In this work, we exclusively use fenchone molecules as a benchmark system to compare different ionization schemes, shown in Fig. 2: single photoionization by high-order harmonics of a 400 nm laser, resonant-enhanced multiphoton ionization by 400 nm pulses, above-threshold ionization by 800 nm pulses, and tunnel ionization by 1850 nm pulses.

2.1 Single-photon ionization from quasi-circular high-harmonics

High-order harmonic generation (HHG) occurs when an intense laser pulse is focused into a gas jet. The highly non-linear interaction of the strong field with the atoms or molecules results in the emission of bright, coherent, ultrashort (femtosecond to attosecond) pulses in the XUV range. HHG has been used for decades as a source of radiation for pump–probe spectroscopy and would be a very good source for PECD studies. Unfortunately, the HHG mechanism has an intrinsic preference for linearly polarized light. The high harmonics are emitted by a three step process.[27–29] When the laser field is maximum, part of the electron wavefunction tunnels into the continuum; the wavepacket is accelerated by the strong field, which drives it back towards the parent ion; lastly, the wavepacket can recombine radiatively with this ion, emitting a short burst of extreme ultraviolet light. This last step is the reverse process of XUV photoionization. If the driving laser field is elliptical, then the minor component of the electric field drives the electron wavepacket away from its parent ion, strongly suppressing recombination. Using 20–30% ellipticity of the driving laser typically lowers the harmonic signal by one order of magnitude.[30] Furthermore, the ellipticity of the harmonics emitted in these conditions remains lower than the driving laser ellipticity.[31]

Converting the polarization state of high-harmonics from linear to circular can be achieved by multiple reflections on metallic surfaces.[32,33] However, this technique is not so easy to implement and results in a strong decrease of the signal, due to the poor reflectivity of the surfaces in this wavelength range. In the past few years, a few solutions have emerged to solve this issue and directly produce bright highly elliptical high-order harmonics. The first one relies on shaping the laser electric field in the time domain. Using a combination of counter-rotating fundamental and second harmonic fields results in the emission of circularly polarized high harmonics with alternatively left or right polarizations.[34] While this configuration would be inadequate for molecular photoionization studies, due to the difficulties of deciphering the spectrum, it is certainly interesting for the condensed phase to investigate X-ray magnetic circular dichroism. The second solution is based on shaping of the laser field in the spatial domain. Generating high-harmonics from two interfering non-collinear counter-rotating circularly polarized fields produces highly elliptical harmonic beams.[35] The third solution, which we use here, is based on shaping the recollision process in the HHG mechanism using resonant high-harmonic generation.[36]

Autoionizing states and shape resonances are known to have a strong influence in XUV photoionization, where they induce structures in the photoelectron spectrum, changes in the photoelectron angular distribution and scattering phase shifts.[37] By performing a complete characterization of the high-order harmonic emission in the vicinity of a shape resonance in SF_6 molecules, we have shown that the resonance had a similarly strong influence on the harmonic spectrum. Besides enhancing the harmonic yield, the resonance creates a strong