Scientific impact and international visibility

Major scientific contributions – goal attainment and impact

MUST stands for Molecular Ultrafast Science and Technology and highlights the two pillars of the NCCR. Ultrafast technology at the forefront is often a prerequisite for breakthrough scientific advances and hence a fundamental pillar of the NCCR MUST. Over the past 12 years, NCCR MUST researchers have pioneered or substantially contributed to a variety of ultrafast technologies, among them:

- **High field THz generation**: High field THz sources are instrumental in exciting specific low frequency modes in molecules and condensed matter systems and allow studying their influence on structure, phase, or couplings to other degrees of freedom. Wolf has demonstrated record energy (50 uJ) single cycle THz pulses using pulse front tilted optical rectification in MgO:PPLN.
- **Multi-dimensional THz or mixed THz-IR spectroscopy**: Nonlinear and multi-dimensional THz spectroscopy (Staub, Johnson, Feurer, Fiebig) boosts our capabilities to study electronic dynamics in solids. In addition mixed THz-IR spectroscopy (Hamm) is instrumental to investigate couplings in solvents, such as water but also deep eutectic solvents, and further relevant systems.
- **2D DUV spectroscopy**: The extension of this technique, pioneered by Hamm in the IR and extended to the visible by many groups, was pushed to the UV and DUV by Cannizzo and Chergui to investigate couplings in organic systems, such as multichromophoric systems.
- **Ultrafast electron diffraction**: Carbone demonstrated new methods to observe the nm-fs resolved dielectric response of an individual nanoparticle, to provide combined attosecond/nm resolution in imaging plasmonic near fields, to dynamically control the chirality of the wavefunction of individual electrons at the attosecond scale, to modulate the longitudinal component of the wavefunction of individual electrons at the attosecond and zeptosecond speed, to achieve meV energy resolution combined with fs time resolution in electron energy loss spectroscopy, to perform diffractive imaging with incoherent electron beams, or to perform ultrafast energy filtered imaging in a TEM.
- **Time-domain ptychography**: This phase reconstruction modality pioneered by Feurer allows for boosting most known ultrafast nonlinear measurement schemes, for instance, reconstructing the phase of a system's response function from a homodyne measurement.
- **Attosecond spectroscopy**: Starting from Keller's expertise in attosecond gas phase spectroscopy, with the first high harmonic generation (HHG) beamline and COLTRIMS in Switzerland, NCCR MUST groups developed several variants, for instance, to investigate surfaces or liquids, but also by combining attosecond with photoelectron spectroscopy.

Various NCCR MUST initiatives, for instance, the Student Exchange Program, the Inter-MUST Women Postdoc Award, or intensified collaborative research projects, very efficiently disseminated these technological advances, thereby multiplying the network's scientific progress. For instance, at the beginning of the NCCR MUST, only the group of Keller was running a HHG attosecond spectroscopy experiment and thanks to her initial momentum and technology transfer, these activities have bloomed. Today, Switzerland stands as one of the most prominent countries in HHG and attosecond spectroscopy. Along similar lines, high field THz generation was initially only done in Feurer's group but has become an essential ingredient in many other activities within the NCCR MUST.

NCCR MUST researchers have also been instrumental in developing key technology for XFEL beamlines fostering research in the X-ray spectral domain and bridging from laboratory-based table-top sources to the accelerator based large-scale facilities. Starting with key experiments at the Swiss Light Source (PSI), to the early hard X-ray research at the SwissFEL Aramis line, and most recently also the soft X-ray Athos line, NCCR MUST allowed building collaborations across the Swiss ultrafast community and establish world-leading ultrafast research.

Similarly important and key to many of the scientific breakthroughs achieved are the developments in novel theoretical concepts and computational methods. During the 12 years of the NCCR MUST, a wide range of computational methods have been developed, extended, and implemented to provide comprehensive theoretical support for the ongoing experimental activities. This helped to obtain a better fundamental understanding of ultrafast molecular processes. These range from the developments of 1) accurate multipolar force fields for use in simulating linear and multidimensional spectroscopies; 2) reactive molecular dynamics (MD) simulations to follow chemical reactions in the gas phase and in solution; 3) diverse semiclassical methods for first principles-based simulations in ground and electronically excited states including nonadiabatic effects, or 4) approaches that take the quantum nature of the nuclei explicitly into account. In more detail:

- **Quantitative Force Fields**: During Phase I, Meuwly developed multipolar force fields (MPFF) and implemented them into CHARMM. This was also combined with an effort to automate the fitting process, which yielded the “Fitting Wizard” during Phase II. These MPFFs were shown to give much improved infrared spectroscopy and vibrational relaxation dynamics of hydrated ions or peptide building blocks. In a second phase, the distributed charge model (DCM) was developed, which yields the accuracy of a rigorous multipolar representation at considerably reduced computational cost.
- **Reactive Molecular Dynamics**: Adiabatic Reactive Molecular Dynamics (ARMD) is a broadly applicable computational framework to follow chemical reactions in the gas and in the condensed phase. This method was developed by Meuwly during the first phase and then applied to numerous problems. The approach was used together with both, empirical (parametrized) energy functions and with machine-learned (ML) potential energy surfaces (PES) represented as a reproducing kernel Hilbert space (RKHS). A general toolkit for RKHS-based PES was released and PhysNet, a neural network-based approach for ML energies of molecular systems or multidimensional reactive PES was published. Initially, PhysNet was used for dynamics in the gas phase. More recently, it was also used in a QM/MM fashion for following reactions in solution.
- **Nonadiabatic excited state dynamics in external fields**: Röthlisberger extended nonadiabatic on-the-fly dynamics approaches in electronically excited states; (i) real-time propagation time dependent density functional theory (P-TDDFT) combined with mean-field (Ehrenfest) dynamics of the nuclei and (ii) linear response TDDFT (LR-TDDFT) based fewest switches surface hopping (SH) through the inclusion of an external field. This was followed by the formulation and implementation of a local control method for on-the-fly pulse shaping within LR-TDDFT-SH simulations, the theoretical basis for the calculation of nonadiabatic coupling vectors within LR-TDDFT5, or the on-the-fly version of Bohmian dynamics to include the quantum dynamics of the nuclei. As part of an international consortium, they developed a completely new, highly flexible interface for general multiscale simulations called MiMiC and devoted considerable effort to make these simulation methods both more accurate and more computationally efficient. The accuracy of DFT calculations was improved by extending the library for atom-centered dispersion correction potentials and by developing a coordinate-scaling based method for highly efficient exact exchange calculations within the framework of plane waves that enabled the extended use of hybrid functionals. Furthermore, the entire suite of Minnesota functionals was implemented in the CPMD code with the possibility to generate range-separated hybrid functionals à-la-carte. In addition, they developed a stochastic algorithm for the evaluation of MP2 correlation energies within a plane wave basis with speedups of up to 3 orders of magnitude, thus not only enabling the possibility of MP2 based

