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Monitoring Conical Intersection Signatures with Time-Resolved X-Ray Spectroscopy and Enhancing Them with Quantum Optimal Control

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Conical intersections are ubiquitous features in molecular photophysics that enable ultrafast relaxation channels. Wavepacket bifurcation in these regions gives rise to vibronic coherences, emerging as unique signatures of the non-adiabatic passage. Recently, we put forward several spectroscopy techniques to monitor these signatures on different molecular examples [1-3]. The signals are enabled by X-ray laser sources, available both from free-electron lasers and tabletop setups with different properties. Particularly, high temporal resolution provides access to the necessary timing windows of conical intersection passages, and a high bandwidth enables e.g. stimulated Raman processes between electronic states within a single pulse.

We present several time-resolved X-ray signals that exploit the capabilities of X-ray sources. The molecular examples range from small molecules with interesting photochemistry (uracil [1] and azobenzene [2]) to a large synthetic heterodimer with more than 100 atoms exhibiting photovoltaic properties [3]. Stimulated Raman and time-resolved diffraction signals are used to sensitively monitor vibronic coherences at conical intersections, retrieving different physical aspects.

In addition to this, we explore how quantum optimal control of the UV/Vis pump pulse can be employed to prepare the molecule in favourable states for spectroscopic detection. The coherence signatures are inherently weak and can be masked by the dominant population contributions. By shaping the pump pulse and thereby steering the molecular wavepacket, these signatures can be enhanced, allowing for better spectroscopic detectability.

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[3] D. Keefer, V. M. Freixas, H. Song, S. Tretiak, S. Fernandez-Alberti, S. Mukamel, in revision (2020)

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