several ionizing energies in the same measurement. Combined with a forthcoming purely circular ($S_3 = 1$) synchrotron radiation calibration of the molecular chiroptical response at harmonic photon energies, this PECD measurement will allow the disentangling of Stokes parameters S_3 (circular) and S_4 (unpolarized radiation) of the harmonic emission. In a first approximation, assuming a fully polarized elliptical radiation with vertical ellipse axis, and a zero anisotropy parameter β, we can extract a value for the first-order Legendre polynomial coefficient $b_1 = \mathrm{PECD}/(2S_3)$ by using the ellipticities measured by optical polarimetry (Fig. 2). For the HOMO this gives $b_1 \approx 4 \pm 2 \times 10^{-3}$ at a photon energy of 15.5 eV (harmonic 5) and $b_1 \approx 1.1 \pm 0.5 \times 10^{-2}$ at a photon energy of 21.7 eV (harmonic 7). This is in decent agreement with synchrotron radiation measurements performed at neighbouring energies: $b_1 \approx 7 \pm 5 \times 10^{-3}$ at 14 and 16 eV, and $b_1 \approx 2 \pm 1 \times 10^{-2}$ at 22 eV (ref. 34).

By enabling the extension of the current frequency-resolved experiments carried out with synchrotron radiation to the time domain via pump–probe experiments, resonant HHG sources enable a very large avenue of research for 'femtochirality'. In particular, the transition states of enantioselective photochemical processes could be directly addressed by applying standard pump–probe femtochemistry methods. Other femtosecond probes of chirality in the gas phase have been demonstrated recently. Coulomb explosion imaging enables the absolute configuration of molecules to be determined[35], but is restricted to small systems. Compared to multiphoton ionization[36,37], XUV PECD has the advantage of being a universal direct ionization probe, involving no intermediate resonant state. Many photochemical processes could therefore be mapped out in the time domain by means of PECD, which is known to be extremely sensitive to static[2] and dynamical[3] molecular structures. Elliptical HHG also opens the path to attosecond metrology of circular dichroism. The temporal profile associated with the superposition of consecutive harmonics is an attosecond pulse train. Using an additional probe laser field enables resolving the phase of the molecular photoionization process[15], giving access to attosecond time delays of the photoelectrons[14]. It will thus be possible to resolve the different photoionization times of photoelectrons emitted from a chiral molecule forward or backwards relative to the direction of the light propagation, thereby obtaining a unique insight into the fundamental dynamics of electrons in chiral potentials.

Methods

The experiments were performed using the Aurore laser system at CELIA, which delivers 8 mJ, 25 fs, 800 nm pulses at 1 kHz. Frequency doubling was achieved using a 200-μm-thick type I BBO crystal (4 mJ of 800 nm gives 1 mJ of 400 nm light). The polarization state of the fundamental radiation was shaped by rotating a broadband zero-order half-waveplate in front of a quarter-waveplate, which enabled the laser ellipticity ε_0 to be varied while keeping the major axis of the ellipse fixed. The laser was focused by a thin 50 cm SiO_2 lens into a vacuum chamber and interacted with a continous jet (300 μm nozzle) at 100 mbar or a static gas cell (3 mm long) filled at 5 mbar. Optical polarimetry using the two sources gave similar results. Note that SF_6 has the advantage of being non-toxic, non-corrosive and gaseous at room temperature, with a high vapour pressure. The harmonic polarization state was characterized using an XUV polarizer consisting of three bare gold mirrors under 75°–60°–75° incidence, leading to a contrast of 5–20 between S and P polarizations for harmonics 5 to 9 of the 400 nm light. A second half-waveplate was used to rotate the laser polarization, which is equivalent to rotating the XUV polarizer, to record the Malus' law.

For the PECD experiment, a reservoir of enantiopure fenchone (Sigma Aldrich) at room temperature was connected through a microleak to a heated metallic nozzle (120 °C) of 300 μm diameter located 7 cm away from the interaction zone. The pressure in the interaction region was 2×10^{-6} mbar (5×10^{-8} mbar background pressure).

Received 11 March 2014; accepted 27 November 2014; published online 22 December 2014

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