



Abschließender Sachstandsbericht  
Leibniz-Wettbewerb

**Electron Dynamics and Charge Correlations Studied by Ultrafast  
Soft X-Ray Absorption Spectroscopy**

Antragsnummer: **SAW-2016-MBI-1**

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**Berichtszeitraum:** 02.2016 – 01.2020

**Federführendes Leibniz-Institut:** Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie

**Projektleiter/in:**

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## 1. Goals and Milestones

The main aim of this project is to develop ultrafast soft X-ray spectroscopy with table-top sources as a tool to locally probe optically induced charge flow dynamics, both in structurally ordered metal hydrides (materials used for hydrogen storage in hydrogen fuel cell technologies) and cathode materials (as used in Li-batteries), and in push-pull donor-acceptor polyenes, used as a means for charge transport over extended ranges in energy transport and storage devices. Soft X-ray spectroscopy monitors core excitations to unoccupied molecular orbitals, and provide a direct means of locally probing electronic structure. Development of laser sources delivering femtosecond soft X-ray pulses allows for a direct access into the underlying mechanisms of photo-induced charge flow by following the elementary steps responsible for the electron dynamics. The following goals have been pursued, that each led to marked milestones:

**Goal 1:** Laser-driven source of femtosecond soft X-ray pulses: We aim to develop a soft X-ray source spanning the photon energy range from 50 to 600 eV.

**Milestone 1a:** Two-colour driving pulses tuned at 800 nm and 1.3  $\mu\text{m}$  have been used to generate a continuous HHG spectrum in 100 mbar Ar ranging from 40 – 80 eV.

**Milestone 1b:** One-colour driving pulses tuned at 1.8  $\mu\text{m}$  have been used to generate extreme HHG pulses in up to 6 bar He covering a spectral range from 200 – 450 eV.

**Goal 2:** Electric field driven electron dynamics in solids. With ultrashort light pulses we aim to induce or modify the electronic structure and the couplings of electrons in different quantum states in crystalline matter containing light elements such as Li. Ultrafast soft X-ray absorption will be used to characterize the electric field driven electron dynamics.

**Milestone 2:** Impact of lattice motions in crystalline solids on electronic structure; laser driven coherent phonon excitations, resulting in ultrasmall atomic displacements, have been recorded with ultrashort X-ray pulses tuned at the Li K-edge.

**Goal 3:** Photo-induced electron transfer in donor-acceptor molecular systems. We aim to monitor the associated transient charge flow dynamics in push-pull chromophores by ultrafast soft X-ray absorption spectroscopy at the C, N, and O K-edges.

**Milestone 3a:** Simultaneous measurement of C and N K-edge absorption of organic molecules in aqueous solution has been achieved with HHG pulses.

**Milestone 3b:** Design and installation of a new “Hettrick-Underwood” like reflective zone-plate spectrometer with 45 times higher photon flux transmission and 5.5 times higher spectral resolution than “traditional” grating-based spectrometer with multi-channel plate detector.

## 2. Activities and Challenges

**Goal 1:** Laser-driven source of femtosecond soft X-ray pulses.

WP1 and WP2 were first pursued in conjunction with WP3. Hence a beamline for HHG using two-colour driver pulses was first constructed and tested, followed by the construction of a grating-based X-ray spectrometer. HHG photon flux and stabilities have allowed for extremely sensitive time-resolved XAS experiments at the Li K-edge around 60 eV, planned in WP3.

**Goal 2:** Electric field driven electron dynamics.

The activities planned in WP3 have been focused on  $\text{LiBH}_4$ , as sample handling issues have hampered a proper exploration of the electronic structural dynamics of LiH. In the successful experiments on  $\text{LiBH}_4$  absorbance changes as small as  $\Delta A = 10^{-4}$  have been recorded at the Li K-edge around 60 eV.

**Goal 3:** Photo-induced electron transfer in donor-acceptor molecular systems.

Going to larger HHG photon energies above 200 eV necessitates further improvements in the performance of the laser output (driver pulse energy and pointing stabilities), before starting activities in WP5. For WP5 we have established a proper procedure for recording steady-state X-ray spectra between 200 – 450 eV of solutes in aqueous solution using flatjet technology.

