Contribution ID: **4** Type: **not specified**

Ultrafast X-ray Stimulated Raman and Diffraction for Probing Molecular Coherences at Conical Intersections

Wednesday, 13 January 2021 18:10 (30 minutes)

X-ray laser sources provide unprecedented temporal and spectral resolutions, thereby enabling access to ultrafast phenomena during conical intersection dynamics. There, coherences emerge as a unique feature of the non-adiabatic passage. We present several spectroscopy techniques that are sensitive to these molecular coherences and provide different windows into their physics.

The first application is TRUECARS, where a hybrid broadband/narrowband probing scheme records the coherence signature free from the usually dominating population contributions. On the RNA-nucleobase uracil, we present the sensitivity of the TRUECARS signal to the underlying physics [1]. Through its Wigner representation, the signal directly maps the topology of the potential energy surface around the conical intersection explored by the wavepacket coherence and gives the vibronic energy distribution of the latter.
In the second application, time-resolved X-ray diffraction is simulated for the photoisomerization of azobenzene, a textbook photochemical process [2]. Besides monitoring the isomerization reaction via its diffraction patterns, mixed elastic/inelastic scattering from coherences emerges as a weak contribution in the total signal. This can be amplified by employing hard X-rays, realizing high momentum transfer amplitudes, where the coherence contribution is stronger. This signature gives access to the transient real-space molecular charge density, providing a movie of the conical intersection passage.

X-ray free-electron lasers (FELs) relying on the self-amplified spontaneous emission (SASE) mechanism generate stochastic x-ray pulses lacking phase control. This has represented a major bottleneck, since most time-resolved multidimensional nonlinear x-ray spectroscopy schemes are based on sequences of coherent, phase-controlled pulses. We show that suitable correlation signals averaged over independent realizations of stochastic FEL pulses can retrieve the same joint temporal and spectral resolutions of signals with phase-controlled pulses [3]. This is demonstrated both for Raman spectroscopy and imaging signals described above and can be extended to additional complex multidimensional nonlinear x-ray spectroscopy experiments.

Primary author: MUKAMEL, Shaul (University of California, Irvine)

Co-authors: DANIEL, Keefer (University of California, Irvine); STEFANO, Cavaletto (University of California, Irvine)

Presenter: MUKAMEL, Shaul (University of California, Irvine)

Track Classification: WavemiX 2021