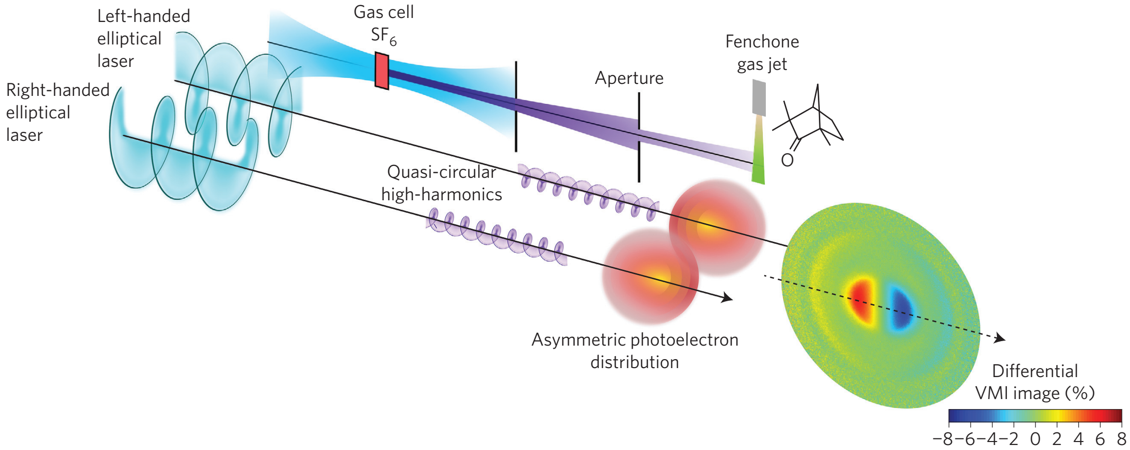

Figure 3 | Experimental set-up and principle of the PECD measurement. Left- and right-handed elliptical 400 nm pulses are used alternately to generate high harmonics in SF_6. An aperture selects the central part (2 mm diameter) of the harmonic beam, which photoionizes enantiopure fenchone molecules in a VMIS. The photoionization of chiral molecules results in asymmetric forward/backward photoelectron emission. This asymmetry appears clearly in the differential photoelectron image (corresponding to fenchone (+)), which is the normalized difference between the electron images obtained using left- and right-handed fundamental pulses: $2(S_{\text{left}} - S_{\text{right}})/(S_{\text{left}} + S_{\text{right}})$.

$\varepsilon_0 = 45\%$. Using shorter wavelengths for HHG also has the advantage of increasing the generation efficiency[32]. We measured 2×10^6 photons per pulse for harmonic 5 when driven by 30% ellipticity, that is, 2×10^9 photons per second. This is lower than the $\sim 1 \times 10^{12}$ photons per second of a quasi-continuous synchrotron beamline such as DESIRS, but still permits pump–probe experiments on dilute matter to be performed. The photon flux could be further increased by optimizing the generating conditions (more energetic laser pulses, longer focal length) without any drastic change in the polarization quality.

As a test case to characterize our elliptical harmonic source, we performed a PECD experiment on a previously studied chiral system. PECD arises when circular radiation photoionizes pure enantiomers of a chiral molecule in the gas phase. The emitted electrons exhibit a large forward/backward asymmetry along the propagation direction of the light, even for randomly oriented molecular samples[2]. The harmonics of the 400 nm laser pulse were directly sent to a velocity map imaging spectrometer (VMIS) where they photoionized enantiopure chiral fenchone molecules (Fig. 3). To avoid modification of the XUV polarization state, no optical element was introduced between XUV generation and the VMIS. An aperture selected the central part of the harmonic beam to maintain good resolution in the VMIS. We checked that the fundamental beam was not intense enough in the detection zone to ionize the fenchone or produce two-photon two-colour transitions. The VMIS projects the angular distribution of ionized electrons onto a set of microchannel plates imaged by a charge-coupled device (CCD) camera. Photoelectron spectra were measured alternately using left-handed and right-handed driving laser ellipticities $\varepsilon_0 = \pm 30\%$. Calculating the normalized difference between the left and right images, $\text{PECD} = 2(S_{\text{left}} - S_{\text{right}})/(S_{\text{left}} + S_{\text{right}})$, provides a direct visualization of the dichroism in the measurement (as seen in Fig. 3): in fenchone (+), when the light is left-handed, more low-energy electrons (around the centre of the detector, electrons predominantly ionized by harmonic 3) are emitted in the backward direction than the forward direction. Switching the handedness of the light reverses the effect. The sign of the PECD switches when the electron energy increases, that is, as we move away from the centre of the detector.

Quantitative evaluation of the observed PECD requires Abel-inverting of the projected images. This data treatment procedure is described in detail in ref. 33. The PECD is shown in Fig. 4, which compares measurements performed in fenchone (+) and (–). The data show a quasi-perfect mirroring between the two enantiomers, as expected from theory, showing the excellent signal-to-noise ratio that can be reached in an acquisition time of a matter of 15 min for each helicity. The PECD peaks at energies associated with the ionization of the two highest occupied molecular orbitals of fenchone (HOMO and HOMO-1). Interestingly, the responses of the two orbitals have opposite signs, which is consistent with synchrotron radiation measurements[34] and highlights the sensitivity of PECD to the ionized orbital. Harmonic 3, which is produced below the ionization threshold of SF_6, produces a significant PECD. This harmonic could not be characterized in the optical polarimetry experiment because of the bandpass of the spectrometer, but the PECD measurement indicates that it is highly elliptical. The PECD changes sign between harmonic 3 and harmonics 5 or 7. This could be either due to the ionization dynamics of fenchone or to an opposite helicity of H3 and H5. These results demonstrate the possibility of performing high-quality PECD measurements with elliptical HHG, with the advantage of probing

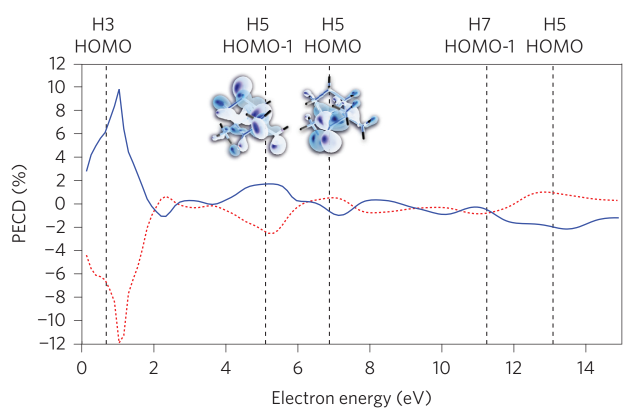

Figure 4 | Photoelectron circular dichroism in fenchone. PECD from fenchone (+) (red dots) and (–) (blue solid line) molecules ionized by high harmonics of a 400 nm fundamental pulse with $\varepsilon_0 = 30\%$ as a function of electron energy. Three harmonics photoionize the system at 9.3 (harmonic 3), 15.5 (harmonic 5) and 21.7 eV (harmonic 7). The dichroism peaks at positions corresponding to the ionization of the two highest occupied molecular orbitals HOMO (ionization potential 8.6 eV) and HOMO-1 (10.4 eV).