MD but also paving the way for the use of rung 5 double-hybrid functionals, introduced a variety of multiple time step (MTS) based algorithms, implemented MTS dynamics for ground state MD combining different rung DFT functionals or combining DFT with force fields or with wavefunction based semi-empirical and *ab initio* methods, formulated and implemented an MTS approach for speeding up nonadiabatic MD in the form of surface hopping simulations, implemented approaches from artificial intelligence for an unbiased analysis of MD data via feature selection, and developed a machine-learning approach for predicting forces enabling speedups of first-principles and QM/MM MD of several orders of magnitude.

The key difficulty of simulating ultrafast molecular processes is that the dynamics are typically nonadiabatic, meaning that the electronic and nuclear degrees of freedom are strongly coupled. Unfortunately, neither of the most commonly used methods, Ehrenfest and surface hopping, is rigorously valid in all cases, and can show significant discrepancies compared with benchmark quantum calculations. It was thus necessary to develop new methods, which bridge the quantum and classical worlds by including the most important quantum effects but retaining as much as possible of the simplicity, computational efficiency and interpretability afforded by classical mechanics.

- **Spin-mapping approaches**: By mapping a two-level quantum system onto a phase-space representation of a spin-½, Richardson developed a mixed quantum-classical approach to simulating nonadiabatic dynamics. The method is in many cases far superior to surface hopping, especially for spectroscopy. This is because surface hopping is designed to reproduce populations of states, whereas the coherences give the spectroscopic signal. The spin-mapping method is basis-independent and thus equally accurate at predicting coherences as it is for populations and is thus the method of choice for theoretical simulations of linear and nonlinear spectroscopy. To describe the effects of entanglement, a path-integral version of the approach was developed.
- **Gaussian wavepacket approaches**: Some ultrafast processes can be simulated most efficiently using semiclassical Gaussian wavepacket approaches developed by Vaníček. Initially, he developed several multi-trajectory semiclassical methods (namely, the dephasing representation, cellular dephasing representation, cellular dephasing representation with a pre-factor, Gaussian dephasing representation, and multi-surface dephasing representation) for computing time-resolved electronic spectra of molecules described by analytical model potentials. Later, they implemented less expensive, single-trajectory methods, which still treat Duschinsky effects exactly and can be efficiently combined with on-the-fly *ab initio* evaluation of electronic structure. These can be used to simulate time-resolved stimulated emission and 2D electronic spectra.

Vaníček and Bostedt joined forces to develop theoretical tools to predict and interpret femto- and attochemistry experiments. Specifically, they developed a theoretical framework to investigate the coupled electron and nuclear dynamics in molecules induced by ultrashort laser pulses used in time-resolved X-ray spectroscopy.

Finally, it was shown that a simple, single-trajectory semiclassical scheme can accurately evaluate the electronic coherence time in polyatomic molecules. In contrast to numerical quantum methods, the semiclassical approach reveals the physical mechanism of decoherence beyond the general blame on nuclear motion. They performed a thorough theoretical scan of many small polyatomic molecules searching for specific structural and dynamical properties, which can be useful for the experimental measurements of ultrafast electronic dynamics and its coupling to the nuclear motion. Long-lasting electronic coherence was found in several new molecules, which have thus become promising candidates for experimental studies.

- **Nonadiabatic molecular quantum dynamics**: Vaníček developed a series of efficient high-order geometric numerical integrators for nonadiabatic molecular quantum dynamics in both diabatic and adiabatic representations, including interactions with a time-dependent electromagnetic field. He also implemented an efficient and accurate semiclassical method (multi-state dephasing representation) for evaluating the adiabaticity, which includes effects beyond population transfer between electronic states.
- **Path-integral methods for kinetic isotope effects**: A collaboration between Richardson, Meuwly, and Vaníček developed and implemented improved quantum-instanton approaches for calculating rate constants using the multipolar force-field code to analyse the kinetic isotope effect on the hydrogen transfer. They also explored the formal relation between the quantum and semiclassical instanton approximations for the reaction rate constant. It was found that the quantum instanton approximation breaks down for asymmetric barriers and required a modification, which has a stronger connection to semiclassical instanton theory, giving numerically accurate predictions even for very asymmetric systems in the low temperature limit.

All of these pioneering experimental, theoretical and computational concepts were instrumental in addressing the scientific challenges formulated by the NCCR MUST, which were grouped under two umbrellas, namely Electron Dynamics and Structural Dynamics even though the two fields cannot always be strictly separated.

The field of Electron Dynamics uses a variety of the above-mentioned ultrafast techniques and theoretical concepts to initiate, follow, and even control Electron Dynamics in molecular and condensed matter systems. Electron Dynamics investigated by NCCR MUST researchers spanned length scales from a few Angstrom, i.e. chemical bonds and atoms (Bostedt, Cavalieri, Keller, Wörner) to macroscopic systems, such as organic photovoltaic devices and perovskite solar cells (Banerji, Moser) or electrodes for photocatalysis (Osterwalder), passing through small molecules, such as amino acids and nucleic acids (Chergui, Wolf), metal complexes (Cannizzo, Chergui, Milne, Moser) and acceptor donor dyads (Cannizzo, Feurer, Häner/Liu); middle-size systems including DNA related assemblies (Cannizzo, Feurer, Häner), water clusters (Signorell), and biomolecules (Chergui, Hamm, Standfuss), nanometric sized systems, such as transition metal oxide nanoparticles (Chergui, Milne, Moser, Wolf), carbonaceous nanodots (Cannizzo, Feurer, Hamm, Osterwalder), functionalized nanoparticle for chemical recognition (Cavalieri) and condensed matter with bulk and 2D materials moving from THz- to PHz-driven dynamics (Fiebig, Keller).

