configuration could offer a simple picture for dynamical measurements, but has the disadvantage of showing a rather low sensitivity and of being based on the use of strong laser fields, which can significantly perturb the probed molecule.

3 Time-resolved photoelectron circular dichroism

The resonance-enhanced multiphoton ionization of fenchone studied above was carried out through the excitation of Rydberg states around 6.1 eV. We conducted time-resolved measurements to follow the ultrafast relaxation of these Rydberg states and to investigate the sensitivity of PECD as a probe of the molecular dynamics. After summarizing the results of our first pump–probe study in which we used a single photon process for both the pump and probe steps,[1] we investigate the case of multiphoton absorption.

3.1 Single photon excitation and single-photon ionization

The first (3s) Rydberg states of fenchone lie slightly above 6 eV (Fig. 7). We thus generated the fourth harmonic of our 800 nm pulses to produce 6.17 eV (201 nm) pulses with 30 meV bandwidth and ~2 μJ energy. The pulses were linearly polarized, and were focused around 5×10^{11} W cm^{-2} by a lens into the VMIS.

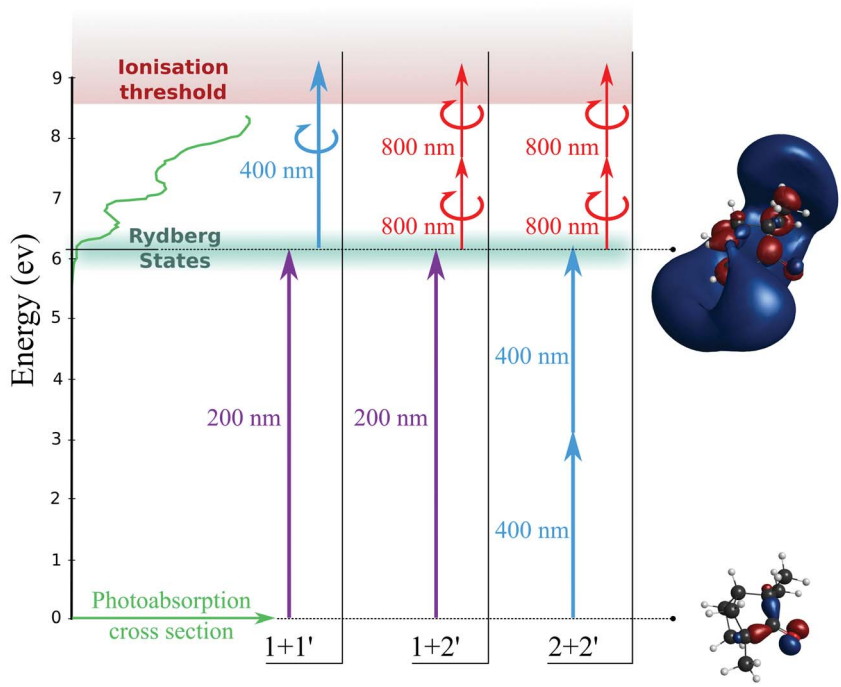

Fig. 7 Pump and probe configuration for time-resolved photoelectron circular dichroism in fenchone molecules. The right panel shows the highest-occupied and 3s Rydberg state molecular orbitals.

