Simulation of optical-pump Xray-probe NEXAFS spectroscopy to track photo-induced dynamics of organic molecules

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X-ray spectroscopy represents a versatile and powerful experimental toolbox for probing the dynamics of both core and valence electronic excitations, nuclear motions and material structure, with element and site specificity.[1-6] Following the achievements of a recent UV-pump X-ray probe time resolved NEXAFS (near-edge X-ray absorption fine structure) experiment,[6] in this contribution we explore the capabilities of this technique to track molecular excited state dynamics, providing complementary information with respect to the more widely employed optical spectroscopy.
The theoretical approach for the simulation of NEXAFS spectra, based on the multi-configurationl restricted active space self consistent field (RASSCF/RASPT2) method, is presented, and the *cis-trans* photo-isomerization of the azobenzene molecule is employed as a testbed case.[7]
Ground state and excited state NEXAFS spectra are computed on selected azobenzene molecular geometries (*cis*, *trans* and conical intersection(s) structures) as well as along the key isomerization coordinates. The origin of the simulated NEXAFS signals is explained, highlighting the specific signatures that make it possible to follow the excited state evolution from the Franck Condon point, towards the conical intersection(s).

References

1. J. Stöhr, NEXAFS Spectroscopy, Springer Berlin Heidelberg, 1992.
2. X-Ray Absorption and X-Ray Emission Spectroscopy, ed. J. A. V. Bokhoven and C. Lamberti, John Wiley & Sons, Ltd, 2016.
3. M. Gühr, *Synchrotron Radiation News*, **29** (2016) 8-12.
4. P. Wernet et. al, *Nature*, **520** (2015) 78-81.
5. A. R. Attar et. al, *Science*, **356** (2017) 54-59.
6. T. J. A. Wolf et al., *Nature Communication*, **8** (2017) 1.
7. F. Segatta et. al., *submitted to Faraday Discussion.*