "Molecular movie"-type studies of model enzymes in normal or heavy water environment will be performed to understand the role of H_2O vs D_2O in active site of proteins/enzymes (*challenge 2, challenge 4*). The effect of normal and heavy water with respect to the hydration shell of proteins will be compared by combining small-angle X-ray and neutron scattering (SAXS/SANS), on properly folded, globular proteins (*challenge 2, challenge 4*) and intrinsically disordered proteins (IDPs, *challenge 1, challenge 2*).

New technical developments are necessary and envisioned to enable the research for the biochemical and biological molecular water research within CMWS. The developments will allow us the quantification of solvation characteristics – from the 1st solvation shell up to the solvation continuum around biomolecules (*challenge 2, challenge 3*). For example new methods to produce defined water attachment (H_2O, D_2O) to biomolecules in the gas phase combined with ion mobility and X-ray mass spectroscopy will be developed (*challenge 1–challenge 4*) as well as novel structural dynamics tools to study the biological mesoscale – protein droplets formed through phase transitions, where proteins spontaneously self-associate into liquid-dense clusters that are distinct and separated from the surrounding solvent (*challenge 1, challenge 3, challenge 4*). The use of new and advanced "molecular-movie" methods with serial X-ray crystallography and time-resolved X-ray scattering techniques will make it possible to study the fundamental question of biochirality in a novel kinetic and mechanistic context in the aqueous phase (*challenge 3, challenge 4*).

To emphasise is the great advantage of our broad and strong spectroscopy expertise within CMWS, which will enable us to develop and use combined multi-spectroscopies for an integrated experimental approach using X-ray scattering from liquid and film samples and IR, Raman and 2D-IR studies, ideally *in situ* (*challenge 1–challenge 4*), as well as improved deconvolution methods for water and macromolecular dynamics (using techniques including X-ray scattering, THz spectroscopy, neutron spectroscopy, X-ray spectroscopy, advanced correlation methods, mid-IR and multidimensional spectroscopies and Raman spectroscopy). The development of tools for modelling and simulation of single-particle coherent diffractive imaging experiments of hydrated biomolecules will be considered as well (*challenge 3* to *challenge 5*).

Our small-molecule–solvent investigations will help to resolve the structural dynamics of intrinsically disordered proteins (IDPs) or intrinsically disordered regions (IDRs) in viral proteins, e.g. relevant for influenza or corona viruses (*challenge 1*). Furthermore, this research will lead to the development of small molecules that disrupt the protein dynamics of quorum communication within microbiological biofilms (*challenge 1, challenge 3* and *challenge 4*) and boosts new approaches for pharmaceutical research, for example the inclusion of small-molecule 'boosters' to increase the efficacy of formulations with respect to disrupting emerging pathogenic resis-

tance. Biomimetic hydrogels are a potential game-changer for drug delivery of sensitive drugs in anti-viral treatment, e.g. against COVID-19, or against multiresistant gram-negative germs naming two urgent actual medical examples (*challenge 1*). In the context of crystallography and radiation therapy the understanding of radiation damage around high-Z atoms in biomolecules with water on the molecular level is needed. The investigation of the increase of radiation damage by radiosensitizers and radical formation in water by secondary processes will thereby help to improve radiotherapy (*challenge 4*).

III.5.4 Methodologies

In order to solve the scientific challenges, it is absolutely necessary to bundle and further develop the methods applied so far, in particular the laboratory-based ones with those at the large-scale facilities as well as the theoretical ones. Integrated structural biology relies on the ability to combine all experimentally and theoretically obtained data. This correlation of all results allows assessing complex changes in the aqueous environment and how those impact molecular structure, function and reactivity in all detail. The results can be further used to develop translational-research applications. The following methods will be employed and further developed. The combination of structure-resolving X-ray methods with ultrafast nonlinear spectroscopy, e.g. surface-selective sum frequency generation, multidimensional infrared (2D-IR) and terahertz–infrared–visible (THz-IR-Vis) spectroscopy, holds strong potential for mapping structural dynamics at the molecular scale, at biological interfaces similar to that used for active centres of enzymes (among others) and will allow to gain information on biomolecular (thermo)dynamics. The spectroscopic approach requires non-invasive probes sensitive to changes in local geometries and interactions. The suggested experiments will help to improve our physical descriptions of water and solvent interactions, and movements in biomolecular systems that may go on to provide details on how to intentionally fine-tune such interactions, be it to fine-tune the solvent, or to engineer new protein functions (tailored organic-solvent or temperature stable homologues).

Following on, experimental approaches will be established for rationalising the driving forces of chemical selectivity, including systematic and model-based studies in the field of disordered to well organised and interacting bio-systems. To this end, the comparative application of light and heavy water (H_2O or D_2O) throughout all investigations will provide valuable information regarding the kinetics, thermodynamics and stability/structural integrity, i.e. mechanics, of biological systems. This approach also affords unique opportunities for collaborative projects between the CMWS and neutron facilities throughout Europe (ILL, FRM-II and ESS) as H/D isotope substitution can be exquisitely monitored using neutron spectroscopy and scattering techniques.

X-ray crystallography, cryo electron microscopy and NMR are excellent tools to study macromolecules with rigid structures and it goes without saying that these will be critical for all aspects requiring high-resolution structures. However, as biochemical function in aqueous solution, i.e. conformational dynamics, structural disorder or solvation dynamics at surfaces, by their very definition excludes the determination of single structures, research will rely heavily on alternative approaches for obtaining structure information. These include small- and wide-angle X-ray and neutron scattering (SAXS, WAXS and SANS), combined multi-spectroscopies like X-ray Raman spectroscopy (to be developed further), light-scattering experiments, e.g. Raman, IR, DLS and SLS, and fluorescence resonance energy transfer studies to resolve structural constraints from ensemble-states of macromolecules in solution. We will combine the different time-resolved methods to gain insight into the change of *molecular*, e.g. by crystallography and 2D-IR, and *mesoscale structures*, e.g. by solution scattering experiments or electron microscopy, and their dependence on altered solvation potentials.

With respect to probing dynamics, ordered-to-disordered or phase transitions, all of the above-mentioned tools will prove useful in combination with time-resolved experimental capacities at the European XFEL. High through-put structure determination methods (SFX and single particle imaging) at FEL sources combined with new mixing liquid jets will enable watching functional

motion of molecular machines. Mass spectrometry, neutron spectroscopy and CD-spectropolarimetry will be key methods in correlating bound and hydration layer states to structural transitions and dynamics. For example, we plan to use results from different experimental approaches to correlate the rotational and translational degrees of freedom of hydration-layer water to each other and understand how those are related to alterations in protein stability, such as for co-solute addition to the bulk solvent and the subsequent induction of amyloid formation.