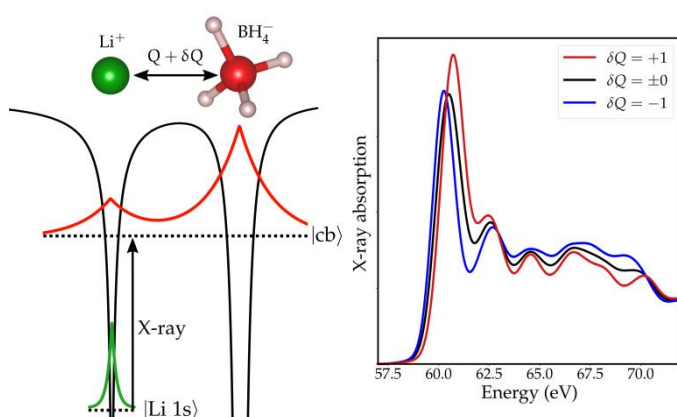
Still the photon flux for the extreme HHG pulses (200-450 eV) determined after transmission through the grating spectrometer remained too small to record the differential transient soft X-ray absorbance signals (on the order of  $10^{-4}$  –  $10^{-3}$  for most photoexcited samples). To prepare for successful time-resolved experiments, further improvement in X-ray pulse throughput and in X-ray detection appeared necessary, hence the construction of a new X-ray spectrometer has been pursued, in collaboration with IAP e.V. Our source combined with the new spectrometer has been tested and first time-resolved soft X-ray absorption experiments have been carried out in various gas samples, ionized by a strong near infrared laser pulse.

### 3. Results and Achievements

#### 3.1 Ultrafast modulation of electronic structure by coherent phonon excitations

X-ray absorption is an important method for mapping equilibrium structures at atomic length scales. The fine structure of X-ray absorption bands reflects distances between neighboring atoms in condensed-phase molecular systems and in crystalline environments. Transient X-ray absorption in the ultrafast time domain thus allows for observing atomic motions and rearrangements in real-time (Figure 1). In the following, we present new results from a femtosecond X-ray absorption study in which periodic motions of atoms over an extremely small length of  $10^{-15}$  m have been recorded using ultrashort X-ray pulses [1,2]. This novel experiment is based on a pump-probe scheme with optical excitation and high-harmonics probe pulses.

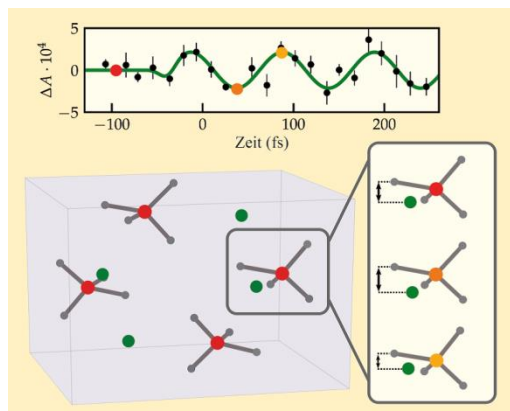
In the experiment, lattice vibrations or phonons are excited in small crystallites. The spatial elongation of nuclei in a vibration is much smaller than the distance between atoms, the latter being determined by the equilibrium distribution of electrons. Nevertheless, the vibrational motions act back on the electrons, modulate their spatial distribution and change the electric and optical properties of the crystal on a time scale which is shorter than 1 ps ( $10^{-12}$  s). To understand these effects and exploit them for novel, e.g., acousto-optical, devices, one needs to image the delicate interplay of nuclear and electronic motions on a time scale much shorter than 1 ps.



**Figure 1** In an X-ray absorption experiment light excites a strongly bound core electron into a conduction band state. On the left of the figure such a transition is shown. An electron which is strongly bound to a Lithium nucleus (green) is excited into a conduction band state (red) that interacts with both the lithium nucleus and borohydride group. This conduction band state is therefore sensitive to a modulation of the distance  $Q$  between Lithium nucleus and borohydride group and as a result the X-ray absorption process is sensitive to such a modulation (cf. Figs. 2(b) and 3(d) in Ref. [1]). On the right side of the figure the Lithium K-edge X-ray absorption spectrum for different strongly exaggerated displacements is shown.

