potential of fenchone). The PES does not show any significant shift as a function of pump–probe delay, and decays monotonically with a 3.3 ps characteristic time. This evolution reflects the lifetime of the 3s Rydberg states.

A significant PECD is observed, which is remarkable given the high level of excitation of the molecule: even though the electron lies initially in a Rydberg state, orbiting quite far away from the ionic core, its scattering into the chiral potential as it leaves the molecule during ionization by the probe pulse is sufficient to imprint a strong forward/backward asymmetry. This asymmetry has the same sign and amplitude as the ones shown in Fig. 4 and 5 in single-photon and one-color REMPI respectively. Our PECD studies on static molecules have suggested that in REMPI, the effective order of the Legendre decomposition may be set by the number of photons absorbed from the resonance. The linear + circular experiment that we perform here gives an opportunity to test this hypothesis. The APECD is not only constituted of b_1 but also b_3 terms, despite the fact that a single circularly polarized photon is involved in the ionization process from the 3s Rydberg state. The evolution of the Legendre coefficients with pump–probe delay provides an explanation to this apparent paradox. At short delays, the interplay of negative b_1 and b_3 leads to a rather sharp PECD distribution around the laser propagation direction (see snapshot at 0.5 ps). As the pump–probe delay increases to 6 ps, b_3 almost vanishes and the PECD distribution has a much broader angular extension, very similar to the single-photon ionization case (Fig. 4). Exponential fittings of the Legendre coefficients (averaged around the maximum of the photoelectron spectrum) give a 3.9 ps decay time for b_1 and 1.4 ps for b_3. Why would the b_3 component decay faster than the Rydberg state population? The excitation process by the linearly polarized pump pulses introduces an anisotropy in the sample, because the excitation probability is maximized for a given molecular orientation. This anisotropy in the molecular excitation means that the ionized molecules are not randomly oriented. Orientation effects have been shown theoretically to strongly modify the angular structure of PECD,[46] and probably cause the appearance of higher order Legendre polynomials in our experiment. The molecules being at non-zero temperature, they rotate with time. This rotation results in a loss of the excitation orientation after a certain time, determined by the moment of inertia of the molecules and rotational temperature of the gas jet.[47]

The PECD can be quantified by integrating the Legendre coefficients around the peak of the PES and calculating the multiphoton MPPECD defined in eqn (5), where the sum is here restricted to its first two terms since the transition is a two-photon process. The MPPECD is found to experience a fast decrease with a minimum around 0.4 ps, followed by an increase to reach the limit value of 14.6%. These results can be found in another publication.[1] If PECD was simply sensitive to the population decay of the Rydberg states, then the MPPECD, which is a normalized quantity, should remain constant with the pump–probe delay. This evolution is thus a first demonstration of the sensitivity of TRPECD to vibronic dynamics.

3.2   Single photon excitation and two-photon ionization

Our measurements on static molecules have illustrated the dependence of the PECD angular distributions on the number of ionizing photons. Following this