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

D Keefer[1], S Cavaletto[1], and S Mukamel[1]

[1]*Department of Chemistry and Department of Physics & Astronomy, UCI, 1102 Natural Sciences II, Irvine CA, USA. Contact Phone: +9498247600*
Contact Email: smukamel@uci.edu

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.

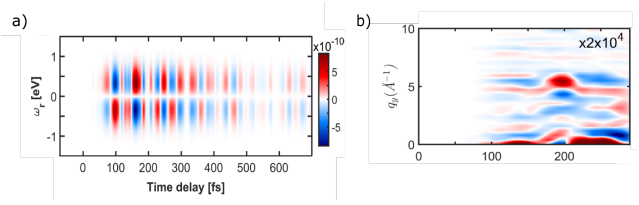

Figure 1: Coherence signatures during conical intersection dynamics. a) TRUECARS signal for the ultrafast photo relaxation of uracil, recorded with a hybrid broadband/narrowband X-ray probe. b) Coherence contribution to the time-resolved X-ray diffraction signal, recorded by mixed elastic/inelastic scattering

The first application is TRUECARS, where a hybrid broadband/narrowband probing scheme records the coherence signature free from the usually dominating population contributions. We present the sensitivity of the TRUECARS signal to the underlying physics for the RNA-nucleobase uracil [1] and a large heterodimer [2]. 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 [3]. 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. This is demonstrated both for Raman spectroscopy [4] and imaging signals [5] described above and can be extended to additional complex multidimensional nonlinear X-ray spectroscopy experiments.

All these signals rely on intrinsically weak signatures from coherence that can be hard to detect. We present a novel approach using optimal control theory to directly amplify desired spectral features and potentially bring them above the detection threshold [6].

References

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