Producing defined water attachment strategies and analysing the attachment of water to biomolecules in the gas phase, combined with ion mobility measurements (*challenge 4*), will be further developed. In particular, mass spectrometry combined with X-ray spectroscopy and FEL-based technologies can contribute to studies of structural influences of water on proteins. In order to investigate the real-time movements of ensembles of water down to sizes as small as possible, pump-probe experiments as in pillar 4 will be applied to model real-time water exchange mechanisms and understand how water mobility is affected by temperature, pressure and alterations to bulk solvent activity.

With today's technology, MD simulations of biological interfaces are particularly challenging due to long (µs–ms) required simulation times, large simulation volumes and the lack of realistic force field and ion parameters for which stringent experimental tests are required. We will use experimental results now available for model systems, e.g. from molecular movie type experiments, to improve existing force fields by benchmark simulations of water in these biological systems.

Ideally, results from all studies mentioned above should be comparable as much as possible. Thus, experiments should be performed on similar, or best, same samples under related conditions. To achieve this difficult aim for a majority of the described techniques, it will be necessary to develop new sample delivery standards, which are interchangeable at least between a subset of experiments, i.e. vibrational spectroscopy and SAXS. On a related note, standardised data formats and handling approaches, i.e. including the setup of databases for integrated biological data sets, can be envisioned.

III.5.5 References

[5.1] P. Ball, Water is an active matrix of life for cell and molecular biology, PNAS 114, 13327–13335 (2017).

[5.2] H.-X. Zhou, X. Pang, Electrostatic Interactions in Protein Structure, Folding, Binding, and Condensation, Chem. Rev. 118, 1691–1741 (2018).

[5.3] M. M. Teeter, Water-Protein Interactions: Theory and Experiment, Annu. Rev. Biophys. Biophys. Chem. 20, 577–600 (1991).

[5.4] A. Frölich, F. Gabel, M. Jasnin, U. Lehnert, D. Oesterhelt, A. M. Stadler, M. Tehei, M. Weik, K. Wood, G. Zaccai, From shell to cell: neutron scattering studies of biological water dynamics and coupling to activity, Faraday Discuss. 141, 117–130 (2008).

[5.5] D. Laage, T. Elsaesser, J. T. Hynes, Water Dynamics in the Hydration Shells of Biomolecules, Chem. Rev. 117, 10694–10725 (2017).

[5.6] S. K. Pal, A. H. Zewail, Dynamics of Water in Biological Recognition, Chem. Rev. 104, 2099–2124 (2004).

[5.7] A. Warshel, Energetics of enzyme catalysis, Proc. Natl. Acad. Sci. U. S. A. 75, 5250–5254 (1978).

[5.8] S. Elbaum-Garfinkle, Y. Kim, K. Szczepaniak, C. Chih-Hsiung Chen, C. R. Eckmann, S. Myong, C. P. Brangwynne, The disordered P granule protein LAF-1 drives phase separation into droplets with tunable viscosity and dynamics, Proc. Natl. Acad. Sci. U. S. A. 112, 7189–7194 (2015).

[5.9] K. Meyer, M. Kirchner, B. Uyar, J.-Y. Cheng, G. Russo, L. R. Hernandez-Miranda, A. Szymborska, H. Zauber, I.-M. Rudolph, T. E. Willnow, A. Akalin, V. Haucke, H. Gerhardt, C. Birchmeier, R. Kühn, M. Krauss, S. Diecke, J. M. Pascual, M. Selbach, Mutations in Disordered Regions Can Cause Disease by Creating Dileucine Motifs, Cell 175, 239–253.e17 (2018).

[5.10] E. R. Tamarozzi, S. Giuliatti, Understanding the Role of Intrinsic Disorder of Viral Proteins in the Oncogenicity of Different Types of HPV, Int. J. Mol. Sci. 19, 198 (2018).

[5.11] Y. Cheng, T. LeGall, C. J. Oldfield, A. K. Dunker, V. N. Uversky, Abundance of intrinsic disorder in protein associated with cardiovascular disease, Biochemistry. 45, 10448–10460 (2006).

[5.12] V. N. Uversky, V. Davé, L. M. Iakoucheva, P. Malaney, S. J. Metallo, R. R. Pathak, A. C. Joerger, Pathological Unfoldomics of Uncontrolled Chaos: Intrinsically Disordered Proteins and Human Diseases, Chem. Rev. 114, 6844–6879 (2014).

[5.13] K. Henzler-Wildman, D. Kern, Dynamic personalities of proteins, Nature 450, 964–972 (2007).

[5.14] T. Chouard, Structural biology: Breaking the protein rules, Nature 471, 151–153 (2011).

[5.15] M. Petri, S. Frey, A. Menzel, D. Görlich, S. Techert, Structural characterization of nanoscale meshworks within a nucleoporin FG hydrogel, Biomacromolecules 13, 1882–1889 (2012).

[5.16] D. J. Kushner, A. Baker, T. G. Dunstall, Pharmacological uses and perspectives of heavy water and deuterated compounds, Can. J. Physiol. Pharmacol. 77, 79–88 (1999).

[5.17] V. Kselíková, M. Vítová, K. Bišová, Deuterium and its impact on living organisms, Folia Microbiol. (Praha) 64, 673–681 (2019).

[5.18] L. D. Marco, W. Carpenter, H. Liu, R. Biswas, J. M. Bowman, A. Tokmakoff, Differences in the Vibrational Dynamics of H_2O and D_2O: Observation of Symmetric and Antisymmetric Stretching Vibrations in Heavy Water, J. Phys. Chem. Lett. 7, 1769–1774 (2016).

[5.19] Y. M. Efimova, S. Haemers, B. Wierczinski, W. Norde, A. A. van Well, Stability of globular proteins in H_2O and D_2O, Biopolymers 85, 264–273 (2007).

[5.20] P. Cioni, G. B. Strambini, Effect of heavy water on protein flexibility, Biophys. J. 82, 3246–3253 (2002).

[5.21] E. A. Disalvo, Ed., Membrane Hydration: The Role of Water in the Structure and Function of Biological Membranes (Springer International Publishing, 2015; https://www.springer.com/gp/book/97833191 90594), Subcellular Biochemistry.

[5.22] K. Kubarych, V. P. Roy, K. R. Daley, in Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry (Elsevier, 2018), pp. 443–461.

[5.23] L. B. Dreier, Y. Nagata, H. Lutz, G. Gonella, J. Hunger, E. H. G. Backus, M. Bonn, Saturation of charge-induced water alignment at model membrane surfaces, Sci. Adv. 4, eaap7415 (2018).

[5.24] J. Lipfert, S. Doniach, R. Das, D. Herschlag, Understanding nucleic acid-ion interactions, Annu. Rev. Biochem. 83, 813–841 (2014).

[5.25] E. Yamamoto, T. Akimoto, M. Yasui, K. Yasuoka, Origin of subdiffusion of water molecules on cell membrane surfaces, Sci. Rep. 4, 4720 (2014).

