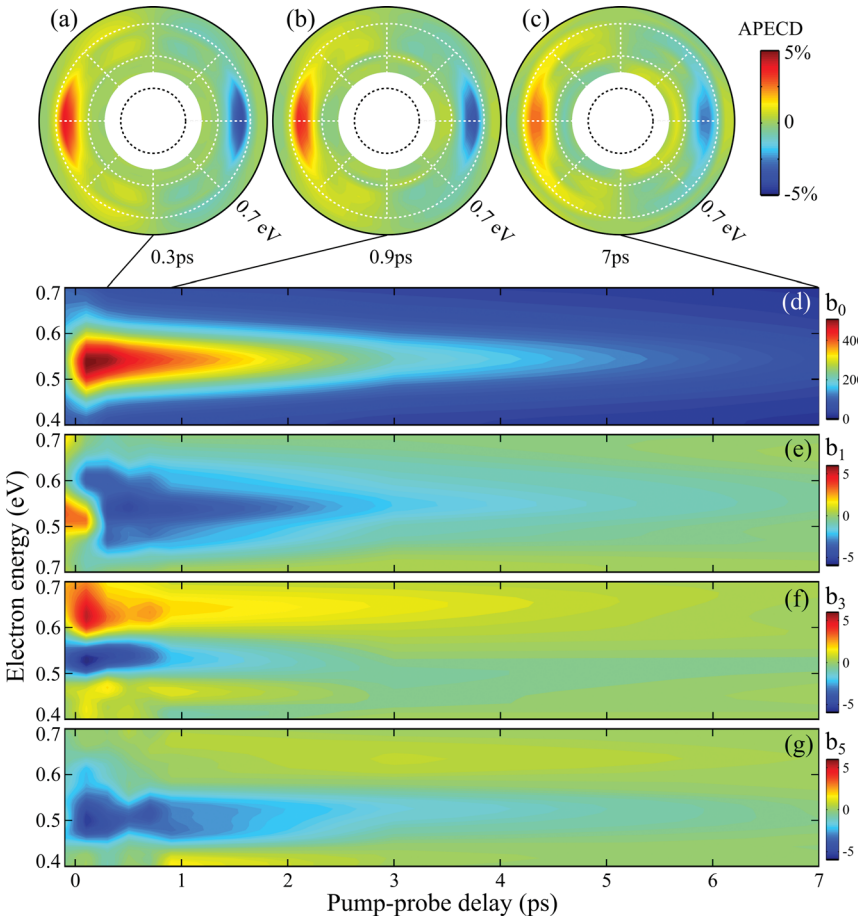

Fig. 9 Time-resolved PECD measurements in fenchone in a 1 + 2′ configuration (201 nm linearly polarized pump and 800 nm circularly polarized probe). The top polar plots show the APECD recorded at three pump–probe delays: 0.3 ps (a), 0.9 ps (b) and 7 ps (c). The light propagation direction is horizontal and the radius extends from 0 to 0.7 eV. The lower contour plots depict the evolution of the Legendre coefficients b_0 (d), b_1 (e), b_3 (f) and b_5 (g) as a function of electron kinetic energy and pump–probe delay.

observation, we have repeated the pump–probe measurements of the relaxation of the 3s Rydberg states using two 800 nm photons as a probe (1 + 2′ configuration). This change is accompanied by an improvement of the temporal resolution of the experiment (~100 fs cross correlation time), since the 800 nm pulses are only 30 fs long. The two-photon ionization here is a REMPI process, with a strong resonance around 7.7 eV to the 3d Rydberg states mixed with the second valence state (Fig. 7).

Fig. 9 shows the temporal evolution of the Legendre coefficients as well as snapshots of the APECD at three pump–probe delays. The PES (b_0) is centered at the same energy as in the 1 + 1′ scheme (0.52 eV) but is significantly broader, reflecting the broader bandwidth of the probe pulses. The signal decays in 3.2 ps, in agreement with the 3s Rydberg lifetime measured above. The APECD is much