The field of Structural Dynamics characterizes, queries, and interprets atomic and molecular motions with a focus on understanding the consequences of the dynamics and linking them to function. The origin of Structural Dynamics can be a temperature jump, a vibrational quantum, or a change in the distribution of the electrons. Structural Dynamics investigated by NCCR MUST researchers ranged from small molecules (Bacellar/Milne, Chergui, Wörner, Wolf) to condensed phase systems (Beaud, Johnson, Staub, Fiebig) via solvents (Meuwly, Hamm, Feurer), proteins (Hamm, Chergui, Standfuss), nanoparticles (Bostedt, Rupp), and surfaces (Osterwalder).

Electron Dynamics

An improved understanding of Electron Dynamics at the fundamental level was made possible by NCCR MUST advances in attosecond science. Keller developed the first cold-target recoil-ion momentum spectrometer (COLTRIMS) with attosecond front-end to explore the photoionization dynamics in gas targets using a short attosecond pulse for ionization. This enabled for the first time a 3D angular resolution and showed an anisotropy in attosecond ionization dynamics around Fano resonances in atoms and the peculiarities of its spatial dependence for symmetric (H_2) and asymmetric (CO) small molecules. This measurement knowhow was also transferred to Wörner who measured the longer photoionization delays in shape resonances when comparing N_2O with H_2O. Extending the attoclock technique, Keller confirmed evidence for a probabilistic but finite electron tunnelling delay time. They also developed attosecond transient absorption spectroscopy (ATAS) from a high-fidelity gas-phase tool into a sensitive technique for studying field-driven electron dynamics in solids moving from THz to PHz spectroscopy initially used to directly observe the dynamical Franz-Keldysh effect in the optical domain. ATAS uses a broadband XUV pulse to probe the transition between core hole and excited states with attosecond temporal resolution. With the probe being resonant with a particular core level, ATAS becomes inherently element specific while its broad bandwidth allows to disentangle the carrier dynamics of the excited state by carrier type. This has been used with the qualitative agreement with state-of-the-art TDDFT simulations to show that strong real-space electron localization takes place around the d-orbitals initially observed in titanium and more recently confirmed with 2D transition metal dichalcogenides such as $MoSe_2$. A collaboration between Keller and Hengsberger/Osterwalder demonstrated an attosecond beamline with angularly resolved photoemission spectroscopy (ARPES) for surface science in a unique two-focus geometry, which enabled the study of energy-resolved photoemission dynamics from various noble metal surfaces and calibrated against a gas-phase reference. This knowhow was also transferred to the Wörner group to extend attosecond science to liquids and clusters, reporting the first attosecond time-resolved measurements in liquids, i.e., photoionization delays between liquid and gaseous water, which amount to 50-70 as.

Electron dynamics becomes particularly complex when it is coupled to nuclear dynamics. Many NCCR MUST groups contributed to the understanding of this so-called nonadiabatic quantum dynamics. Keller explored this regime in ionization dynamics with H_2 using *ab initio* theories. Theoretical methods outlined above were used to explain the unusual photophysics of azulene investigated experimentally by Moser. Simulations by Röthlisberger helped to interpret the attoclock experiments of Keller and the attosecond timescale electron dynamics of iodoacetylene was investigated by Wörner. At the opposite limit, accuracy of even adiabatic molecular dynamics was improved by the development of multipolar force fields and of the distributed charge model by Meuwly.

Nonadiabatic dynamics is closely associated with the processes of charge transfer, migration, and decoherence. Röthlisberger and Banerji characterized the charge-transfer relaxation in donor-acceptor organic photovoltaics, while Röthlisberger and Feurer described the charge transfer process of 4-(dimethylamino)benzonitrile in deep eutectic solvents. Systematic development of the multi-dimensional high-harmonic spectroscopy (HHS) by Wörner led to the first observation and reconstruction of attosecond charge migration and to the demonstration of laser control over charge migration. Experimental observation of the charge migration is made difficult by decoherence. Vaníček, therefore, proposed a single-trajectory semiclassical scheme to evaluate the electronic coherence time in polyatomic molecules, explaining the detailed physical mechanism of decoherence.

Coherent energy transfer processes involving higher excited states were observed for the first time by Cannizzo and Feurer in DNA-organized polyphenanthrene arrays conceived by Häner. Chergui's investigation and discovery of ultrafast spin cross-over transitions has improved the comprehension of intersystem crossing processes in transition metal complexes, proving their key role in ultrafast structural dynamics launched upon photoexcitation. Häner and Liu, in collaboration with Cannizzo and Feurer, designed acceptor-donor assemblies with charge transfer properties, as lifetimes and direction, that can be either chemically or optically regulated, paving the way for photocurrent modulation and switching with a highly stimuli-responsive ON/OFF ratio. Concerning biomolecules, Chergui unravelled hitherto unknown electron transfer processes between the tryptophan amino acid and the haem in haemoproteins, whereas Wolf and Röthlisberger showed that the physiological response of the retina in living mice can be modulated by steering the dynamics of a vibronic wavepacket evolving on the S1 excited state of the rhodopsin.

