weaker than in the $1 + 1'$ case, and shows rich angular structures. The high-order asymmetric coefficients of the Legendre decomposition, b_3 and b_5, reveal the existence of two energetic components with very different behaviors. Below 0.6 eV, b_3 is negative with a 1.1 ps decay. This is very similar to what was observed in the $1 + 1'$ scheme (Fig. 8). In this energy range, a strong b_5 component exists. The combined effect of b_3 and b_5 is visible in the angular distribution of the PECD, which shows lobes peaking around $\theta \approx \pm 60°$ and 120°. These lobes disappear above 0.6 eV, where b_3 is positive, with a slower 3.3 ps decay, and b_5 is null.

The PECD measurements show a transition below and above 0.6 eV between two energy components separated by ~ 100 meV, which are invisible in the PES. What could be the origin of these components? There are two main differences compared to the $1 + 1'$ scheme. First, the ionization process is here a 2-photon REMPI. In the 3-photon REMPI with the 3s Rydberg as the intermediate state, the main effect of the resonance seemed to be the decrease of the effective number of ionizing photons contributing to the Legendre decomposition of the PECD, leading to a dominant b_1 term. However as we stressed before, this effect depends on the nature of the intermediate state since in camphor, strong b_1 and b_3 were measured.[20] Here, the Rydberg states involved in the 2-photon REMPI are higher in energy, such that we cannot draw any simple conclusion on the effect of the resonance on the Legendre decomposition, even if it probably plays an important role.

The second difference compared to the $1 + 1'$ measurement is the broader bandwidth of the ionizing pulses, which enables a larger range of electron kinetic energies to be reached. Since PECD results from the scattering of the electrons in the molecular potential, it is very sensitive to the electron kinetic energy. For instance, the b_1 parameter in single-photon ionization from the HOMO of camphor or fenchone was predicted to vary abruptly between 0 and 1 eV.[17] The single-photon ionization measurements from Fig. 4 are not able to resolve this effect, since the detection cannot isolate the contribution from the HOMO. By contrast the $2 + 1$ REMPI ionization measurements at 400 nm show a clear electron kinetic energy effect.

The $1 + 2'$ scheme selects a well defined ionization channel through the excitation and REMPI detection. It is thus likely that the transition observed at 0.6 eV is a near-threshold kinetic energy effect. In that case, why would the different component show a different time-dependence? The low energy part of the b_3 reflects the decay of excitation anisotropy, meaning that this component is enhanced by the partial selection of molecular orientations operated by the excitation process, as observed in the $1 + 1'$ scheme. The high energy component is not affected by this decay, which shows that it is more robust to orientation averaging. These observations provide precious information to understand and to model the electron scattering in the chiral molecular potential, near the ionization threshold.

In addition to the picosecond dynamics, the time-resolved PECD measurements show a faster and spectacular evolution in the first few hundreds of femtoseconds (see Fig. 9(e), with a rapid sign change of the recorded asymmetry). As in the $1 + 1'$ case, this demonstrates the high sensitivity of the technique. In order to achieve optimal resolution of these fast dynamics, we performed $2 + 2'$ measurements through the same Rydberg resonances using shorter laser pulses.