[5.26] D. Krepkiy, M. Mihailescu, J. A. Freites, E. V. Schow, D. L. Worcester, K. Gawrisch, D. J. Tobias, S. H. White, K. J. Swartz, Structure and hydration of membranes embedded with voltage-sensing domains, Nature 462, 473–479 (2009).

[5.27] P. K. Agarwal, A Biophysical Perspective on Enzyme Catalysis, Biochemistry 58, 438–449 (2019).

[5.28] M. C. Bellissent-Funel, A. Hassanali, M. Havenith, R. Henchman, P. Pohl, F. Sterpone, D. Van Der Spoel, Y. Xu, A. E. Garcia, Water Determines the Structure and Dynamics of Proteins, Chem. Rev. 116, 7673–7697 (2016).

[5.29] J. N. Dahanayake, K. R. Mitchell-Koch, How Does Solvation Layer Mobility Affect Protein Structural Dynamics?, Front. Mol. Biosci. 5, 65 (2018).

[5.30] T. Oroguchi, M. Nakasako, Changes in hydration structure are necessary for collective motions of a multi-domain protein, Sci. Rep. 6, 1–14 (2016).

[5.31] P. Mehrabi, E. C. Schulz, R. Dsouza, H. M. Müller-Werkmeister, F. Tellkamp, R. J. Dwayne Miller, E. F. Pai, Time-resolved crystallography reveals allosteric communication aligned with molecular breathing, Science 365, 1167–1170 (2019).

[5.32] Y. Xu, M. Havenith, Perspective: Watching low-frequency vibrations of water in biomolecular recognition by THz spectroscopy, J. Chem. Phys. 143, 170901 (2015).

[5.33] C. Bostedt, S. Boutet, D. M. Fritz, Z. Huang, H. J. Lee, H. T. Lemke, A. Robert, W. F. Schlotter, J. J. Turner, G. J. Williams, Linac Coherent Light Source: The first five years, Rev. Mod. Phys. 88, 015007 (2016).

[5.34] M. Levantino, B. A. Yorke, D. C. F. Monteiro, M. Cammarata, A. R. Pearson, Using synchrotrons and XFELs for time-resolved X-ray crystallography and solution scattering experiments on biomolecules, Curr. Opin. Struct. Biol. 35, 41–48 (2015).

[5.35] H. N. Chapman, P. Fromme, A. Barty, T. A. White, R. A. Kirian, A. Aquila, M. S. Hunter, J. Schulz, D. P. Deponte, U. Weierstall, R. B. Doak, F. R. N. C. Maia, A. V. Martin, I. Schlichting, L. Lomb, N. Coppola, R. L. Shoeman, S. W. Epp, R. Hartmann, D. Rolles, A. Rudenko, L. Foucar, N. Kimmel, G. Weidenspointner, P. Holl, M. Liang, M. Barthelmess, C. Caleman, S. Boutet, M. J. Bogan, J. Krzywinski, C. Bostedt, S. Bajt, L. Gumprecht, B. Rudek, B. Erk, C. Schmidt, A. Hömke, C. Reich, D. Pietschner, L. Ströder, G. Hauser, H. Gorke, J. Ullrich, S. Herrmann, G. Schaller, F. Schopper, H. Soltau, K. U. Kühnel, M. Messerschmidt, J. D. Bozek, S. P. Hau-Riege, M. Frank, C. Y. Hampton, R. G. Sierra, D. Starodub, G. J. Williams, J. Hajdu, N. Timneanu, M. M. Seibert, J. Andreasson, A. Rocker, O. Jönsson, M. Svenda, S. Stern, K. Nass, R. Andritschke, C. D. Schröter, F. Krasniqi, M. Bott, K. E. Schmidt, X. Wang, I. Grotjohann, J. M. Holton, T. R. M. Barends, R. Neutze, S. Marchesini, R. Fromme, S. Schorb, D. Rupp, M. Adolph, T. Gorkhover, I. Andersson, H. Hirsemann, G. Potdevin, H. Graafsma, B. Nilsson, J. C. H. Spence, Femtosecond X-ray protein nanocrystallography, Nature 470, 73–78 (2011).

[5.36] T. A. White, R. A. Kirian, A. V. Martin, A. Aquila, K. Nass, A. Barty, H. N. Chapman, CrystFEL: A software suite for snapshot serial crystallography, J. Appl. Crystallogr. 45, 335–341 (2012).

[5.37] D. Oberthuer, J. Knoška, M. O. Wiedorn, K. R. Beyerlein, D. A. Bushnell, E. G. Kovaleva, M. Heymann, L. Gumprecht, R. A. Kirian, A. Barty, V. Mariani, A. Tolstikova, L. Adriano, S. Awel, M. Barthelmess, K. Dörner, P. L. Xavier, O. Yefanov, D. R. James, G. Nelson, D. Wang, G. Calvey, Y. Chen, A. Schmidt, M. Szczepek, S. Frielingsdorf, O. Lenz, E. Snell, P. J. Robinson, B. Šarler, G. Belšak, M. Maček, F. Wilde, A. Aquila, S. Boutet, M. Liang, M. S. Hunter, P. Scheerer, J. D. Lipscomb, U. Weierstall, R. D. Kornberg, J. C. H. Spence, L. Pollack, H. N. Chapman, S. Bajt, Double-flow focused liquid injector for efficient serial femtosecond crystallography, Sci. Rep. 7, 1–12 (2017).

[5.38] M. O. Wiedorn, D. Oberthür, R. Bean, R. Schubert, N. Werner, B. Abbey, M. Aepfelbacher, L. Adriano, A. Allahgholi, N. Al-Qudami, J. Andreasson, S. Aplin, S. Awel, K. Ayyer, S. Bajt, I. Barák, S. Bari, J. Bielecki, S. Botha, D. Boukhelef, W. Brehm, S. Brockhauser, I. Cheviakov, M. A. Coleman, F. Cruz-Mazo, C. Danilevski, C. Darmanin, R. B. Doak, M. Domaracky, K. Dörner, Y. Du, H. Fangohr, H. Fleckenstein, M. Frank, P. Fromme, A. M. Gañán-Calvo, Y. Gevorkov, K. Giewekemeyer, H. M. Ginn, H. Graafsma, R. Graceffa, D. Greiffenberg, L. Gumprecht, P. Göttlicher, J. Hajdu, S. Hauf, M. Heymann, S. Holmes, D. A. Horke, M. S. Hunter, S. Imlau, A. Kaukher, Y. Kim, A. Klyuev, J. Knoška, B. Kobe, M. Kuhn, C. Kupitz, J. Küpper, J. M. Lahey-Rudolph, T. Laurus, K. Le Cong, R. Letrun, P. L. Xavier, L. Maia, F. R. N. C. Maia, V. Mariani, M. Messerschmidt, M. Metz, D. Mezza, T. Michelat, G. Mills, D. C. F. Monteiro, A. Morgan, K. Mühlig, A. Munke, A. Münnich, J. Nette, K. A. Nugent, T. Nuguid, A. M. Orville, S. Pandey, G. Pena, P. Villanueva-Perez, J. Poehlsen, G. Previtali, L. Redecke, W. M. Riekehr, H. Rohde, A. Round, T. Safenreiter, I. Sarrou, T. Sato, M. Schmidt, B. Schmitt, R. Schönherr, J. Schulz, J. A. Sellberg, M. M. Seibert, C. Seuring, M. L. Shelby, R. L. Shoeman, M. Sikorski, A. Silenzi, C. A. Stan, X. Shi, S. Stern, J. Sztuk-Dambietz, J. Szuba, A. Tolstikova, M. Trebbin, U. Trunk, P. Vagovic, T. Ve, B. Weinhausen, T. A. White, K. Wrona, C. Xu, O. Yefanov, N. Zatsepin, J. Zhang, M. Perbandt, A. P. Mancuso, C. Betzel, H. Chapman, A. Barty, Megahertz serial crystallography, Nat. Commun. 9, 1–11 (2018).