Studies of excitons in nanoparticles, such as TiO_2, ZnO, and carbonaceous dots has triggered a larger cooperative effort by several groups (Chergui, Cannizzo, Feurer, Hamm, Milne, Moser, Osterwalder). Chergui identified a new, strongly bound exciton in anatase TiO_2 material and evidence of excitons in the case of amorphous TiO_2. They were the first to identify electron trapping sites in anatase and amorphous TiO_2 using ps-XAS. Wolf, in collaboration with Moser, succeeded to follow charge dynamics in TiO_2 colloidal suspension probed at Ti $L_{2,3}$-edge with a new soft X-ray transient absorption beamline, developed in Geneva in collaboration with Wörner. Milne, in collaboration with Chergui, investigated the excitonic dynamics and detected the electron trapping sites in ZnO by using ps-XAS at the Zn K-edge absorption. In collaboration with Cannizzo, he has extended this study to Mn doped ZnO nanoparticles, to elucidate the mechanism of electron trapping in such systems. Electronic dynamics in the new family of Cdots have been mainly investigated by Cannizzo. In collaboration with Feurer he unveiled the details of their photophysics in conventional and deep eutectic solvents. The role of the molecular groups decorating the dot surface and of their vibrational modes was investigated in tight collaboration with Hamm. The capability of CD films to enhance the photo-catalytic efficiency of TiO_2 electrodes was successfully investigated by Osterwalder, while Cavalieri designed functionalized nanoparticles that exploited emission quenching or gain for detection of biological molecules.

Molecular dynamics induced by electronic transitions can be investigated by pump-probe or two-dimensional electronic spectroscopy. To compute such spectra, Richardson and Vaníček proposed different methods as outlined above.

The relevance of X-ray spectroscopy within NCCR MUST was not limited to the study of excitons in nanoparticle described above. Chergui, Abela, and Röthlisberger used DFT-based QM/MM molecular simulations in combination with nuclear quantum dynamics and the simulation of X-ray absorption spectra to characterize the photophysics of iodide and several transition metal complexes in aqueous solution. Wörner and Wolf used the aforementioned table-top soft-X-ray setup to resolve the dynamical evolution of unoccupied molecular orbitals on the femtosecond timescale of photo-dissociation reactions with element selectivity and site specificity. In 2021, Bostedt completed several pilot experiments at the SwissFEL Maloja endstation on time-resolved core-level and nonlinear soft X-ray spectroscopies. The experiments were performed by the Maloja team headed by Schnorr and involved experimental and theoretical collaborations with Wörner and Vaníček.

Signorell investigated the ultrafast dynamics of the formation of the ground state of the solvated electron in large water clusters after excitation below and above the bandgap, using a new femtosecond velocity map photoelectron spectrometer with HH pump and ultraviolet probe pulses. Their comparative study between ice and liquid clearly revealed that the electron scattering cross sections in the liquid water and amorphous ice are identical within uncertainties, thus solving one of the most debated issues regarding electron scattering in water.

The investigation of perovskite materials and related systems, such as hybrid organic-inorganic perovskite solar cells, is another good example of the synergies within the NCCR MUST (Banerji, Chergui, Feurer, Moser). Banerji compared excited-state properties of 2D-perovskites with those of organic solar cell materials and demonstrated the emission of THz radiation from unbiased films, due to the rocking motion of ions within the lattice. Chergui demonstrated the existence of Mahan excitons in inorganic perovskites and monitored the ultrafast transport of electrons into the bulk and the formation of hole polarons around halogen atoms in these systems. Feurer recorded the first THz Stark spectra from perovskites and Moser applied ultra-broadband time-resolved THz spectroscopy to hybrid lead halide perovskite films of various morphologies with the aim of studying exciton delocalization and carrier scattering by grain boundaries, impurities, and phonons. These results are already guiding efforts towards the synthesis of novel materials with improved functionalities and designing of more efficient photonic devices.

Scaling up to bulk and nanostructured solid materials, the ultrafast methods developed in the NCCR MUST offered a unique platform to control and follow the evolution of the bonding electrons in out of equilibrium conditions ensuing an external excitation. Beaud, within a collaborative effort with Johnson and Staub, reported a comprehensive study of the metal insulator transition in a charged and orbitally ordered manganite driven by optical pulses. These results were enabled by state-of-the-art ultrafast X-ray diffraction methods. To investigate phase transitions driven by quantum fluctuations, Fiebig developed a new approach to excite heavy-fermion systems with a THz pulse and track the heavy fermion formation and quantum criticality. Besides the understanding of the fundamental physics governing the emergent properties of quantum materials, their coherent control has been a subject of intense development within the NCCR MUST. Always in manganites, Johnson demonstrated that high-intensity THz excitation can coherently excite large-scale magnetic dynamics in a multiferroic material. These results also involved a strong NCCR MUST collaboration (Beaud, Johnson, Staub). Staub has shown that resonant driving of the ferroelectric soft mode using THz excitations leads through nonlinear phonon-phonon coupling to a phonon up conversion in $SrTiO_3$.

From a technique development point of view, X-ray and XUV transient grating experiments are known to allow creating patterned photo-excitations in materials. These are particularly useful for studying electron diffusion phenomena and collective excitations (Cannizzo, Milne, Feurer, Knopp). Moreover, Beaud, Staub, and Chergui reported transient grating experiments using hard X-rays for the first time, highlighting the possibility to pattern an electronic excitation in solids at the nanometric scale.

At reduced dimensionality, Osterwalder investigated the electron dynamics on surfaces by transient photoemission experiments, performing an orbital tomography of molecular absorbates on surface and pushing the limits of photoemission to the attosecond regime to investigate the fundamental aspects of light-matter interaction, together with Keller. Collective electronic modes were also investigated via electron scattering techniques, demonstrating the possibility to image and control plasmonic waves at the attosecond and nanometer scale by Carbone. In a proof-of-concept study, Rupp reported the formation and evolution of a nanoplasma in individual atomic clusters, imaged by coherent diffractive imaging methods.

