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PhD THESIS DEFENSE: Attosecond soft X-ray absorption revealing the ultrafast non-adiabatic dynamics of furan

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One of the fundamental goals of the physical chemistry community has always been to be able to follow the details of the evolution of chemical reactions in real-time. Besides the extreme temporal resolution (sub-femtoseconds) required, a blurred picture of the dynamics often arises from the difficulties of spectroscopically disentangling the interplay between the electronic and nuclear degrees of freedom in complex compounds. This depends on the observable used for the experiments, which defines the direct and indirect information that can be retrieved. For example, electron diffraction or X-ray scattering methods directly track the structural changes of a species during a reaction. X-rays Absorption Fine Structure

(XAFS) spectroscopy, instead, follows the dynamics from the electron perspective by probing transitions from a core orbital to an empty valence orbital. Especially when applied to the soft X-ray wavelength region, the core-hole transitions minimize the spectral congestion and provides inherent element, charge and state sensitivity. At the same time, the observable is strongly dependent on the geometrical changes and, hence, provides information regarding the nuclear dynamics.

With the emergence of attosecond science, the remarkable properties of XAFS spectroscopy were combined with unprecedented temporal resolution matching the natural timescales of electronic motion in matter. This equipped the scientific community with a tool capable of disentangling the details of the intricate dynamics that arise from the interaction between light and matter, and initiated a revolution in the field of ultrafast spectroscopy. Among the many chemical dynamics that can be investigated, Attosecond XAFS (AttoXAFS) spectroscopy is very appealing for the study of non-adiabatic processes of polyatomic systems involving degeneracy points of the potential energy surfaces, i.e., conical intersections (CIs), in which electronic and vibrational coherence play a crucial role. In these phenomena, the ability to disentangle the nuclear and electronic degrees of freedom is fundamental for a correct interpretation of the process.

In this thesis, AttoXAFS in the soft X-rays is applied to the study of the complex non-adiabatic dynamics of a prototypical heterocyclic molecule, furan. Analysis of the experimental data, with the support of high-level simulations, provides a clear interpretation of the ultrafast coupled electron and nuclear dynamics. The temporal resolution and sensitivity to both electronic occupancies and structural changes allow following the dynamics step by step, revealing information about the nuclear and electronic configuration of the molecule with an unprecedented level of detail. The resulting picture shows how the passage through subsequent CIs defines the flow of the electronic population through transient dark states and the complete relaxation to the ground state, as well as the interplay between electronic and vibrational coherence dynamics.

In chapter 1 of this thesis, I will provide the framework for these results. This consists, on the one hand, of the recent development of attosecond science and its achievements in the study of light-matter interaction and, on the other, the coupled nuclear and electronic dynamics that characterize the photoinduced chemical reaction of polyatomic systems. In chapter 2 I will present the experimental setup developed in Prof. Dr. Jens Biegert's lab with which the results of this thesis were obtained. In chapter 3, I will discuss the importance of high photon energy pulses for materials science, focusing on XAFS and its capabilities, and show its exemplary applications on various solid state and gas phase samples achieved during my PhD. The core of this thesis is presented in chapter 4, where I will describe the experimental data on furan and the main results of the combined theoretical and experimental investigation. Finally, I will conclude with a summary and an outlook.

Thesis Director: Prof Dr. Jens Biegert

Hosted by: Prof. Dr. Jens Biegert