

Electronic Supporting Information

**Photo-isomerization of the isolated photoactive yellow protein
chromophore: What comes before the primary step?**

Cate S. Anstöter, Basile F. E. Curchod, and Jan R. R. Verlet

Department of Chemistry, Durham University, Durham DH1 3LE, United Kingdom.

Experimental Details

Time-resolved photoelectron imaging of mass-selected *para*-coumaric ketone (*p*CK) was performed using an instrument that has been described previously.¹⁻³ Deprotonated anions of *p*CK, *p*CK⁻, were produced by negative-mode electrospray ionisation of a ~1 mM solution of *p*CK in methanol. Ions were transferred into vacuum through a stainless steel capillary and guided through 3 differentially pumped vacuum regions using a series of ring-electrode RF ion guides. Ions were trapped at the end of these guides and extracted collinearly into a time-of-flight mass-spectrometer at 100 Hz. At the focus of the mass-spectrometer (1.3 m from extraction), the mass-selected ion packet was irradiated with femtosecond pulses at the centre of a perpendicular velocity-map imaging photoelectron spectrometer.² Emitted electrons were detected in the spectrometer using a position sensitive detector (dual multichannel plate coupled to phosphor screen with output monitored using a CMOS camera). Images were analysed using polar onion peeling⁴ to yield the central slice through the 3D electron distribution, which offered the photoelectron spectrum and photoelectron angular distributions. The spectra were calibrated using the well-known photoelectron spectrum of iodide and the spectral resolution as ~5% of the electron kinetic energy (eKE). The raw data is available from at <https://doi.org/10.5281/zenodo.3750967>

Femtosecond pulses were derived from a commercial femtosecond laser system (2.5 W, 800 nm, 35 fs pulses, 1 kHz). Part of the output was used directly as probe pulses (~450 μJ pulse⁻¹). Pump pulses were produced by 4th harmonic generation of the idler output of an optical parametric amplifier, yielding ~5 μJ pulse⁻¹ at 444 nm. Probe pulses were delayed relative to the pump pulses using a motorized optical delay line and recombined collinearly using a dichroic mirror before being directed into the instrument unfocused (beam diameter ~ 3 mm). Pump and probe polarizations were set parallel to the detector.

Computational Details

Energetic minima corresponding to the critical points on the $p\text{CK}^-$ S_0 and S_1 potential energy surfaces were optimized using $\omega\text{B97X-D/aug-cc-pVDZ}$.⁵ Specifically, Density Functional Theory (DFT) was used to optimize the Franck-Condon minimum of the S_0 state, $\text{FC}(S_0)$, while linear response time-dependent DFT (LR-TDDFT) with the Tamm-Dancoff Approximation (TDA)⁶ was used to optimize the S_1 planar minimum, $S_{1,\text{PM}}$. The nature of each stationary point located was confirmed by frequency calculations. All optimization and frequency calculations were carried out using Gaussian 09 (rev D.01).⁷

The vertical excitation energies of the S_0 , S_1 and D_0 states were recalculated using multi-state extended multi-configurational quasi-degenerate perturbation theory (MS-XMCQDPT2).⁸ An (aug)-cc-pVTZ basis set⁹ was used, in which the augmented function was affixed to only the oxygen atoms. Inclusion of the D_0 state in the active space (and therefore detachment to the D_0 plus free electron continuum) was achieved through addition of an orbital characterised by an extremely diffuse p-function ($\alpha = 1\text{E}-10$), transitions to this state were included in the 6-state averaging procedure to mimic detachment to the continuum. Following previously established protocols,¹⁰⁻¹² a DFT/PBE0-based one-electron Fock-type matrix was used to obtain energies of the MCSCF semicanonical orbitals used in perturbation theory. All MS-XMCQDPT calculations were carried out using the Firefly quantum chemistry package.¹³

Dyson Orbitals

The Dyson orbitals were calculated using the equation-of-motion coupled cluster singles and doubles method for electronically excited and ionisation potential energies (EOM-EE/IP-CCSD),^{14,15} using the Pople 6-31+G** basis set.^{16,17} The Dyson orbitals were

then used to model the trends in PADs as a function of changing energy of the photodetached electron. The EOM-EE/IP-CCSD calculations were carried out using the QChem 5.2 computational package¹⁸ and the PADs were modelled using ezDyson v4.¹⁹



Figure S1: Dyson orbitals for S_1 in FC geometry (left) and $S_{1,PM}$ geometry (right).

Energies are calculated for the EOM-EE/IP-CCSD Dyson orbital calculation but, given the reduced basis set used, these are of lower accuracy as those calculated with the XMCQDPT2 level of theory. The EOM-EE/IP-CCSD energies were calculated to be 2.8657/2.6407 eV and 2.8041/2.5220 eV, for the FC and $S_{1,PM}$ geometry, respectively.

References

- 1 J. Lecointre, G. M. Roberts, D. A. Horke and J. R. R. Verlet, *J. Phys. Chem. A*, 2010, **114**, 11216–11224.
- 2 D. A. Horke, G. M. Roberts, J. Lecointre and J. R. R. Verlet, *Rev. Sci. Instrum.*, 2012, **83**, 063101.
- 3 L. H. Stanley, C. S. Anstöter and J. R. R. Verlet, *Chem. Sci.*, 2017, **8**, 3054–3061.
- 4 G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede and J. R. R. Verlet, *Rev. Sci. Instrum.*, 2009, **80**, 053104.
- 5 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- 6 S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **314**, 291–299.
- 7 *Gaussian 09, Revision D.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson,

- D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc., Wallingford CT, 2016.*, .
- 8 A. A. Granovsky, *J. Chem. Phys.*, 2011, **134**, 214113.
- 9 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 10 A. V. Bochenkova, B. Klærke, D. B. Rahbek, J. Rajput, Y. Toker and L. H. Andersen, *Angew. Chem. Int. Ed.*, 2014, **53**, 9797–9801.
- 11 A. V. Bochenkova, C. R. S. Mooney, M. A. Parkes, J. L. Woodhouse, L. Zhang, R. Lewin, J. M. Ward, H. C. Hailes, L. H. Andersen and H. H. Fielding, *Chem. Sci.*, 2017, **8**, 3154–3163.
- 12 C. S. Anstöter, T. E. Gartmann, L. H. Stanley, A. V. Bochenkova and J. R. R. Verlet, *Phys. Chem. Chem. Phys.*, 2018, **20**, 24019–24026.
- 13 A. A. Granovsky, .
- 14 C. M. Oana and A. I. Krylov, *J. Chem. Phys.*, 2009, **131**, 124114.
- 15 C. Melania Oana and A. I. Krylov, *J. Chem. Phys.*, 2007, **127**, 234106.
- 16 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654.
- 17 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265–3269.
- 18 Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. W. III, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. D. Jr, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyayev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O’Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. G. III, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. S. III, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. V. Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184–215.
- 19 S. Gozem and A. I. Krylov, EzDyson, [Http://Iopenshell.Usc.Edu/Downloads/Ezdyson](http://Iopenshell.Usc.Edu/Downloads/Ezdyson).