[5.39] R. L. Owen, D. Axford, D. A. Sherrell, A. Kuo, O. P. Ernst, E. C. Schulz, R. J. D. Miller, H. M. Mueller-Werkmeister, Low-dose fixed-target serial synchrotron crystallography, Acta Crystallogr. Sect. D Struct. Biol. 73, 373–378 (2017).

[5.40] E. C. Schulz, P. Mehrabi, H. M. Müller-Werkmeister, F. Tellkamp, A. Jha, W. Stuart, E. Persch, R. De Gasparo, F. Diederich, E. F. Pai, R. J. D. Miller, The hit-and-return system enables efficient time-resolved serial synchrotron crystallography, Nat. Methods. 15, 901–904 (2018).

[5.41] B. A. Yorke, G. S. Beddard, R. L. Owen, A. R. Pearson, Time-resolved crystallography using the Hadamard transform, Nat. Methods. 11, 1131–1134 (2014).

[5.42]   D. Johansen, C. M. J. Jeffries, B. Hammouda, J. Trewhella, D. P. Goldenberg, Effects of macromolecular crowding on an intrinsically disordered protein characterized by small-angle neutron scattering with contrast matching, Biophys. J. 100, 1120–1128 (2011).

[5.43]   C. J. Sahle, M. A. Schroer, C. M. Jeffries, J. Niskanen, Hydration in aqueous solutions of ectoine and hydroxyectoine, Phys. Chem. Chem. Phys. 20, 27917–27923 (2018).

[5.44]   R. Jain, M. Petri, S. Kirschbaum, H. Feindt, S. Steltenkamp, S. Sonnenkalb, S. Becker, C. Griesinger, A. Menzel, T. P. Burg, S. Techert, X-ray scattering experiments with high-flux x-ray source coupled rapid mixing microchannel device and their potential for high-flux neutron scattering investigations, Eur. Phys. J. E. 36, 109 (2013).

[5.45]   S. Magazù, F. Mezei, P. Falus, B. Farago, E. Mamontov, M. Russina, F. Migliardo, Protein dynamics as seen by (quasi) elastic neutron scattering, Biochim. Biophys. Acta - Gen. Subj. 1861, 3504–3512 (2017).

[5.46]   R. L. Owen, B. A. Yorke, J. A. Gowdy, A. R. Pearson, Revealing low-dose radiation damage using single-crystal spectroscopy, J. Synchrotron Radiat. 18, 367–373 (2011).

[5.47]   Z. Yin, L. Inhester, S. Thekku Veedu, W. Quevedo, A. Pietzsch, P. Wernet, G. Groenhof, A. Föhlisch, H. Grubmüller, S. Techert, Cationic and Anionic Impact on the Electronic Structure of Liquid Water, J. Phys. Chem. Lett. 8, 3759–3764 (2017).

[5.48]   G. Öhrwall, R. F. Fink, M. Tchaplyguine, L. Ojamäe, M. Lundwall, R. R. T. Marinho, A. N. De Brito, S. L. Sorensen, M. Gisselbrecht, R. Feifel, T. Rander, A. Lindblad, J. Schulz, L. J. Sæthre, N. Mårtensson, S. Svensson, O. Björneholm, The electronic structure of free water clusters probed by Auger electron spectroscopy, J. Chem. Phys. 123, 054310 (2005).

[5.49]   N. Ottosson, K. J. Børve, D. Spångberg, H. Bergersen, L. J. Sæthre, M. Faubel, W. Pokapanich, G. Öhrwall, O. Björneholm, B. Winter, On the origins of core-electron chemical shifts of small biomolecules in aqueous solution: Insights from photoemission and ab initio calculations of glycine(aq), J. Am. Chem. Soc. 133, 3120–3130 (2011).

[5.50]   J. Werner, I. Persson, O. Björneholm, D. Kawecki, C. M. Saak, M. M. Walz, V. Ekholm, I. Unger, C. Valtl, C. Caleman, G. Öhrwall, N. L. Prisle, Shifted equilibria of organic acids and bases in the aqueous surface region, Phys. Chem. Chem. Phys. 20, 23281–23293 (2018).

[5.51]   S. Bari, D. Egorov, T. L. C. Jansen, R. Boll, R. Hoekstra, S. Techert, V. Zamudio-Bayer, C. Bülow, R. Lindblad, G. Leistner, A. Ławicki, K. Hirsch, P. S. Miedema, B. von Issendorff, J. T. Lau, T. Schlathölter, Soft X-ray Spectroscopy as a Probe for Gas-Phase Protein Structure: Electron Impact Ionization from Within, Chem. - A Eur. J. 24, 7631–7636 (2018).

[5.52]   L. Schwob, S. Dörner, K. Atak, K. Schubert, M. Timm, C. Bülow, V. Zamudio-Bayer, B. Von Issendorff, J. T. Lau, S. Techert, S. Bari, Site-Selective Dissociation upon Sulfur L-Edge X-ray Absorption in a Gas-Phase Protonated Peptide, J. Phys. Chem. Lett. 11, 1215–1221 (2020).

[5.53]   F. Dahms, B. P. Fingerhut, E. T. J. Nibbering, E. Pines, T. Elsaesser, Large-amplitude transfer motion of hydrated excess protons mapped by ultrafast 2D IR spectroscopy, Science 357, 491–495 (2017).

[5.54]   J. Schauss, F. Dahms, B. P. Fingerhut, T. Elsaesser, Phosphate–Magnesium Ion Interactions in Water Probed by Ultrafast Two-Dimensional Infrared Spectroscopy, J. Phys. Chem. Lett. 10, 238–243 (2019).

[5.55]   T. Siebert, B. Guchhait, Y. Liu, B. P. Fingerhut, T. Elsaesser, Range, Magnitude, and Ultrafast Dynamics of Electric Fields at the Hydrated DNA Surface, J. Phys. Chem. Lett. 7, 3131–3136 (2016).