In collaborative work of MBI, the Swiss Federal Laboratory for Materials Science and Technology in Dübendorf (Switzerland), and the National Institute of Standards and Technology, Gaithersburg (USA), a novel method of optical pump-soft X-ray probe spectroscopy was applied for generating coherent atomic vibrations in small  $\text{LiBH}_4$  crystals,

and reading them out via changes of X-ray absorption. More specifically, an optical pump pulse centered at 800 nm excited a coherent optical phonon with  $A_g$  symmetry via impulsive Raman scattering (Figure 2). The resulting motion that corresponds to a modulation of the distance between the  $\text{Li}^+$  and  $(\text{BH}_4)^-$  ions, with the vibrational frequency of 10 THz, was directly mapped into a modulation of soft X-ray absorption on the Li K-edge around 60 eV (Figures 1 and 2, upper panel).



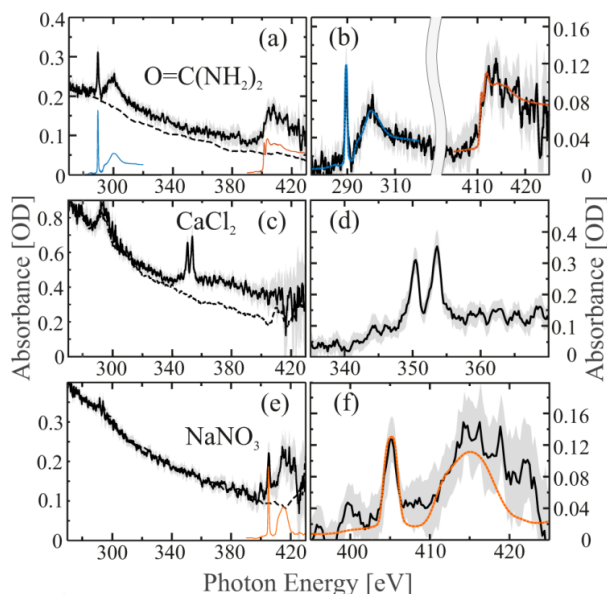
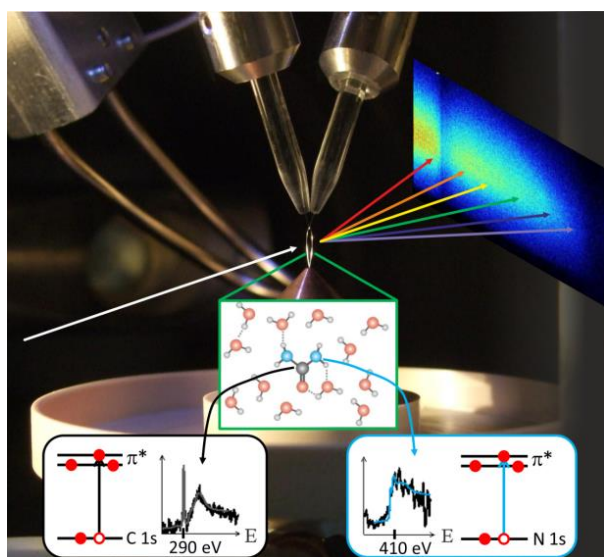
**Figure 2** What happens in the unit cell of crystalline  $\text{LiBH}_4$  after impulsive Raman excitation with a femtosecond laser pulse? Upper panel: measured transient absorption change  $\Delta A(t)$  (symbols) as we vary the time delay between infrared pump pulses and soft X-ray probe pulses at photon energy of  $\hbar\omega = 61.5$  eV (cf. Fig. 3(a) in Ref. [1]). The lower box shows the atoms in the unit cell of  $\text{LiBH}_4$  with red boron atoms, gray hydrogen atoms, and green Li atoms. The moving blue circle in the upper panel is synchronized with the moving atoms in the lower panel. The amplitude of the motion is strongly exaggerated (i.e. times 30000) to visualize the pattern of the motion.

