Electronic Supplementary Material (ESI) for Chemical Science

Taking the green fluorescence out of the protein: dynamics of the isolated GFP chromophore anion

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1 Experimental Analysis

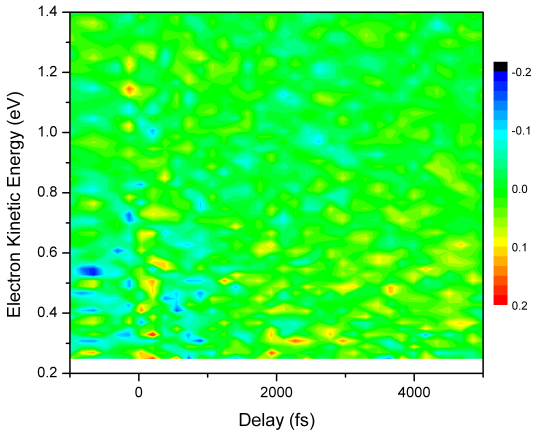

Figure 1: A plot of the difference between the experimental and modelled photoelectron spectra, Figs 4(a) and 4(b) in the paper. The numerical scale is the same as that shown in Figure 4; however the colour scale has been adjusted to make the features more visible.

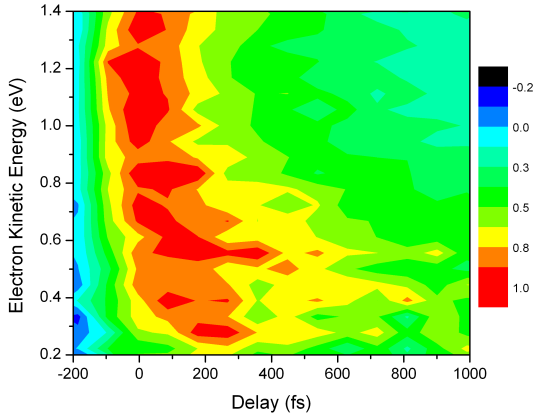

Figure 2: Enlarged portion of the experimental spectra from Fig. 3 in the paper in which each energy slice has been normalised to its maximum intensity.

1.1 Global fit

$$S(e\mathrm{KE}, t) = \sum_i g(t) \otimes c_i(e\mathrm{KE}) e^{-t/\tau_i} \tag{1}$$

When $t = 0$, this expression can be rewritten,

$$S(e\mathrm{KE}, 0) = \sum_i g(t) \otimes c_i(e\mathrm{KE}), \tag{2}$$

showing that the photoelectron spectrum of the initial excited state population is the sum of the decay associated spectra.

2 *Ab initio* Calculations

Structure	State	CASSCF (au)	CASPT2 energy (au)	reference weight[a]
FC	S_0	-641.58927	-643.44721	0.61
	S_1	-641.45926	-643.34034	0.60
	D_0	-641.54655	-643.33445	0.62
FS	S_0	-641.58238	-643.44597	0.61
	S_1	-641.46749	-643.34726	0.60
	D_0	-641.54238	-643.33390	0.62
TI	S_0	-641.53817	-643.40090	0.61
	S_1	-641.48565	-643.35810	0.60
	D_0	-641.52780	-643.31457	0.62

Table 1: Ground and Excited state CASSCF CASPT2 absolute energies for the model GFP chromophore anion and radical.

Structure	State	Configuration	Coefficient	Weight[a]
FC	S_0	22222200000	-0.91210	0.83192
	S_1	22222ud0000	0.89274	0.79699
	D_0	22222u00000	-0.87599	0.76736
FS	S_0	22222200000	-0.90627	0.82133
	S_1	22222ud0000	-0.88658	0.78602
	D_0	22222u00000	-0.86119	0.74164
TI	S_0	22222200000	0.91354	0.83455
	S_1	22222ud0000	-0.91818	0.84306
	D_0	22222u00000	0.87890	0.77247

Table 2: Table showing summary of wavefunction printout of CASSCF calculation from MOLCAS (2, fully occupied; 0, empty; u, spin up; d, spin down). [a] Showing contributions with a weight > 0.05

2.1 Nuclear Geometries

XYZ Coordinate files from CASSCF optimisations and potential energy surface scan.

