Theoretical beamlines to unravel electronic structures and ultrafast relaxation pathways in functional molecules

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Spectroscopy, the most far-reaching analysis tool in chemistry, exploits the interaction of light with matter to probe molecular and electronic structures. This interaction is also the foundation of photochemistry, optogenetics, phototherapy, photocatalysis, optical devices, solar cells, and other use cases in chemistry, life sciences, and material design. The theoretical modelling and simulation of the molecular response to light thus provides crucial fundamental insight into the microscopic mechanisms behind all spectroscopies and light-energy conversion processes. Understanding, e.g., at the molecular level which excited states are initially populated by light irradiation and through which ultrafast electron relaxation pathways they evolve is a fundamental enabling step to decode molecular functionalities and to be able to exploit such processes in technological applications.

Therefore, the last two decades have witnessed a proliferation of experimental techniques to investigate excited-state dynamics in real time, and hereby shed light on fundamental photochemical processes like, e.g., ultrafast internal conversion and intersystem crossing in RNA/DNA-bases, singlet fission, metal-to-ligand and metal-to-metal charge transfer in transition metal complexes, ring opening, H-bonding networks in solvated species. X-ray free electron lasers, for instance, have opened an extraordinary window for imaging individual events in chemical reactions with (sub-)femtosecond time resolution via techniques like time-resolved X-ray absorption (XAS) and photoelectron (XPS) spectroscopy. However, experiments alone are not sufficient: theory and computational simulations are indispensable for unravelling the information encoded in the spectra.

In my talk, I will present some of our work on the development and application of rigorous and accurate quantum chemical methods to simulate steady-state and time-resolved spectroscopy across different frequency regimes, in particular soft x-ray, and their application to the interpretation of cutting-edge experimental studies that investigate electronic structure and relaxation mechanism following electronic excitation and/or ionization of functional molecules. Among them are steady-state and time-resolved XAS, XPS, x-ray emission, normal and resonant Auger-Meitner. Depending on the functional molecule, the objective of these studies was either to probe fundamental processes like IC, ISC, symmetry breaking, electron transfer and photochemistry, or to demonstrate the applicability of new types of experiments to image the above mentioned photophysical/chemical processes, or both.