Abstract ID : **31**

Time-resolved chiral X-Ray photoelectron spectroscopy of fenchone with transiently enhanced atomic site-selectivity

Content

Chirality plays a fundamental role across the physical and biological sciences. A chiral molecule lacks both a plane of symmetry and a center of symmetry and thus can occur in two non-superimposable mirror-image forms called enantiomers. Despite having the same chemical structure, most enantiomers exhibit different properties when interacting with other chiral objects, such as other chiral reagents or circularly polarized light. While chirality has been a subject of deep investigation in biology and chemistry, its ultrafast dynamics are mostly unexplored. One of the most promising time-dependent investigation techniques of chiral dynamics is Time-Resolved Photo-Electron Circular Dichroism (TR-PECD), which provides a sensitive probe of the structural relaxation of the molecule on the femtosecond time scale [1]. In standard TR-PECD, an ultrashort circular pulse ionizes the molecule from a photo-excited state of the system, and the transient dichroism emerges from the forward-backward asymmetry of the photoelectron emission along the propagation axis of the pulse. However, the non-local character of this approach makes the interpretation of TR-PECD experiments challenging. In this respect, time-resolved X-ray Photoelectron Spectroscopy (TR-XPS) from the core level of a molecule would permit accessing the local relaxation dynamics of electronically excited states in a chemical- and site-selective way, through their transient excited-state chemical shifts (ESCS) [2].

We combined the chemical- and site-specificity of TR-XPS with the enantio-sensitivity of TR-PECD, studying the relaxation dynamics of photoexcited fenchone molecule at the carbon K-edge [3]. With this experiment, we demonstrate that femtosecond chiral dynamics can be probed using core level spectroscopy with circularly polarized XUV light provided by the FERMI free-electron laser. In addition, we demonstrate that core-level PECD spectroscopy of transient excited states allows us to isolate different carbon atoms inside the molecule through their different ESCS. This permit enhancing the site-specificity of the technique allowing to further separate and identify the PECD from different sites in the molecule that otherwise would not be accessible.

[1] A. Comby et al., "Relaxation Dynamics in Photoexcited Chiral Molecules Studied by Time-Resolved Photoelectron Circular Dichroism: Toward Chiral Femtochemistry", J. Phys. Chem. Lett. 7, 4514 (2016)

[2] D. Mayer et al., "Following excited-state chemical shifts in molecular ultrafast x-ray photoelectron spectroscopy", Nature Communications 13, 1 (2022).

[3] D. Faccialà et al., "Time-resolved chiral X-Ray photoelectron spectroscopy with transiently enhanced atomic site-selectivity: a Free Electron Laser investigation of electronically excited fenchone enantiomers." arXiv preprint arXiv:2202.13704 (2022).

Primary authors: FACCIALÀ, Davide (CNR-IFN Milano, IT); DEVETTA, Michele (CNR-IFN Milano, IT); BEAUVARLET, Sandra (CELIA, Université de Bordeaux-CNRS-CEA, FR); BESLEY, Nicholas (University of Nottingham, UK); CALEGARI, Francesca (CFEL, DESY, Hamburg, DE); CALLEGARI, Carlo (Elettra-Sincrotrone Trieste, IT); CATONE, Daniele (CNR-ISM Roma, IT); CINQUANTA, Eugenio (CNR-IFN Milano, IT); CIRIOLO, Anna G. (CNR-IFN Milano, IT); COLAIZZI, Lorenzo (CFEL, DESY, Hamburg, DE); CORENO, Marcello (CNR-ISM Roma, IT); CRIPPA, Gabriele (Politecnico Milano, IT); DE NINNO, Giovanni (Elettra-Sincrotrone Trieste, IT); DI FRAIA, Michele (Elettra-Sincrotrone

Trieste, IT); GALLI, Mara (CFEL, DESY, Hamburg, DE); GARCIA, Gustavo (Synchrotron Soleil, Gif sur Yvette, F R); NEGRO, Matteo (CNR-IFN Milano, IT); MAIRESSE, Yann (CELIA, Université de Bordeaux-CNRS-CEA, FR); PLEKAN, Oksana (Elettra-Sincrotrone Trieste, I T); PRASANNAN GEETHA, Prabhash (CNR-IFN Milano, IT); PRINCE, Kevin (Elettra-Sincrotrone Trieste, I T); PUSALA, Aditya (CNR-IFN Milano, IT); STAGIRA, Salvatore (Politecnico Milano, IT); TURCHINI, Stefano (CNR-ISM Roma, IT); UEDA, Kiyoshi (Tohoku University, JP); YOU, Daehyun (Tohoku University, JP); ZEMA, Nicola (CNR-ISM Roma, IT); BLANCHET, Valerie (CELIA, Université de Bordeaux-CNRS-CEA, FR); NAHON, Laurent (Synchrotron Soleil, Gif sur Yvette, F R); POWIS, Ivan (University of Nottingham, UK); VOZZI, Caterina (CNR-IFN Milano, IT)

Presenter: FACCIALÀ, Davide (CNR-IFN Milano, IT)

Contribution Type: Hot topic contribution