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  21
MOLPRO CASSCF FC OPT - 6-31G*
C         -0.0000002370       -0.1756586901       -3.6449534381
C         -0.0000115581       -1.2130418447       -2.6244916432
C         -0.0000090666       -0.9261949528       -1.3009138326
C          0.0000032666        0.4084248508       -0.8010151223
C          0.0000141330        1.4464387280       -1.7931161790
C          0.0000144860        1.1910978861       -3.1306844949
O         -0.0000020672       -0.4224742499       -4.8507991840
H         -0.0000210319       -2.2334389368       -2.9685878637
H         -0.0000177546       -1.7295936096       -0.5882556776
H          0.0000253239        2.4712517863       -1.4548318753
H          0.0000221027        1.9886546445       -3.8540971652
C          0.0000022601        0.7588204306        0.5612333256
C         -0.0000090123        0.0145864480        1.7284391915
N         -0.0000147168       -1.3859353746        1.8506379738
C         -0.0000033488       -1.6395162620        3.1082289545
N          0.0000612231       -0.4992745364        3.8927942288
C          0.0000014912        0.6103725689        3.0527359257
H          0.0000054025       -2.6205746547        3.5408467743
H         -0.0001295696       -0.4471726834        4.8829690575
O         -0.0000335734        1.7633833931        3.4396250818
H          0.0000062283        1.8194887882        0.7585874641
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MOLPRO FS OPT  CASSCF 6-31G*
C          0.2082302009       -0.0000077759       -3.6389737034
C          1.2174367975       -0.0000054089       -2.6214614587
C          0.9025713827        0.0000060232       -1.2596434070
C         -0.4431325006        0.0000162234       -0.8095029566
C         -1.4634473202        0.0000136133       -1.8328037023
C         -1.1717283031        0.0000029398       -3.1430252226
O          0.4389442661       -0.0000181655       -4.8621477481
H          2.2454018470       -0.0000130344       -2.9397817537
H          1.6880562790        0.0000071428       -0.5324911536
H         -2.4947607709        0.0000212380       -1.5170024342
H         -1.9517335747        0.0000017132       -3.8856008629
C         -0.8637766943        0.0000285421        0.5783029127
C         -0.0376888343        0.0000132371        1.7413909392
N          1.3424252424       -0.0000065649        1.7999541788
C          1.6683570282       -0.0000208791        3.0581587177
N          0.5591033865        0.0000534331        3.8808614950
C         -0.5784438741       -0.0000011350        3.0918784704
H          2.6676568923       -0.0000171618        3.4405228977
H          0.5450671299       -0.0002194297        4.8723971240
O         -1.7311563816       -0.0000456147        3.5056430495
H         -1.9197597083        0.0000398743        0.7753873181
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MOLPRO 5 Degrees OPT  CASSCF 6-31G*
C          0.2077584595        0.0156167349       -3.6384506798
C          1.2169651816       -0.0254692388       -2.6216764537
C          0.9021472124       -0.0499800831       -1.2600775026
C         -0.4429283660       -0.0316421648       -0.8094055256
C         -1.4631135982        0.0100926852       -1.8316733985
C         -1.1717425567        0.0317158363       -3.1419323124
O          0.4386056533        0.0376449605       -4.8614091835
H          2.2446723077       -0.0400660380       -2.9404716912
H          1.6875872651       -0.0804121396       -0.5334758883
H         -2.4941712598        0.0232621539       -1.5153279472
H         -1.9517105829        0.0633500608       -3.8838671511
C         -0.8633394081       -0.0645419647        0.5788968309
C         -0.0377012867       -0.0219036326        1.7412331310
N          1.3424910122       -0.0074303261        1.7993581099
C          1.6684458865        0.0294567621        3.0569649385
N          0.5592513458        0.0396515567        3.8798040023
C         -0.5783002247        0.0078670180        3.0915042466
