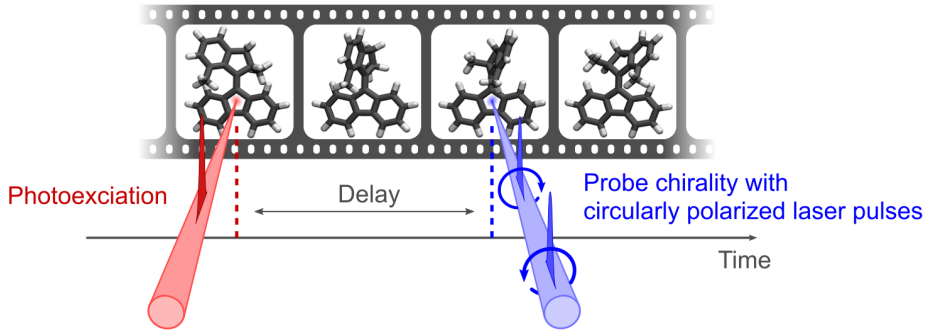
Molecules in motion: Capturing and controlling molecular dynamics through chirality

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The ability to follow changes in molecular structure during a chemical reaction or biological activity has been a dream of scientists for decades. However, resolving the molecular motion that drives the fastest (bio-)chemical processes has remained a formidable challenge in their native solution phase, where even established methods reach important limitations: nuclear magnetic resonance is limited to millisecond real-time resolution while time-resolved X-Ray scattering requires large-scale free-electron laser facilities. A promising laboratory-based alternative is circular dichroism (CD) spectroscopy, which measures the absorption difference of left- and right-handed circularly polarized light in chiral molecules. CD is especially attractive in the far and middle ultraviolet (UV) <300 nm, where it is routinely used to characterise the chiral equilibrium structures of proteins, DNA and chiral organic complexes. However, taking this technique to the time-domain has remained a challenge for over three decades, with only few isolated reports with sub-nanosecond time-resolution [1].

In this talk, I will present a novel time-resolved CD spectrometer that combines ultra-sensitive broadband detection in the deep-UV (250-370 nm) with sub-picosecond time-resolution [2]. This has finally opened the path to measure the CD spectra of photoexcited chiral molecules in solution and to follow the encoded structural dynamics with ultrafast time-resolution. In my talk I will illustrate these exciting new experimental capabilities with an investigation of Fe(II) spin-crossover complexes, where – despite decades of research – the relaxation mechanism of their excited high-spin state has remained unresolved. By combining ultrafast CD with transient absorption and anisotropy measurements of a prototypical chiral Fe(II) complex [3], we now show that the spin-relaxation mechanism involves a torsional twisting mode that breaks the chiral symmetry of the compound [4]. Quite remarkably, suppressing the vibrational population of this mode then slows down the spin-relaxation.



[1] P. Changenet, F. Hache, *Eur. Phys. J. Spec. Top.,* **2022.**
[2] M. Oppermann, B. Bauer, T. Rossi, F. Zinna, J. Helbing, J. Lacour, and M. Chergui, *Optica,* 6, 1, 56-60, **2019.**
[3] J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann, *Angew. Chem. Int. Ed.,* 37, 2379, **1998.**
[4] M. Oppermann, F. Zinna, J. Lacour, and M. Chergui, *Nat. Chem.*, 14, 739-745, **2022.**