Structural Dynamics

Various approaches have been implemented to probe photo-induced Structural Dynamics in molecules, proteins, and nanoparticles. In the field of molecules, a rich harvest of results has been obtained on spin cross-over (SCO) systems combining ultrafast optical and X-ray spectroscopies (absorption and emission) and deep-ultraviolet circular dichroism spectroscopy (Bacellar/Milne, Chergui). These have unravelled the details of the SCO and back-SCO dynamics, but most importantly, the generality of this mechanism to a large class of iron-containing molecular systems, including haem proteins. The development of ultrafast X-ray absorption spectroscopy in the water window (Wörner, Wolf) has allowed new phenomena to be observed, such as the gradual emergence of state-mixings or the fastest reported electronic intramolecular relaxation event in the ethylene cation. Using HHS in a 2-colour counter-rotating circularly polarized pulse scheme, an exceptional chiral discrimination of ca. 13% has been demonstrated and traced back to the sub-fs dynamics of the molecular cation, in what is the first observation of attosecond charge migration in chiral molecules (Wörner). Finally, using a transient grating configuration (Wörner), the photo-dissociation of a chiral molecule was monitored showing a persistence of its chirality over relatively long times (250 fs) and distances (≥7Å).

Concerning nano-systems, much of the activity has been focusing on the study of metal oxide and perovskite nanoparticles, for which the dynamics of hole and electron trapping have been characterized by ultrafast X-ray absorption and emission spectroscopy, shedding new light into the nature of the trapping sites and their structure (Bacellar/Milne, Chergui). The dynamics of charge carriers has also been characterized by 2-dimensional visible to deep-UV spectroscopy, along with their localization as polaritons or the emergence of new quasi-particles such as Mahan excitons (Chergui). Further studies have been performed on the light-induced phase transition of metallic nanoparticles using hard X-ray Bragg scattering and coincidence ion time-of-flight spectroscopy showing that the timescale of crystalline disordering scales inversely to the average speed of the ejected ions (Bostedt).

The central aim of structural biology is to understand protein function based on protein structure, but in many ways, this is an oversimplification since proteins are not static entities but require timed structural rearrangements to fulfil their biological roles. Time-resolved structural biology resolves these changes to better understand biological activity. In this regard, Standfuss has pioneered time-resolved serial crystallography using synchrotrons and X-ray free electron lasers, mostly at the new SwissFEL at PSI. These experiments can produce a molecular movie of light-induced processes in photo-active proteins, as they observe snap-shot structures in the most direct manner over a wide range of timescales. The initial photochemical reaction of the active chromophore in these proteins (in most cases a photo-induced isomerization) is taking place on a very fast femtosecond timescale. This molecular switch then triggers a cascade of responses in the embedding protein that continues into the millisecond regime. Standfuss investigated both natural protein systems (bacteriorhodopsin, G coupled protein receptors), and artificial ligand-protein constructs, in which the light-active chromophore is an azo-benzene moiety.

The protein work of Hamm is highly complementary to that of Standfuss, looking at very similar problems with the help of transient IR spectroscopy. While the strength of time-resolved serial crystallography is the very detailed structures it can reveal, these experiments are time demanding and only a few snapshots at distinct time-points can be taken. Transient IR spectroscopy, in contrast, is structure-sensitive, albeit in an indirect manner. That is, even very minor structural changes (as small as 0.3 Å) of a protein will result in a measurable spectroscopic response of the amide I band, but one cannot say what those structural changes are. The strength of transient IR spectroscopy is determining the timescales of structural transitions, an information that then can be used to pick important time-points for time-resolved serial crystallography.

Nonlinear THz spectroscopy played an important role in the NCCR MUST, as the stable funding over 12 years allowed us to develop conceptually novel spectroscopy techniques. THz excitations concern the intermolecular modes, e.g., phonons in solids or hydrogen bonds in liquids. Strong-field, or nonlinear THz excitations have been used to control the directionality of charge transfer reaction between molecules (Feurer, Wolf), to manipulate small molecules on catalytic surfaces (Osterwalder, Meuwly), or in the context of nonlinear phononics to drive phase transitions in strongly correlated solids (Johnson, Beaud, Staub). Furthermore, 2D-Raman-THz spectroscopy has been developed as the first realization of multidimensional spectroscopy in this spectral range to unravel the dynamics underneath the strongly smeared THz spectra of liquids (Hamm). The heterogeneous dynamics of complex liquids, such as water or deep eutectic solvents (DES), have been investigated with the help of nonlinear as well as linear THz methods, often in combination of 2D-IR spectroscopy (Hamm, Feurer, Meuwly).

Computational characterization of motion at the molecular and atomic scale is an important complement for the interpretation of experimental characterizations. Meuwly, Röthlisberger, and Vaníček developed computational approaches for applications to problems in gas- and condensed-phase structural dynamics to provide molecular-level understanding of chemical and physical processes.

Approximate quantum dynamics based on (semi-) classical concepts was pursued by Vaníček, which explored and developed *ab initio* semiclassical thawed Gaussian methods for two-dimensional electronic spectroscopy. In a more recent effort, time-resolved core-level X-ray spectra were determined for methyl-iodide and compared with experimental results obtained at PSI. In addition, a path-integral Monte Carlo implementation of the quantum instanton approximation was used together with a reactive force-field (Meuwly) to determine the isotope effect of hydrogen transfer in malonaldehyde, one of the paradigmatic systems for tunnelling dynamics in the gas phase for which accurate experimental data is available as a benchmark.

For applications to larger systems, Röthlisberger engaged in the development of multiple time step methods that yield a speed-up of a factor of 5 to 10 compared with conventional molecular dynamics approaches. Nonadiabatic on-the-fly dynamics simulations were further developed and applied to dynamics in the gas- and in the condensed phase in direct collaboration with a wide range of experimental groups within the network. Particularly strong collaborations were forged with the groups engaged in the characterization of solvated metal complexes (Chergui, Abela) for which the structural dynamics was studied. These systems were also studied by Meuwly. Hamm and Meuwly characterized the structural dynamics of fluorinated phenol in the condensed phase and the structural dynamics of the first steps in the vision process were investigated together with Wolf.

