



Fig. 11 Modification of the fenchone molecule from the ground electronic state to the equilibrium geometry of the 3s Rydberg state. The stronger bond length changes from the TDDFT calculations are indicated.

( $b_0$ ) decays smoothly while the Legendre coefficients and MPPECD show some oscillations. The MPPECD maximizes at 80 fs, with equally strong but opposite  $b_1$  and  $b_3$ , and at 320 fs, with a dominant contribution of  $b_3$ . At 600 fs, the PECD is almost a pure  $b_3$  term.

The drastic change of the  $b_1/b_3$  ratio between  $1 + 2'$  and  $2 + 2'$  is quite fascinating and opens interesting questions that need to be addressed both experimentally and theoretically:

- With a 2-photon excitation, a stronger selectivity is expected in the orientation of the excited molecules. Does this type of alignment effect enhance the  $b_3$  contribution?

- A 2-photon excitation means that antisymmetric vibrational modes can be excited. Does this type of excitation in the 3s Rydberg states enhance the  $b_3$  contribution compared to the fully symmetric vibrational wavepacket created in one-photon excitation?

These fast oscillations of the PECD reflect rapid changes in the molecular geometry. We have performed TD-DFT calculations to determine the dominant motion of the wavepacket launched by the pump pulse on the 3s potential energy surface. The main gradient of this surface corresponds to the C1–C2 stretching, in the vicinity of the carbonyl group. The main modifications of bond lengths as the molecule goes from the ground electronic state to the equilibrium geometry of the 3s Rydberg state are indicated in Fig. 11. We expect that this main vibrational motion will be accompanied by energy transfers to other vibrational modes, as