Supplementary Information

Mapping the photochemistry of cyclopentadiene: From theory to ultrafast x-ray scattering

Lauren Bertram,^{*a*} Peter M. Weber,^{*b*‡} and Adam Kirrander^{**a*}

^a Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK.

^b Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA.

E-mail: Adam.Kirrander@chem.ox.ac.uk

Fax: +44 (0)1865 275400; Tel: +44 (0)1865 275400

1 Ground state geometries of CP and BP



Figure S1 Ground state minimum energy geometries of CP (a) and BP (b), optimised at the XMS(3)-CASPT2(4,4)/cc-pVDZ level, with numbering of the C atoms shown.

2 Benchmarking DFT functionals for ground state dynamics



Figure S2 Benchmarking different DFT functionals compared to XMS(3)-CASPT2(4,4)/cc-pVDZ energies along the LIIC pathway from the S₀ minimum energy geometry of CP to the S₁/S₀ MECI to BP. All DFT functionals were computed with the def2-SV(P) basis set.



Figure S3 Benchmarking different DFT functionals compared to XMS(3)-CASPT2(4,4)/cc-pVDZ energies along the LIIC pathway from the S₀ minimum energy geometry of CP to 1,2-hydrogen shift product. All DFT functionals were computed with the def2-SV(P) basis set.

3 Internal coordinate dependence during dynamics simulations



Figure S4 Time-dependence of the C(1)-C(5)-C(4) bond angle throughout the dynamics simulations. The bond distances in the trajectories have been convoluted by a narrow Gaussian for the benefit of plotting.

4 Minimum energy pathway calculation from BP to CP



Figure S5 The minimum energy pathway from BP to CP was calculated using the nudged-elastic band (NEB) method at the PBE0/def2-SVP level of theory. The highest energy geometry was used as a starting point for the transition state optimisation for this pathway.