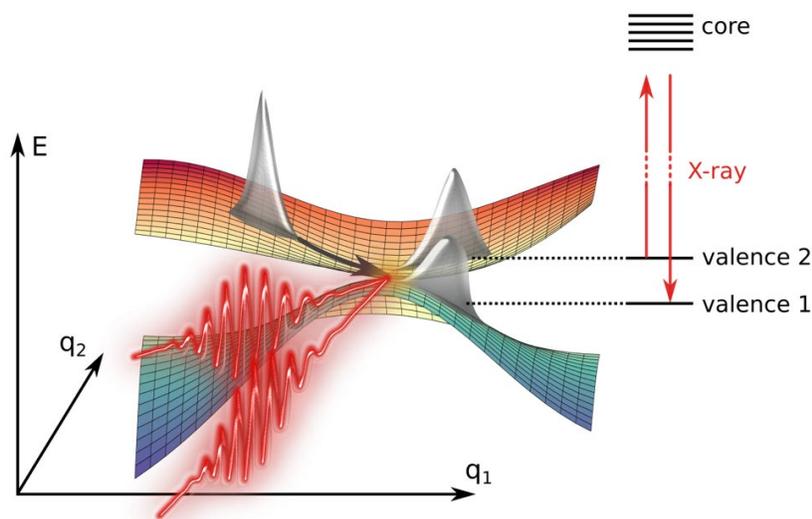


# Monitoring Elementary Molecular Events by Ultrafast Nonlinear X-ray Spectroscopy

Daniel Keefer, Haiwang Yong, Shichao Sun, Stefano Cavaletto, Jeremy R. Rouxel, Shaul Mukamel

Department of Chemistry and Department of Physics & Astronomy, University of California, Irvine, Irvine, California 92697-2025, USA

Novel X-ray pulse sources, specifically from free-electron lasers (FELs) and high-harmonic generation (HHG) setups make it possible to monitor molecular events on unprecedented temporal, spatial and energetic scales. The attosecond duration of X-ray pulses, their large bandwidth over a large tunable energy range, and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal selectivity. In this talk, we survey recent theoretical developments that design, simulate and predict spectroscopic signals that reveal detailed information about different aspects of ultrafast molecular transformations. The first technique is TRUECARS and based on an X-ray stimulated Raman process between electronic states to probe their coherences in a background-free measurement (see Fig. 1).<sup>[1]</sup> A hybrid broadband/narrowband X-ray probe field provides the necessary joint temporal and spectral resolutions.<sup>[2]</sup> The measurement can be performed in different modes, either with two phase-controlled coherent X-ray pulses,<sup>[1,2]</sup> or with stochastic, SASE-generated X-ray fields in a