[5.56]   E. M. Bruening, J. Schauss, T. Siebert, B. P. Fingerhut, T. Elsaesser, Vibrational Dynamics and Couplings of the Hydrated RNA Backbone: A Two-Dimensional Infrared Study, J. Phys. Chem. Lett. 9, 583–587 (2018).

[5.57]   L. B. Dreier, C. Bernhard, G. Gonella, E. H. G. Backus, M. Bonn, Surface Potential of a Planar Charged Lipid–Water Interface. What Do Vibrating Plate Methods, Second Harmonic and Sum Frequency Measure?, J. Phys. Chem. Lett. 9, 5685–5691 (2018).

[5.58]   C. Bernhard, K. N. Bauer, M. Bonn, F. R. Wurm, G. Gonella, Interfacial Conformation of Hydrophilic Polyphosphoesters Affects Blood Protein Adsorption, ACS Appl. Mater. Interfaces 11, 1624–1629 (2019).

[5.59] H. M. Müller-Werkmeister, J. Bredenbeck, A donor-acceptor pair for the real time study of vibrational energy transfer in proteins, Phys. Chem. Chem. Phys. 16, 3261–3266 (2014).

[5.60] L. J. G. W. van Wilderen, D. Kern-Michler, H. M. Müller-Werkmeister, J. Bredenbeck, Vibrational dynamics and solvatochromism of the label SCN in various solvents and hemoglobin by time dependent IR and 2D-IR spectroscopy, Phys. Chem. Chem. Phys. 16, 19643–19653 (2014).

[5.61] A. Creon, I. Josts, S. Niebling, N. Huse, H. Tidow, Conformation-specific detection of calmodulin binding using the unnatural amino acid p-azido-phenylalanine (AzF) as an IR-sensor, Struct. Dyn. 5, 064701 (2018).

[5.62] A. Wagner, T. A. Le, M. Brennich, P. Klein, N. Bader, E. Diehl, D. Paszek, A. K. Weickhmann, N. Dirdjaja, R. L. Krauth-Siegel, B. Engels, T. Opatz, H. Schindelin, U. A. Hellmich, Inhibitor-Induced Dimerization of an Essential Oxidoreductase from African Trypanosomes, Angew. Chem. Int. Ed. 58, 3640–3644 (2019).

[5.63] B. Goretzki, N. A. Glogowski, E. Diehl, E. Duchardt-Ferner, C. Hacker, R. Gaudet, U. A. Hellmich, Structural Basis of TRPV4 N Terminus Interaction with Syndapin/PACSIN1-3 and PIP 2, Structure 26, 1583–1593 e5 (2018).

[5.64] O. Mankinen, V. V. Zhivonitko, A. Selent, S. Mailhiot, S. Komulainen, N. L. Prisle, S. Ahola, V.-V. Telkki, Ultrafast diffusion exchange nuclear magnetic resonance, Nat. Commun. 11, 3251 (2020).

[5.65] R. Shaharabani, M. Ram-On, Y. Talmon, R. Beck, Pathological transitions in myelin membranes driven by environmental and multiple sclerosis conditions, Proc. Natl. Acad. Sci. 115, 11156–11161 (2018).

[5.66] T. J. Simmons, K. E. H. Frandsen, L. Ciano, T. Tryfona, N. Lenfant, J. C. Poulsen, L. F. L. Wilson, T. Tandrup, M. Tovborg, K. Schnorr, K. S. Johansen, B. Henrissat, P. H. Walton, L. Lo Leggio, P. Dupree, Structural and electronic determinants of lytic polysaccharide monooxygenase reactivity on polysaccharide substrates, Nat. Commun. 8, 1064 (2017).

[5.67] K. K. Rasmussen, K. E. H. Frandsen, E. Boeri Erba, M. Pedersen, A. K. Varming, K. Hammer, M. Kilstrup, P. W. Thulstrup, M. Blackledge, M. R. Jensen, L. Lo Leggio, Structural and dynamics studies of a truncated variant of CI repressor from bacteriophage TP901-1, Sci. Rep. 6, 29574 (2016).

[5.68] S. Kesgin-Schaefer, J. Heidemann, A. Puchert, K. Koelbel, B. A. Yorke, N. Huse, A. R. Pearson, C. Uetrecht, H. Tidow, Crystal structure of a domain-swapped photoactivatable sfGFP variant provides evidence for GFP folding pathway, FEBS J. 286, 14797 (2019).

[5.69] I. Josts, J. Nitsche, S. Maric, H. D. Mertens, M. Moulin, M. Haertlein, S. Prevost, D. I. Svergun, S. Busch, V. T. Forsyth, H. Tidow, Conformational States of ABC Transporter MsbA in a Lipid Environment Investigated by Small-Angle Scattering Using Stealth Carrier Nanodiscs, Structure 26, 8, 1072–1079.e4 (2018).

[5.70] K.K. Viet, A. Wagner, K. Schwickert, N. Hellwig, N. Bader, T. Schirmeister, N. Morgner, H. Schindelin, U. A. Hellmich, Structure of the human TRPML2 ion channel extracytosolic/lumenal domain, Structure 27, 1246–1257 (2019).

[5.71] A. Wagner, T. A. Le, M. Brennich, P. Klein, N. Bader, E. Diehl, D. Paszek, A. K. Weickhmann, N. Dirdjaja, R. L. Krauth-Siegel, B. Engels, T. Opatz, H. Schindelin, U. A. Hellmich, Inhibitor-Induced Dimerization of an Essential Oxidoreductase from African Trypanosomes, Angew. Chem. Int. Ed. 58, 3640–3644 (2019).

[5.72] M. Merski and B. K. Shoichet, The Impact of Introducing a Histidine into an Apolar Cavity Site on Docking and Ligand Recognition, J. Med. Chem. 56, 2874–2884 (2013).

[5.73] M. Merski, M. Fischer, T. E. Balius, O. Eidam, B. K. Shoichet, Homologous ligands accommodated by discrete conformations of a buried cavity, Proc. Natl. Acad. Sci. 112, 5039–5044 (2015).

[5.74] B. J. Mietner, M. Fröba, R. Valiullin, Water Transport in Periodic Mesoporous Organosilica Materials, J. Phys. Chem. C 122, 12673–12680 (2018).

[5.75] B. J. Mietner, F. J. Brieler, Y. J. Lee, M. Fröba, Properties of Water Confined in Periodic Mesoporous Organosilicas: Nanoimprinting the Local Structure, Angew. Chem. Int. Ed. 56, 12348–12351 (2017).

[5.76] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Silica-Based Mesoporous Organic–Inorganic Hybrid Materials, Angew. Chem. Int. Ed. 45, 3216–3251 (2006).

[5.77] J. R. Werber, C. O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nat. Rev. Mater. 1, 16018 (2016).