Meuwly set out to improve the accuracy of empirical force fields based on developments suitable to follow dynamics in the gas- and condensed-phase. For the bonded interactions, machine-learning techniques based on reproducing kernels and neural networks were developed and implemented in general-purpose molecular dynamics software. Multipolar representations of the electrostatics improve the description of the anisotropy of the charge distribution, which is of particular relevance for halogenated compounds, ions, and radicals. With these ingredients the structural dynamics of small ions in solution, radicals in proteins, and strongly interacting, heterogeneous mixtures such as eutectic solvents were studied (together with Hamm and Feurer) and molecular-level interpretations of experiments within the network were possible. Furthermore, the structural dynamics of ligands in myoglobin was investigated in the infrared (Meuwly, Hamm) and by using X-ray absorption spectroscopy (Meuwly, Chergui).

Structural dynamics in the condensed phase was conducted using optical spectroscopy in table-top laboratories as well as at large-scale X-ray facilities. The overarching objective of this work has been to determine the couplings between electrons, spins, and the underlying lattice in correlated and quantum materials that exhibit interesting and potentially useful properties. In the future, this research could lead to new methods of optical control and potentially new devices operating with higher efficiency and speed. Below, experiments and results have been selected to highlight advances that were made in two key areas such as electron-phonon coupling in electronic and structural dynamics, which includes phase transitions, and magnetization dynamics.

While experiments were conducted using all-optical spectroscopy with table-top laboratory-based systems, important scientific problems could also be addressed using ultrafast X-rays, which provided new capability to disentangle microscopic structural responses from electronic processes. As a result, many of the scientific achievements were made using experimental methodologies relying on ultrashort X-ray pulses available at large-scale facilities. Initially, the FEMTO slicing source of the SLS at PSI was utilized to access ultrafast dynamics in crystal structures through X-ray diffraction (XRD). Later, using intense X-ray pulses available at XFELs the research was gradually expanded to include investigations on the dynamics of the magnetic and electronic structure of strongly correlated materials. These research pathways – on the table-top and at large-scale facilities – were uniquely enabled by fruitful collaboration within the NCCR MUST network.

Femtosecond X-rays at FEMTO were used to quantitatively probe the time-domain structural response of a material due to electron delocalization associated with metal-insulator transitions. These dynamics were studied in the charge-density wave (CDW) state of $TiSe_2$ (Johnson, Beaud, Staub). By combining measurements from optical spectroscopy with ultrafast X-ray diffraction, it was shown that the charge density wave is melted non-thermally, suggestive of a role for exciton condensation as a main mechanism for stabilizing the charge density wave. More, recently, additional measurements using XFEL sources have indicated that the underlying structural distortion plays a key role, suggesting that this is also a critical component in the stabilization of the CDW (Staub, Johnson). Similar investigations were performed in a range of interesting materials including the prototypical 1-D CDW system $K0.3MoO_3$ (Johnson, Beaud).

Building on the capabilities established at FEMTO, XFELs permit simultaneous determination of the electronic and lattice structure in materials, due to the availability of orders-of-magnitude more intense X-ray pulses across the full X-ray spectral range. A prominent demonstration of this capability was made in an early LCLS study using X-ray resonant diffraction, which determined the hierarchies of the order parameters in the charge and orbital order phase transition in half-doped manganites (Beaud, Staub, Johnson). The different order parameters (charge, orbital, lattice) were accessed through different reflections at resonance. The actual change in crystal symmetry associated with this transition occurs on several different timescales that are characteristic of the various electronic and vibrational coordinates of the system. It was shown that the phase transformation is well described using a single time-dependent order parameter that depends exclusively on the time evolving electronic excitation. The phase transition occurs when the excitation exceeds a critical value. The resemblance of this description to Landau's theory – describing the adiabatic case – points towards a potentially universal description of complex phase transitions in the time domain.

Metal-insulator type phase transitions in manganites and CDW systems have also been compared to purely structural second order phase transitions, such as the octahedral rotation phase transitions that are common in perovskites. Ultrafast XRD, after an above bandgap excitation, showed that the oxygen octahedra in $SrTiO_3$ (Staub, Johnson, Beaud), rotate in the opposite direction when compared to isostructural $EuTiO_3$ (Staub, Johnson). The rotation in $EuTiO_3$ represents an ultrafast increase of the order parameter caused by a change of the Goldschmidt tolerance factor that defines the octahedral rotation angle in perovskites. Inorganic perovskites were also investigated using steady state and time-resolved XAS and X-ray diffraction to monitor temperature- and photo-induced changes. Through these studies, the formation of hole polarons around halogen atoms in these systems was quantified (Chergui).

In parallel to the activities at the large-scale facilities, structural dynamics were also studied in material systems using table-top optical systems. Progress was made in the application of attosecond sources in the XUV, where it was possible to decouple structural and electronic dynamics using time-resolved and angle-resolved photoelectron diffraction. A phase lag was observed between the optically excited coherent phonon mode with respect to the modulation of the electronic structure in Bi (Hengsberger, Osterwalder, Keller). Acoustic phonon modes were also the subject of studies using a new 2-dimensional UV spectroscopy approach in TiO_2. Here, the acoustic phonon was found to couple strongly to the bound exciton, enabling a determination of its oscillator strength and suggesting a means for coherent control (Chergui). On the other side of the optical spectrum, 2-dimensional THz spectroscopy was used to study soft-modes in a ferroelectric perovskite, revealing the origin of the soft-mode nonlinearities (Fiebig). These results established THz spectroscopy as a general approach to unravel the interplay between transient nonlinear electronic motions and macroscopic polarization.

Another area where the NCCR MUST has contributed is in new applications of mid-IR and THz optical fields for excitation. Researchers in the NCCR MUST contributed to the first direct demonstration of nonlinear phonon coupling using X-ray diffraction (Johnson). Researchers in the NCCR MUST also contributed to studies using mid-IR excitation in half doped manganites that showed how electron-phonon coupling directly destroys the charge and orbital ordered ground state. The loss of order could be explained without imposing nonlinear phonon-phonon couplings (Beaud, Staub). Systematic mid-IR pump studies quantified the relative magnitude of ionic Raman scattering *versus* electronic Raman scattering in $LaAlO_3$, a prototypical perovskite oxide (Johnson). Collaborative work was also performed with SLAC using THz excitations in the simple perovskite $SrTiO_3$. Here, the direct excitation of the ferroelectric soft mode has been observed by ultrafast XRD revealing a phonon up-conversion process (Staub).