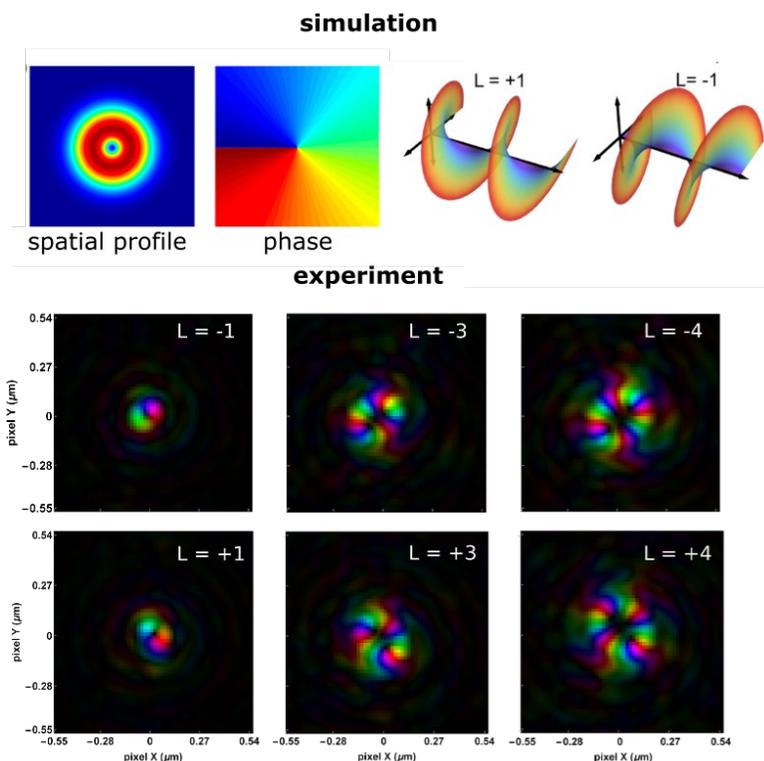


**Fig. 1.** Sketch of a conical intersection between two electronic states in the space of two nuclear degrees of freedom  $q_1$  and  $q_2$ . A hybrid X-ray pulse sequence induces a stimulated Raman transition between the two states. The signal is only present if there is a vibronic coherence that is generated through wavepacket bifurcation at the conical intersection.

covariance-based setup.<sup>[3]</sup> Next, different implementations of ultrafast homodyne- and heterodyne-detected X-ray (XRD) and electron diffraction (UED) are discussed. Besides following photochemical reactions in real-time via a series of femtosecond-resolved diffraction patterns,<sup>[4-6]</sup> a combination of UED and XRD is demonstrated to be sensitive *only* and directly to nuclear wavepackets.<sup>[7]</sup> This results from the fact that while in XRD photons scatter from molecular electron densities, UED is scattering from the total, nuclear+electronic charge density.<sup>[6]</sup> Both for TRUECARS and for XRD, quantum optimal control is presented as a potent tool to

selectively amplify and isolate desired contributions, such as the intrinsically weak coherences that may be buried beneath a stronger, less interesting population background.<sup>[8,9]</sup>

Another class of techniques exploits the orbital angular momentum (OAM) of femto- and attosecond probe fields. While well established in the optical regime, OAM light fields are just recently implemented in the X-ray domain. We demonstrate how in an X-ray scattering setup, two pulses with opposite angular momentum can be employed to suppress the dominating population background that is otherwise observed in scattering experiments and isolate electronic coherences.<sup>[10]</sup> Furthermore, we show how OAM light fields can be employed to monitor transient electronic ring currents in a polycyclic molecule.<sup>[11]</sup> For all techniques, the signal formalism and simulation procedure is discussed, as well as pulse requirements for experimental realization, followed by examples on ultrafast molecular processes such as uracil photorelaxation, azobenzene photoisomerization, thiophenol S-H bond cleavage, electronic coherences in larger dimers and dendrimers, and Mg-phthalocyanine ring current migration.



**Fig. 2.** X-ray light fields with orbital angular momentum (OAM). **Top:** simulated spatial and phase profile with  $l=1$ . **Bottom:** Experiment with different angular momenta generated with Fresnel zone plates.

Most of these examples rely on conical intersections (CoIns) on their operational principle and in this aspect; they stand representative for a large class of photochemical reactions in nature, chemical synthesis, materials and biology. CoIns are energetically degenerate regions on molecular potential energy surfaces causing a breakdown of the Born-Oppenheimer approximation and opening ultrafast non-radiative relaxation channels, thus determining the pathways and outcomes of virtually all photophysical and photochemical molecular processes (Fig. 1). The existence of CoIns is widely accepted, yet their observation is usually based on ultrafast internal conversion rates via electronic state populations. The novel X-ray techniques discussed here contain direct signatures of CoIns and other elementary molecular phenomena which so far remained

elusive, corroborating the unique capabilities and groundbreaking potential of ultrafast X-ray probes.

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**Joint Theory Seminar of European XFEL, CFEL and the University of Hamburg, September 2022**