consequence of this homochirality is that many biological processes are chiral-sensitive. For instance, two enantiomers of a given chemical species can have different flavors or healing properties. The identification of the left or right character of the molecules by chiral biological sensors is called chiral recognition. The understanding of the interaction of chiral species, and in particular the question of chiral recognition, is a central question in analytical chemistry and catalysis. Chiral reactivity is governed by nuclear rearrangements occurring on picosecond to femtosecond timescales. The nuclear motion is driven by electron dynamics which are typically much faster and at the attosecond scale. On what timescale does chirality imprint from nuclear to electronic structure? What are the dynamical mechanisms for the birth and death of chirality in chemical reactions? What are the fundamental processes governing chiral recognition? Answering these questions requires unraveling the dynamical aspects of the processes, which is only possible using ultrashort light pulses. However, this task is so difficult that, until very recently[1] no ultrafast dynamical chiral process had ever been measured in the gas phase, where isolated molecular systems can be studied with a high level of detail. This is due to the lack of a sensitive enough chiral discrimination technique. In the visible range, the differential response of a chiral molecule to left and right circularly polarized light (Circular Dichroism, CD), is related to the interference of electric and magnetic dipole transitions. Consequently, the CD values are generally weak, on the order of 10^{-5} to 10^{-3} in relative values from the visible to the X-ray range,[2] which is prohibitive for gas-phase measurements where absorption is especially weak. High enantio-sensitivity can be achieved by microwave spectroscopy,[3,4] but this spectral range is not suited for ultrafast measurements on the femtosecond timescale.

Moving from an integral measurement such as absorption or total ionization yield, to a differential measurement such as angle-resolved photoemission enabled a strong increase in the sensitivity of chiral detection in the early 2000s through PhotoElectron Circular Dichroism (PECD).[5,6] Unlike conventional CD, this very intense chiroptical effect is allowed within the electric dipole approximation. The ionization of randomly oriented chiral molecules by circular XUV light leads to a forward/backward asymmetry, with respect to the light propagation axis, in the angular distributions of the released electrons. This asymmetry reverses if the light helicity or the enantiomer is changed (Fig. 1) and can be very large – the highest measured value to date is 35%.[7] PECD gives rise to forward/backward asymmetry because of the intrinsic chirality of the target. It should not be confused with the observed asymmetries which arise in the plane perpendicular to the light propagation axis in photoionization from achiral molecules with a well defined orientation, the so called Circular Dichroism in electron Angular Distribution, CDAD.[8]

PECD possesses a number of unique characteristics (for a review see ref. 9) which make it an ideal probe for molecular structural and dynamical investigations: (i) high signal-to-noise ratio – due to its purely electric-dipole nature, PECD is typically on the order of a few percents; (ii) initial molecular orbital sensitivity;[10] (iii) dynamical final (continuum) state sensitivity depending on the electron kinetic energy; (iv) vibrational sensitivity – PECD was found to change sign between ground and vibrationally excited states, in clear violation of the Franck–Condon approximation.[11] Furthermore, PECD is very sensitive to conformation,[12–14] chemical substitutions,[15,16] isomerism[10,17] and to dimerization and clustering. As