[5.78] O. Fisette, C. Päslack, R. Barnes, J. M. Isas, R. Langen, M. Heyden, S. Han, L. V. Schäfer, Hydration Dynamics of a Peripheral Membrane Protein, J. Am. Chem. Soc. 138, 11526–11535 (2016).

[5.79] M. Prieß, H. Göddeke, G. Groenhof, L. V. Schäfer, Molecular Mechanism of ATP Hydrolysis in an ABC Transporter, ACS Cent. Sci. 4, 1334–1343 (2018).

[5.80] H. Singh, S. K. Vasa, H. Jangra, P. Rovó, C. Päslack, C. K. Das, H. Zispe, L.V. Schäfer, Fast Microsecond Dynamics of the Protein-Water Network in the Active Site of Human Carbonic Anhydrase II Studied by Solid-State NMR Spectroscopy, J. Am. Chem. Soc. 141, 19276–19288 (2019).

[5.81] H. Göddeke and L. V. Schäfer, Capturing Substrate Translocation in an ABC Exporter at the Atomic Level, J. Am. Chem. Soc.142, 12791–12801 (2020).

IV. Infrastructure and Organisation

IV.1 CMWS Infrastructure

IV.1.1 The Science Campus Bahrenfeld

The central part of the CMWS science activities shall be located in a research building on the Science Campus Bahrenfeld in Hamburg in close proximity to DESY's on campus light source facilities (PETRA III/IV, FLASH), the European XFEL and the on campus partner institutes and research centres. This involves the EMBL outstation, the Max-Planck Institute for the Structure and Dynamics of Matter (MPSD), the Center for Free-Electron Laser Science (CFEL) and research centres CSSB, CHyN, HARBOR and CXNS.

CMWS has already established close links to the on-site partners by collaborating in ongoing research projects (within the Early Science Programme or, e.g. within the Clusters of Excellence AIM and CUI funded via Germany's Excellence Strategy), by sharing instrumentation and working on access schemes to the light source facilities and through their involvement in the editing of the CMWS research agenda

(Chapter III). Further synergetic effects are expected from the planned relocation of the Physics and Chemistry Departments of the University of Hamburg to the Science Campus Bahrenfeld.

IV.1.2 CMWS Office and Laboratory Building

A future CMWS building shall offer office space (about 1650 m^2) and laboratory space (about 1150 m^2) for a planned number of 150 people. This includes research groups of the five pillars and additional capacities for junior research groups, for example within the framework of the Helmholtz Young Investigator Group (YIG) programme, the Emmy-Noether programme of the DFG, or Starting and Consolidator grants of the ERC. Coworking space for visiting scientists of CMWS partner institutions will be provided by a "research hostel". An integral part of the CMWS concept is the close cooperation and interaction between the research groups within and in between the research pillars and guests from the CMWS partners. For this purpose, communication spaces in form of a lecture hall,

CHyN
Center for
Hybrid Nano-
structures

HARBOR
Hamburg
Advanced
Research
Centre for
Bioorganic
Chemistry

EMBL
European
Molecular
Biology
Laboratory

CSSB
Centre for
Structural
Systems
Biology

MPSD
Max-Planck-
Institut für
Struktur und
Dynamik
der Materie

CFEL
Center for
Free-Electron
Laser Science

CXNS
Centre for
X-ray and
Nano Science

PETRA III/IV   FLASH

European
XFEL

Start-up
Labs
Bahrenfeld

Figure IV.1: Aerial view of the Science Campus Bahrenfeld in Hamburg. Relevant CMWS partners are indicated in the legend.

meeting and seminar rooms of different sizes and common meeting areas will be incorporated in the building. The central CMWS building will thus enable

close cooperation and networking between the research pillars under one roof and combine dedicated experimental resources in a unique way. CMWS will furthermore benefit from the access to the general on-site infrastructures available at the DESY campus such as the mechanical workshops and the IT infrastructure. CMWS will set up its own computing cluster unit named "POSEIDON" operating within the DESY IT infrastructure.

The CMWS building laboratory space shall accommodate standard laboratories (750 m^2) and specialised laboratories (400 m^2) for research and development. The work in the laboratories will be supported by a group of technicians. The standard laboratory portfolio will comprise laboratories for **chemistry, sample synthesis** (e.g. hydrous geo-materials), **sample analysis and microscopy** (AFM, mass spectrometry, DLS, equipment for calorimetric, thermogravimetric and surface tension measurements, special sample environments), and **spectroscopy** (NIR, IR, UV-Vis, Raman, SFG and FTIR spectrometers). Of very high importance is a **dedicated ice laboratory and a cold room** for the controlled preparation, handling, storage and characterisation of low temperature samples.

Specialised laboratories shall be operated by the respective research groups, and access to the dedicated setups will be possible in cooperation with the experts of the research groups. This will include a **liquid jet and sample injection laboratory** for the development, testing and characterisation of liquid jet, aerosols and clusters sources.

An important add-on includes a **laser laboratory** with class IV laser safety clearance and excellent floor stability (VC-C/VC-D classification) and temperature stability (21±0.2 °C) and a **S2 Biological Laboratory** for synthesis, handling and investigation of aqueous biological samples.

It is planned to foresee **"temporary" lab space** for preparation of experiments at the large-scale photon facilities (setting up, testing and pre-alignment of experimental setups and end-stations) in an experimental hall.

IV.1.3 Infrastructure and Competence Hubs

The Centre for Molecular Water Science (CMWS) is supported by a network of Infrastructure and Competence Hubs (Figure IV.2). The Infrastructure Hubs shall offer dedicated access to a hard X-ray facility (PETRA III/IV), soft X-ray facilities (e.g. SOLEIL, ELETTRA, BESSY II), FEL radiation (FLASH, European XFEL), NMR (KU Leuven) and sample preparation and/or characterisation laboratories with complementary experimental techniques. These laboratories can be centralised, such as the CMWS Preparation and Characterisation Laboratory on the Science Campus Bahrenfeld, or decentralised, with different experimental techniques provided by several partners, such as the Complementary Techniques and Spectroscopies Hub. These Hubs complement the CMWS capabilities and give CMWS researchers comprehensive access to a large portfolio of experimental techniques covering a broad range of the electromagnetic spectrum and 18 orders of magnitude in time (Figure IV.3). The Hubs are open for expansions and modifications to new methodologies and techniques and future CMWS partners. Also, Hubs with focus on specific competences, e.g. in data analysis, computer simulations and theory can be developed and implemented within this framework (Competence Hubs).

Access to the facility Hubs may be different from case to case and might happen via CMWS or via the access programme of the respective facility or is based on collaborative projects. The Hub environment comprises:

Hard X-ray Facilities

Hard X-ray radiation plays a central role for structure and dynamics investigations within CMWS. Access to PETRA III and (future) PETRA IV in terms of long-term and Block Allocation Group (BAG) access is under discussion.