This experimental scheme is highly sensitive and allows for the first time to kick off and detect extremely small amplitudes of atomic vibrations. In our case, the  $\text{Li}^+$  ions move over a distance of only 3 femtometers =  $3 \times 10^{-15}$  m which is comparable to the diameter of the  $\text{Li}^+$  nucleus and 100000 times smaller than a distance between the ions in the crystal. The experimental observations are in excellent agreement with in-depth theoretical calculations of the transient X-ray absorption signal. Moreover, these results together with transient electron density maps obtained from previous femtosecond X-ray diffraction [3] give detailed insight in the character of the virtual intermediate state in the Raman excitation process. The 800 nm pump pulse induces a shift of electronic charge between neighboring  $\text{Li}^+$  and  $(\text{BH}_4)^-$  entities which results in a Coulomb force on the nuclei. The force field derived from the transient electron density maps displays local components pointing into the same directions as the local elongations of the 10 THz  $A_g$  mode, explaining the predominance of this phonon in the transient response. The new type of optical pump-soft X-ray probe spectroscopy on a femtosecond time scale holds strong potential for measuring and understanding the interplay of nuclear and electronic motions in liquid and solid matter, a major prerequisite for theoretical simulations and applications to develop novel technologies.

### 3.2 Looking at molecules from two sides with table-top femtosecond soft X-rays

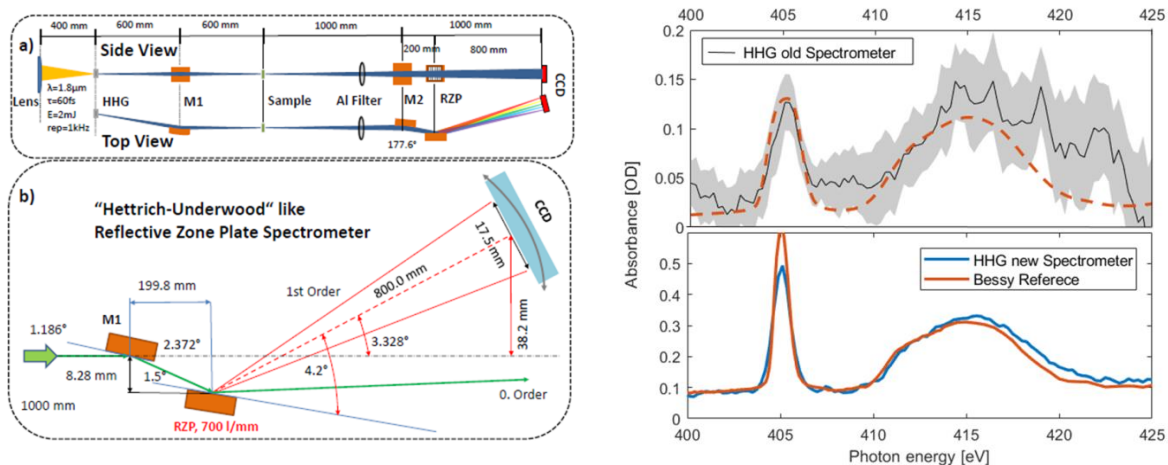
X-ray spectroscopy provides direct access to the electronic nature of chemical bonds, from which the outcome of chemical reactions can be understood. Intense activities are currently pursued at a large number of laboratories to develop new ultrashort X-ray sources and to implement novel measurement methods to explore the structural aspects of ultrafast photoinduced chemical reactions. We have now successfully combined a table-top laser-based HHG source for short-pulse soft X-ray absorption spectroscopy in the water window spectral range [4] with novel flatjet technology [5]. By doing so, we provided the first demonstration of simultaneous probing of carbon and nitrogen atoms in organic molecules in aqueous solution using a table-top soft X-ray source (Figure 3).

Near edge X-ray absorption spectroscopy (XAS) monitors unoccupied electronic orbitals with element, oxidation-state and spin specificity, from which the electronic structure can be derived. For the majority of organic molecules the soft X-ray spectral region (100-1000 eV) is relevant, as the K-edge transitions of low- $Z$  elements (C, N, and O), and the L-edges of 3d metals are located in this spectral range [6,7]. XAS is typically performed at large scale facilities, such as storage rings or free-electron lasers. Table-top laser-based sources have until now only been sparsely used to probe pure materials, e.g., metals and organic films [8,9]. So far, measurements of the carbon or nitrogen K-edges of organic molecules in dilute aqueous solution using the latter approach have not been reported.