X-ray diffraction and optical spectroscopies were applied to study lattice dynamics in magnetic materials. In an early experiment using the FEMTO X-ray source, the structural response of the AFM-FM transition in FeR, driven by femtosecond laser excitation, was clarified to proceed via a route of domain nucleation growing from the surface (Beaud, Johnson). In another study in a pnictide, coherent phonons modifying the Fe-As tetrahedra were measured, allowing the electron-phonon coupling constant to be estimated. This finding underlines the importance of the structural dynamics in driving the transient increase of the Fe magnetic moment (Staub, Johnson, Beaud). Further investigations of magnetic-structural dynamics were performed on Ni_2MnGa, a so-called ”shape memory” compound (Johnson, Beaud). Perhaps, the most glamorous result in this area was the observation of the ultrafast Einstein-de-Hass effect that is associated with the demagnetization of an epitaxial Fe film (Johnson, Staub, Beaud). With ultrafast time-resolution, this seminal experiment showed precisely how angular momentum is transferred from spins to the lattice during laser-driven demagnetization of iron, resolving the 20-year-old problem of how momentum is conserved in the ultrafast demagnetization process in a classical ferromagnet.

In the second key area of magnetization dynamics, ultrafast XRD studies concentrated on the spin structure in correlated materials. One of the first time-resolved experiments that directly addressed the magnetic structure was performed at LCLS. Femtosecond resonant magnetic soft X-ray diffraction showed how an ultrafast laser pulse can drive a phase transition between two ordered antiferromagnetic phases in multiferroic CuO (Johnson, Staub, Beaud). The transition is driven by a fast increase in magnetic disorder that alters the relative stability of the two phases, causing a first-order transition that is characterized by domain growth of the higher entropy phase. It was found that at high fluences, the onset of the growth is limited to 400 fs, which appears to coincide with a half-period of magnetic excitations that govern the change in long-range order. From the spectral change of the magnetic diffraction peak, the electronic temperature of the ordered spin system of several thousand degrees Celsius was obtained, which lies surprisingly an order of magnitude above the static transition temperature (Staub, Johnson, Beaud). In addition, the demagnetization times of a simple 4f anti-ferromagnet, elemental Ho, have been investigated (Staub, Johnson). The 4f and the induced 5d shell moment have been probed in the same experiment by ultrafast resonant magnetic hard XRD. By tuning the X-ray photon energy, the demagnetization timescales in the individual atomic shells were found to be comparable indicating a strong inter-shell magnetic coupling.

A dramatic breakthrough in ultrafast magnetization dynamics occurred with the discovery that a high-intensity THz excitation can lead to large-scale magnetic dynamics in multiferroics, this time in $TbMnO_3$ (Staub, Johnson, Beaud). In this material, a THz excitation in resonance with an electromagnon can drive large-amplitude coherent oscillations. The large magnitude of the motion suggests that realistically achievable THz fields, on the order of 10 MV/cm, may be sufficient to drive persistent switching of the magnetic order, and consequently lead to a reversal of the electric polarization in this multiferroic material.

Main scientific value added by the NCCR

Through technology exchange, collaborative efforts, and the innovative theory developments, the NCCR MUST was able to contribute substantially to some of the grand challenges in ultrafast science. The review panel continuously attested the NCCR MUST to be highly productive with innovative and fundamental work that met high scientific quality standards. Some of the groups excelled due to their exceptional high productivity, technical innovations and/or outreach. Over the years, the progress reports documented internationally leading scientific achievements, indicating that many of the NCCR

MUST teams were operating at the highest level. The individual visibility of the PIs was rated as high and for several PIs exceptional. A few projects in the area of structural dynamics have generated exceptional results and can be considered an outstanding example for concerted efforts within the NCCR MUST. Numerous spectroscopy projects were rated as quite evolutionary following an agenda, which was considered mainstream, but with positive exceptions. For instance, biology has gained relevance over the years, demonstrating how time-resolved ultrafast methods across THz to X-rays were being used in a concerted effort. The use of SwissFEL for time-resolved crystallography to study a light-driven sodium pump from the femto- to the millisecond range represents a demonstration of future opportunities. The work on solar cells develops steadily and other, non-perovskite, systems were investigated.

Table: Overview of scientific outputs / NCCR publications

Peer-reviewed publications*	Open Access	Median citations per peer-reviewed article	Average authors per publication
92.3%	77%	16	3.2

Source: NIRA-data (provided by SNSF), * Only peer-reviewed publications with a valid DOI number and with a match found in the Scopus database are considered.

Table: Distribution of scientific outputs / NCCR publications

	Number of public-cations	Original contribution to science journals	Review articles	Book or contribution to a book	Proceedings	Editors	Other literature/ publication
Phase I	370	350 (95%)	0	9 (2%)	4 (1%)	7 (2%)	0
Phase II	385	374 (97%)	0	5 (1%)	6 (2%)	0	0
Phase III	344	338 (98%)	2 (1%)	3 (1%)	0	0	1 (<1%)
Total	1099	1062 (97%)	2 (<1%)	17 (2%)	10 (1%)	7 (1%)	1 (<1%)

Source: NIRA-data / NCCR (provided by SNSF)