FEL Facilities

Ultrashort hard and soft X-ray pulses for structure but in particular dynamics investigations of water are of prime importance for the centre. Special priority programmes are under discussion at the

European XFEL. FLASH/FLASH2020+ is supporting XUV and Soft X-ray methods.

NMR Facility
KU Leuven (Belgium) will provide access to their NMR centre for enabling research in mixed solid / liquid / gas systems, and for high-throughput applications.

Soft X-ray Facilities
XUV and Soft X-ray methods are accessible at the large-scale synchrotron radiation sources SOLEIL (France), ELETTRA (Italy) and BESSY II in Berlin.

Complementary Techniques Hub
The Complementary Techniques Hub organises access to techniques available at DESY or at partners institutions. This involves access to attosecond sources combined with UV/VIS/IR radiation, laser sources from UV to THz, VMI and mass spectrometry, resistive heated DAC setup for Raman spectroscopy measurements and broadband microwave spectroscopy (DESY).

Further available methods include non-linear spectroscopy (IR–THz) capabilities and ultrafast 2D (IR–THz) spectroscopy (MPIP, Mainz), environmental TEM and atomic probe tomography (Göttingen University). Various sample handling and preparation systems are at hand, e.g. gas-dynamic virtual nozzles, flat jets, dielectrics at surfaces, gas adsorption/desorption techniques (FHI, Berlin and Kassel University), cluster and aerosol sources (ETH Zurich), sample preparation units (UHH), an ice-growing laboratory (MPIP, Mainz), a rotating multi-anvil-press and internally heated pressure vessel for syntheses of hydrous materials (GFZ Potsdam/Potsdam University).

CMWS Preparation and Characterisation Laboratory
Basic on-campus sample characterisation capabilities are accessible (Ion-Mobility Spectrometer, Calorimeter, Cryo-Microscope, Dielectric Spectrometer, Raman Spectrometer, FTIR Spectrometer, UV–VIS Spectrometer).
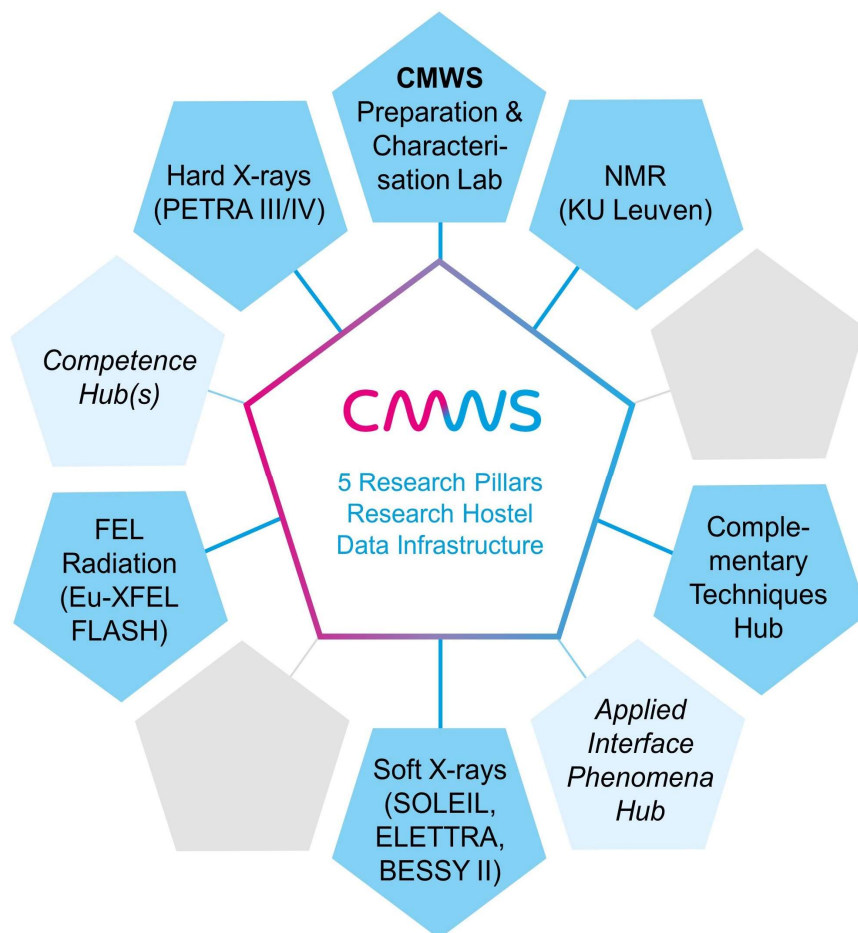
Figure IV.2: Network of Infrastructure Hubs (dark blue) and future Hubs under discussion (light blue and grey).
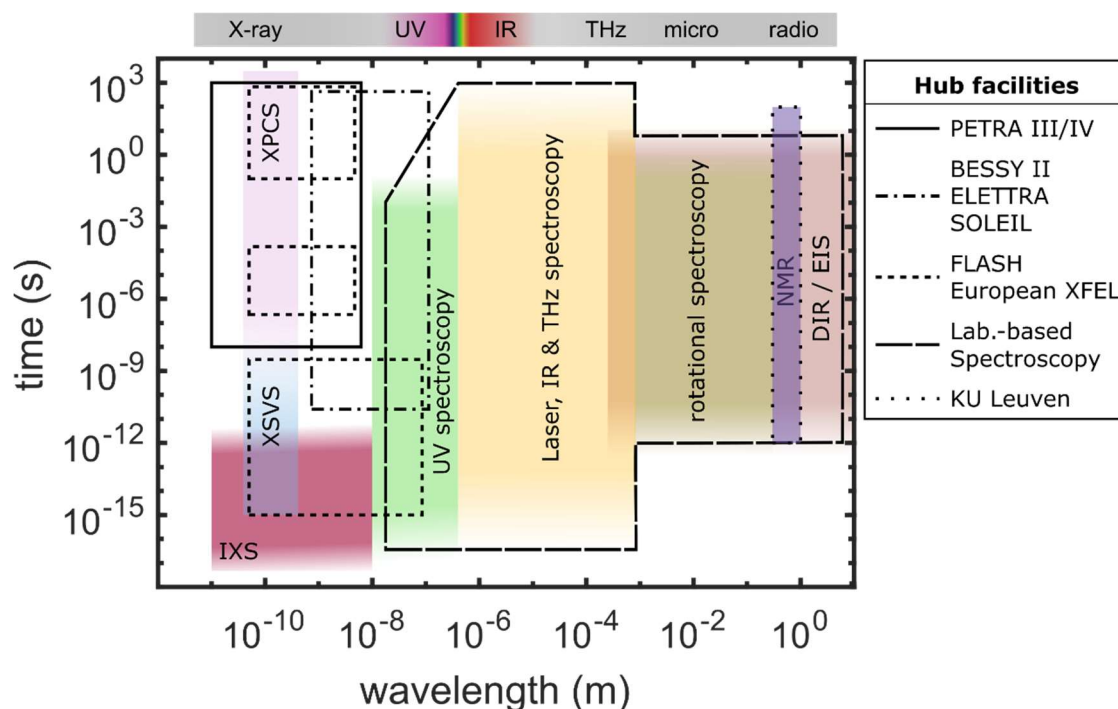
Figure IV.3: Timescales covered by various experimental methods and techniques available within CMWS. X-ray based techniques involve X-ray Photon Correlation Spectroscopy (XPCS), X-ray Speckle Visibility Spectroscopy (XSVS) and Inelastic X-ray Scattering (IXS). DRS/EIS denotes Dielectric Relaxation Spectroscopy/Electrochemical Impedance Spectroscopy. Image: DESY.