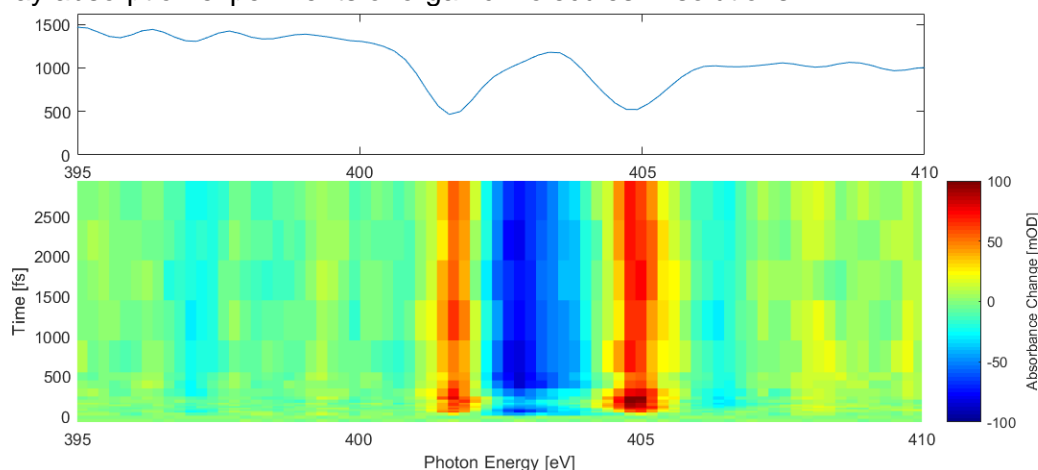
**Figure 3** left: Liquid flatjet (solvated urea) illuminated by a broadband soft X-ray pulse obtained by high-order harmonic generation. The insets show the steady-state absorption of Urea at the C and N K-edges extracted from the measurements. Right: Absorbance of (a)  $\text{O}=\text{C}(\text{NH}_2)_2$ , (c)  $\text{CaCl}_2$ , and (e)  $\text{NaNO}_3$  (black solid lines) recorded with our table-top XAS setup shown together with their corresponding confidence intervals (gray areas). For details, see [10].

We have now developed a bright source of femtosecond soft X-ray pulses, making use of the HHG process. Long-wavelength ( $1.8 \mu\text{m}$ ) driver pulses generated with an amplified Ti:sapphire laser system were used to generate HHG well above the conventional spectral range, now extending up to 450 eV [10]. We have combined this source with liquid flatjet technology fully functioning under vacuum conditions and reported the first steady-state absorption spectra of organic molecules and inorganic salts in a thin ( $\sim 1 \mu\text{m}$ ) sheet of aqueous solution, throughout the so-called water window region between 200-540 eV (Figure 3). In particular, we demonstrated the possibility to simultaneously probe at both carbon and nitrogen sites within the molecules. With this we demonstrated the feasibility of simultaneously following multiple sites within molecular systems (Figure 3), with the potential of probing possible correlations between these sites upon molecular rearrangements [10]. This investigation represents a major step towards the systematic investigation of ultrafast rearrangements of solution phase molecular systems with femtosecond soft X-ray spectroscopy. New insights into ultrafast charge transport processes and photo-induced reactions in chemistry and biology are envisaged to become accessible.



**Figure 4** Left: X-ray spectrometer design for time-resolved soft-X-ray experiments. Right: Comparison of the N K-edge spectra measured on  $\text{NO}_3^-$  using the grating/MCP spectrometer (upper panel) and the new reflective zone plate/CCD spectrometer (lower panel). Reference measurements (orange lines) measured at the BESSYII facility have been convoluted with the corresponding spectral resolution of the spectrometers.

The X-ray spectrometer used for this experiment consisted of a grating and a multi-channel plate detector with a rather low X-ray photon transmission of 0.2% and an energy resolution of only  $\Delta E/E = 220$ , i.e. too low to record transient absorption spectrum in aqueous solutions with enough statistic and energy resolution. To improve these two parameters, a new X-ray spectrometer has been constructed [11], in close collaboration with the Institute für Angewandte Photonik e.V (Berlin-Adlershof) (Figure 4). This X-ray spectrometer design is alike that of a Hettrick-Underwood, equipped with X-ray optics consisting of a spherical mirror and a reflective zone plate. Together with a new X-ray CCD detector purchased from Greateyes GmbH (Berlin-Adlershof) significant improvements have been achieved with a photon transmission efficiency of 9 % and an energy resolution of  $\Delta E/E = 1200$  (Figure 4). In order to test the new spectrometer for time-resolved soft X-ray absorption experiments, we performed near infrared pump - soft X-ray probe experiments in gas-phase  $N_2O$ . A strong laser pulse with intensity above  $10^{14} \text{ W.cm}^2$  was used to ionize a  $N_2O$  gas sample and the change of absorption at the N K-edge resulting from the formation of  $N_2O^+$  ions was monitored as a function of the delay between the ionizing laser pulse and the ultrashort soft X-pulse (see Figure 5). Up to 10 % change of the absorption spectrum was observed over long pump-probe time delays. This last result represents a major step towards time-resolved soft X-ray absorption experiments of organic molecules in solutions.



