well as to internal conversion onto lower valence states. The detailed understanding of the PECD signal would require a complete calculation of the wavepacket dynamics, which is far beyond the scope of this work. Let us stress that the dynamics revealed by the TRPECD measurements are invisible in the TRPES signal, confirming the relevance of photoelectron circular dichroism as a probe of ultrafast dynamics of chiral molecules.

4 Conclusions

We have performed an extended investigation of photoelectron circular dichroism in the photoionization of enantiopure fenchone molecules in different ionization regimes, and found that PECD is a universal effect. Each regime has its specificities in terms of signal strength and ionization channel sensitivity, offering complementary looks at the chiral molecules. We have used time-resolved PECD to track the ultrafast relaxation of a Rydberg wavepacket, proving that this observable could reveal ultrafast dynamics that is invisible in time-resolved photoelectron spectra. The comparison of different pump and probe schemes shows spectacular differences in the angular distribution of the PECD, which are an additional illustration of its sensitivity. These first results mark the birth of ultrafast time-resolved measurements of chirality in the gas phase. Understanding the outcome of the measurements will require an extensive theoretical work, but the parametric study that we have performed should enable determining what key parameters are at play. A essential aspect of future experiments will be to increase the temporal resolution to track the fastest vibronic dynamics with high contrast.

Several other ultrafast chiral discrimination techniques have been developed very recently, that could provide complementary information on the dynamics of chiral molecules. First, high-order harmonic generation by elliptical laser pulses in chiral molecules was shown to be very sensitive to the handedness of the molecules.[48] This technique, which has intrinsic attosecond resolution, could lead to huge contrasts in pump–probe measurement.[49] Second, we have recently shown that chiral wavepackets could be probed with linearly polarized light. We have measured a forward/backward asymmetry in the photoionization of fenchone molecules excited by circularly polarized light and ionized by linear radiation. This process emerges from a macroscopic asymmetry in the photoexcited wavepacket, an effect we called photo excitation circular dichroism. PXCD is an interferometric process and is a very good probe of ultrafast molecular relaxations.

One question remains open: what will be the sensitivity of these different observables to valence state dynamics? The wavepacket spreading over the reaction coordinates often blurs the photoelectron spectra and prevents resolving the dynamics from TRPES. Will TRPECD, chiral HHG or TRPXCD be able to overcome this issue? The very high sensitivity of these methods to vibrations and electronic states leads us to be optimistic.

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