

Description of Additional Supplementary Files

Supplementary Data 1: Data set containing experimental raw CO_2^+ coincidences data, as well as initial and final geometries for all trajectory simulations.

Supplementary Movie 1: Showing a typical $(\text{CO}_2)_2^+$ trajectory, simulated using the DFT/BNL ground state potential and preserving the symmetry between the two CO_2 monomers. The movie also shows the time resolved KER following Coulomb explosion calculated at 25 fs probe delay intervals. It demonstrates that events with high (and low) KER appear at shorter time delays compared with the experimental measurements.

Supplementary Movie 2: Showing a typical $(\text{CO}_2)_2^+$ trajectory, simulated using the CASPT2 ground state potential and exhibiting the symmetry breaking dynamics. The movie also shows the time resolved KER following Coulomb explosion calculated at 25 fs probe delay intervals. It demonstrates that events with high (and low) KER appear at longer time delays compared with the DFT/BNL simulation, similar to the experimental measurements.

Supplementary Movie 3: Showing a typical $(\text{CO}_2)_2^+$ trajectory, simulated initiated on the CASPT2 2nd excited state potential and exhibiting the symmetry breaking dynamics leading to the formation of a CO_3 moiety.

Supplementary Movie 4: Showing typical pump-probe simulation including the cation ground state dynamics probed by a 2nd ionization at a 100 fs time delay, resulting in a rapid Coulomb explosion.

Supplementary Movie 5: Showing formation of the CO_3 moiety on the singly ionized 2nd excited state and the formation of a metastable $\text{C}_2\text{O}_4^{2+}$ formation by a 2nd ionization at a 100 fs time delay.