Applied Interface Phenomena Hub

(proposed by TU Bergakademie Freiberg)

This hub offers to act as an interface for technological applications and shall deal with the interaction of water with technologically relevant surfaces, questions of safety, sustainability and environmental impact. It shall investigate water in technogenic sediments, as carrier of resources, and component in geo-energy applications.

The methods portfolio available within CMWS and the Infrastructure Hubs takes advantage of a large range of the electromagnetic spectrum and gives access to a broad range of timescales (Figure IV.3).

IV.2 Governance

This proto-governance model describes some key elements and functionalities of a future governance structure. Details are in the process of being worked out.

General Assembly

The General Assembly (GA) is the "Decision Making Body" of CMWS. All qualified CMWS partners are represented with voting rights in the General Assembly. The GA elects a Chair and a Vice-Chair and meets at least once a year. It executes its decisions via the Management Board. The General Assembly selects a defined number of the Management Board members. The General Assembly is supported by the CMWS office. It welcomes new qualified partners but offers also the possibility to be joint by associates or collaborating partners.

Management Board

The Management Board is the "Executive Body" of CMWS. It is constituted out of the speakers/deputies representing the (five) CMWS Science Pillars, the representatives of the operational Infrastructure Hubs, the members selected by the General Assembly and the representatives of the Host Lab. It reports to the General Assembly. It supports the operation of the CMWS Pillars and the Infrastructure Hubs.

CMWS Science Pillars

CMWS science is organised around (five) research pillars as defined in the founding White Paper. Each pillar selects a speaker and a deputy

Members and Associates
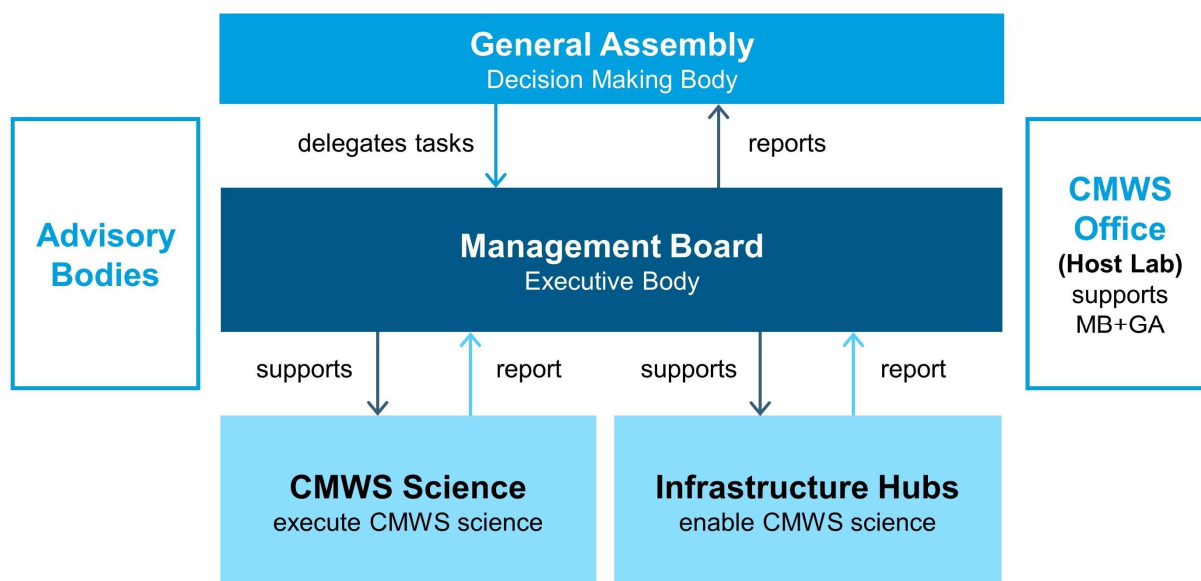
Figure IV.4: Organigram: Centre Molecular Water Science.

and is represented in the Management Board. The speaker/deputy is responsible for the organisation and operation of the pillar.

Infrastructure Hubs

The CMWS infrastructure Hubs provide access to infrastructures (techniques/facilities) not available within CMWS. Hub status requires these capabilities and services to be quantified and specified in terms of manpower, resources, access and regulated within a collaboration contract with the Host laboratory. Infrastructure hubs are represented in the Management Board.

CMWS Office

The Host Laboratory (DESY) supports CMWS by operating the CMWS Office, by providing support for infrastructure and administrative tasks (office and lab space, IT support, controlling), and by managing and co-financing the Early Science Programme (ESP). The Host Laboratory is represented in the Management Board.

CMWS Advisory Committee(s)

The CMWS Scientific Advisory Committee advises the Management Board on all relevant activities, particularly on its research portfolio and strategic plans. It consists of independent international experts in the CMWS activity areas. It meets at least once a year. Additional Advisory Committees may be constituted upon need.

IV.3 Timeline

3/2018	1st Workshop: Research Course Trends in Water Science
12/2018	2nd Workshop: Centre for Molecular Water Science
3/2019	Early Science Programme: Phase I
1/2020	Opening CMWS Office
3/2020	3rd Workshop: DESY Water Week
1/2021	Early Science Programme: Phase II
	Start of operation of first CMWS laboratory
3/2021	4th Workshop: Water Days (online)
Fall 2021	Scientific Evaluation
Spring 2022	MoU and Collaboration Contracts
Fall 2022	Start operation

Glossary

BESSY II	Berliner Elektronenspeicherring für Synchrotronstrahlung
CFEL	Center for Free-Electron Laser Science
CHyN	Centre for Hybrid Nanomaterials
CSSB	Centre for Structural Systems Biology
CUI	Centre for Ultrafast Imaging
Elettra	ELETTRA Sincrotrone, Trieste
EMBL	European Molecular Biology Laboratory
European XFEL	European X-Ray Free Electron Laser
FLASH	Free-Electron Laser for soft X-rays at DESY
HARBOR	Hamburg Advanced Research Centre for Bioorganic Chemistry
PETRA III/IV	PETRA III/IV Synchrotron Radiation Source at DESY
SOLEIL	SOLEIL Synchrotron Facility, Paris
TUHH	Technische Universität Hamburg
UHH	Universität Hamburg

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