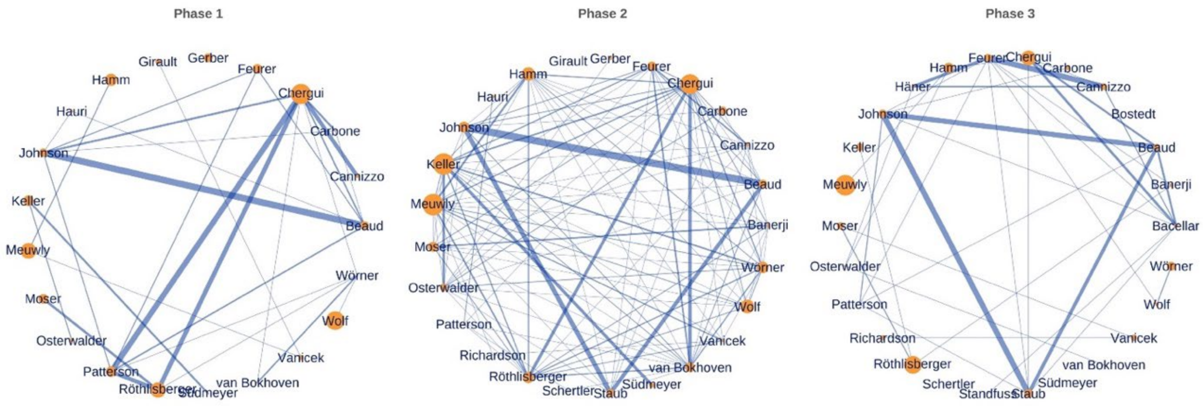

Figure: Co-author networks per phase (Source: NIRA data, provided by SNSF, 14.03.2022)

All NCCR MUST PIs recognized the astonishing added value of the NCCR MUST in stimulating, supporting, and establishing scientific collaborations, facilitating interdisciplinary exchange of ideas, and access to a variety of experimental and theoretical tools. Especially the collaborations between theory and experiment are seen as an invaluable achievement of the NCCR MUST and many research projects involved theoretical support for experiments and *vice versa*. Figure 2 emphasizes this point by illustrating the many different joint projects initiated and conducted only because of the NCCR MUST networking efforts (see also Table 4). The number of co-authors reached a maximum in Phase II, because of a special issue in Structural Dynamics with joint review papers and the fact that a significant knowhow transfer between groups resulted very often in a first joint publication or was acknowledged in the appropriate sections. The latter type of knowhow exchange is not reflected in Figure 2. In addition, bundling of knowhow resulted in shared ultrafast laser infrastructure at the EPFL and the University of Bern and a vision to establish a similar infrastructure within the Department of Physics at the ETHZ and in collaboration with the PSI. To pass knowhow to the next generations, many PIs integrated lectures on different aspect of ultrafast science in different universities or published graduate level textbooks.

International standing – goals, achievements, and perspectives

The scientific drivers of the NCCR MUST were to understand

- How matter functions at the electronic, atomic, and molecular level,
- How matter changes its structure during reaction and light interaction, and
- How quanta of energy are transported on an atomic spatial and ultrafast timescale as short as attoseconds.

The interdisciplinary nature of this research – at the boundaries of physics, chemistry, material science, and biology – made it a crucial and exciting research area.

Prior to 2010, ultrafast science in Switzerland was a relatively small and fragmented effort driven by individual PIs scattered across the different universities and research institutions. Through the NCCR MUST, these individual efforts were linked together resulting in an interdisciplinary network of experimental and theoretical groups working together on challenging problems in ultrafast science. Over the course of 12 years, the NCCR MUST has transformed the Swiss ultrafast science landscape from a speckle pattern to a strong coherent Swiss-wide network with interdisciplinary efforts, shared technologies, and numerous collaborations. By combining complementary expertise, it became possible to tackle problems that could not be addressed before. We elaborated the need for a long-term research effort using a “seeding/cultivating/harvesting” approach.

- In Phase I, we strengthened interdisciplinary connections, implemented new tools, science topics, and methodologies. We promoted active knowhow transfer of new – technically very challenging – observation and measuring techniques, such as electron diffraction and spectroscopy (source and detection development), HHG and attosecond beamlines, multi-D spectroscopy in THz and UV, or nonlinear THz spectroscopy.
- This investment was used in Phase II for proof-of-principle experiments, and
- Were continued in Phase III, by answering our scientific questions and visions, developing new applications, and building a broader ultrafast science community.

In addition, the go-ahead for the new SwissFEL at PSI brought a new focus on ultrafast science, demanded stronger collaborations with the broader ultrafast science community in Switzerland, and gave the ultrafast community a strong growth perspective. The NCCR MUST succeeded in linking university groups and SwissFEL through joint professor positions and collaborations. The NCCR MUST also succeeded to educate the many beamline scientists and was likely key in building the case and scientific expertise, which helped making SwissFEL a success story.

Early on, the NCCR MUST realized the need for university-based infrastructure labs and established the FastLab concept with two branches now at the University of Bern and at EPFL, and we hope that we can still establish a FastLab in the near-future at ETHZ. All these (highly competitive) experimental sources are accessible to our growing research community and bridge the gap between single-PI labs and large-scale infrastructures, such as SwissFEL.

Thanks to the NCCR MUST, many new positions in ultrafast science were created and filled across Switzerland, further strengthening the field. In general, the appeal and visibility of the NCCR MUST helped to attract highly qualified candidates and to grow the community. This sustainably provides a user base with invaluable input and expertise for the Swiss large-scale photon infrastructures. Moreover, the NCCR MUST provides, through training of the next generation and knowhow transfer of key theoretical and experimental research tools, the necessary expertise and new flexible tools with broad adoption. Today, the network is an excellent mix between established top research groups and young group leaders, who could strengthen their profile partially thanks to the NCCR MUST.

Thanks to the concerted efforts and funding of expensive research through the NCCR MUST, Switzerland is in a leading position in ultrafast science as of today. As a result, we regularly see NCCR MUST PIs as invited speakers in key conferences in the field. The network has reached the critical mass for visibility abroad. Internationally, research colleagues commented that they are impressed by the Swiss effort in ultrafast science and technology and many national and international collaborations – also with start-ups, SMEs, and larger companies – were initiated (see also Annex 3). The Swiss network is now established and will be maintained and extended by the Swiss Society for Photon Science. This newly founded society has published, in its first year, the Swiss Roadmap for Photon Science outlining the Swiss national strategy in ultrafast science. This is a sound base for the future of ultrafast science in Switzerland.