**Figure 5:** Top panel: Static soft X-ray absorption spectrum of  $N_2O$  at the N K-edge with the well-known double absorption lines from the two nitrogen atoms. Bottom panel: Transient absorption around the N K-shell following strong field ionization of  $N_2O$  by an intense NIR laser pulse. A strong bleaching of the absorption lines (red color) are observed together with the apparition of new absorption lines (blue color) from the formation of  $N_2O^+$ .

#### 4. Equal Opportunity

Dr. Maria Ekimova played a key role in the application of flatjet technology for X-ray absorption spectroscopy of molecules and ions in aqueous solution. Initially hired on a German Science Foundation project (DFG NI 492-11-1 (2012-2017) ), she continued her activities at the MBI for the SAW-2016-1 project from 2017-2019, setting up a flatjet target chamber, performed the solution phase measurements within WP5, as well as assisted in the construction of the new reflective-zone plate/CCD X-ray spectrometer. She has presented her results at several conferences dedicated to (ultrafast) X-ray spectroscopy: 3rd International Conference on Ultrafast Structural Dynamics ICUSD, ETH, Zürich, Switzerland, June 2015; 39th International Conference on Vacuum Ultraviolet and X-ray Physics VUVX2016, Zürich, Switzerland, July 2016; Helmholtz Virtual institute "Dynamic Pathways in Multidimensional Landscapes", International Conference by Helmholtz Association Virtual Institute, Berlin, Germany, September 2016); 4th International Conference on Ultrafast Structural Dynamics ICUSD 2017, Trieste, Italy, December 2017. She will be further contributing to science and technology in Germany by joining a start-up company in Berlin-Adlershof (Magnosco GmbH) as Senior Developer in Optical Technologies.

## 5. Quality Control

At the Max Born Institute, [the rules of good scientific practice](#) are adhered to in the spirit of the [recommendations](#) of the Deutsche Forschungsgemeinschaft ([see also DFG](#)). By strictly following [these rules of good scientific practice](#) the quality control of the activities are guaranteed.

## 6. Additional Funding Sources

To provide a proper head start in activities on ultrafast soft-X-ray spectroscopy, in 2014 MBI institutional investment funds have been allocated and spent on the purchase of a Ti:sapphire amplified laser system (1288000,- €). In addition to that a flatjet system used in WP5 was purchased 2014 through a German Science Foundation project (DFG NI 492-11-1 (2012-2017; 148,000,- €)). Additional MBI institutional investment funds include X-ray optics (ordered late 2017; 48,000,- €) and further design and testing by IAP e.V. (ordered early 2018; 42,700,- €) for the Hettrick-Underwood spectrometer. Further funding of mostly consumables (~ 20,000,- €) and salary for an additional postdoctoral team member (01/2019-12/2020) have been financed by an ERC Advanced Grant (Nibbering ERC-ADV XRayProton, 2018-2023).

## 7. Structures/Cooperations

Collaborations with research groups supporting theory on our experimental activities have been established with E. L. Shirley (National Institute of Standards and Technology, Gaithersburg, MD, USA), A. Borgschulte (Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Advanced Analytical Technologies, EMPA, Dübendorf, Switzerland), F. de Groot (Utrecht University, the Netherlands) and M. Odelius (Stockholm University, Sweden). Collaborations with the Institute for Applied Photonics e.V. and Greateyes GmbH (both Berlin-Adlershof) will be further intensified for the upcoming years.

## 8. Outlook

Part of the activities initiated within the SAW-2016-1 project (charge flow in metal oxides & charge flow in push-pull chromophores) will be continued using third party funding from the EU (Nibbering ERC-ADV XRayProton, 2018-2023; Rouzée/Nibbering SMART-X, 2020-2023). These activities will certainly benefit from the ongoing development on novel laser systems using optical parametric chirped pulse amplification (OPCPA) schemes, pursued in all three Divisions of the MBI.

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