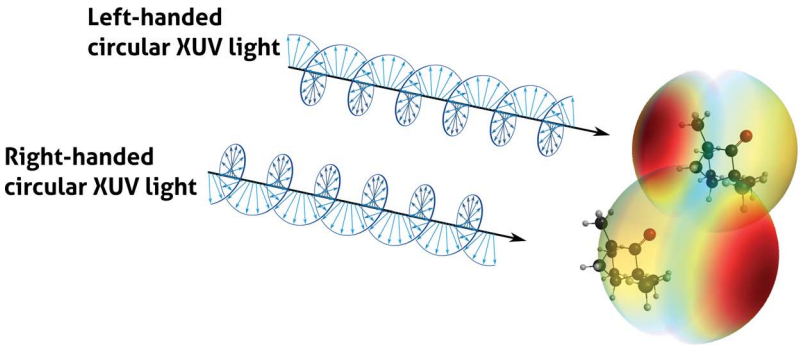

Fig. 1 Principle of photoelectron circular dichroism in XUV photoionization.

a consequence, subtle changes in electronic or nuclear molecular structures are expected to produce large modulations of PECD, which is thus a very good candidate for ultrafast time-resolved measurements on chiral compounds.

Time-resolved measurements of chirality do not only require a sensitive observable but also ultrashort circularly polarized light pulses, which are difficult to produce in the XUV range. One way to circumvent this issue is to use relatively intense circular femtosecond UV-visible pulses to perform multiphoton ionization of the chiral molecules. Several studies based on resonant-enhanced multiphoton ionization have shown that a strong PECD could emerge in this situation, with high sensitivity to isomerism.[18–20] In the first part of the manuscript we compare the PECD obtained using different femtosecond sources, from the extreme ultraviolet to the mid-infrared range, resulting in different ionization regimes: single-photon, resonance-enhanced multiphoton, above-threshold and tunnel ionization. We discuss the advantages and drawbacks of these different cases in the perspective of probing the ultrafast dynamics of chiral molecules. In the second part we study the ultrafast relaxation of the showcase fenchone molecule photoexcited into 3s Rydberg states and show that PECD is a very good probe of the ongoing dynamics, revealing features that are unaccessible in conventional time-resolved photoelectron spectroscopy.

2 Photoelectron circular dichroism using ultrashort light pulses

The vast majority of PECD studies have been carried out in the single-photon XUV ionization regime, using synchrotron radiation. Indeed, synchrotron radiation is bright, tunable over a very large spectral range, and can be fully controlled in polarization – a perfect tool for spectroscopic investigations. However, its long duration prevents ultrafast dynamical studies. Femtosecond lasers can be used to cut temporal slices in the radiation,[22,23] resulting in femtosecond pulses but at the cost of a much lower brightness. Free electron lasers do represent a valuable alternative but so far a single one (FERMI) delivers circular XUV pulses,[24] with