H          2.6677073275        0.0479466886        3.4390015641
H          0.5452790271        0.0677465991        4.8709426534
O         -1.7308689585        0.0071571788        3.5056019382
H         -1.9193700973       -0.0635496671        0.7758737953
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MOLPRO 10 Degrees OPT  CASSCF 6-31G*
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C          0.9006507514       -0.1025972988       -1.2613627284
C         -0.4425833379       -0.0642424645       -0.8091459387
C         -1.4620435024        0.0220479288       -1.8281364347
C         -1.1716286560        0.0660835596       -3.1385451778
O          0.4377306073        0.0747263713       -4.8590520576
H          2.2422573900       -0.0837480568       -2.9424845354
H          1.6858315355       -0.1647388269       -0.5363956956
H         -2.4922987025        0.0503762985       -1.5102510080
H         -1.9515005489        0.1305734463       -3.8784252233
C         -0.8622439611       -0.1286735823        0.5807032192
C         -0.0377612678       -0.0431233221        1.7406808397
N          1.3425533676       -0.0122072270        1.7972145861
C          1.6687355809        0.0610424053        3.0530176015
N          0.5599717524        0.0786959993        3.8765156016
C         -0.5777410721        0.0148086477        3.0903618956
H          2.6679522277        0.0991411588        3.4337946901
H          0.5462490142        0.1365758303        4.8663646578
O         -1.7298119407        0.0120980651        3.5057147859
H         -1.9183798744       -0.1276876689        0.7774885460
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MOLPRO 20 Degrees OPT  CASSCF 6-31G*
C          0.1994797572       0.0573036372      -3.6300732532
C          1.2057277287      -0.1343394165      -2.6255244709
C          0.8906726472      -0.2286601376      -1.2676789491
C         -0.4434401030      -0.1275035003      -0.8086654274
C         -1.4562944205       0.0699813869      -1.8126802468
C         -1.1692839636       0.1548718482      -3.1243151770
O          0.4350805769       0.1396941033      -4.8500312429
H          2.2276007625      -0.2141018981      -2.9530012094
H          1.6726813249      -0.3691032970      -0.5498510634
H         -2.4817097888       0.1477952936      -1.4878065438
H         -1.9469795369       0.3002373757      -3.8548281840
C         -0.8603584253      -0.2420199582       0.5890388473
C         -0.0391209136      -0.0761023698       1.7379127075
N          1.3407517661       0.0060423601       1.7838206099
C          1.6704226915       0.1425652402       3.0329725959
N          0.5661554813       0.1510646211       3.8634060296
C         -0.5732882922       0.0172450205       3.0884022662
H          2.6697720560       0.2279061198       3.4059659185
H          0.5550977010       0.2590533892       4.8490807362
O         -1.7215977601      -0.0077781532       3.5127662856
H         -1.9165003019      -0.2597122279       0.7856777598
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MOLPRO 30 Degrees OPT  CASSCF 6-31G*
C          0.2119493752      -0.0471382262      -3.5938744553
C          1.0715622207      -0.5824858764      -2.5685296715
C          0.6882616622      -0.5984806416      -1.2300590464
C         -0.5377567742      -0.0587729915      -0.8091971568
C         -1.3642591176       0.5278335925      -1.8126801156
C         -1.0395298410       0.5202135172      -3.1271271248
O          0.5222954275      -0.0518602144      -4.8006413507
H          2.0135496997      -0.9992108591      -2.8784904458
H          1.3499741079      -1.0117540314      -0.4940540328
H         -2.3020074711       0.9573747010      -1.5007055948
H         -1.6950739760       0.9437087815      -3.8682451742
C         -0.9827052296      -0.0253760686       0.6218584645
C         -0.1024608259       0.0623528442       1.7150111235
N          1.2267094004       0.4643639957       1.6808814126
C          1.6493318470       0.4754438272       2.9068395160
N          0.6730912532       0.0745205783       3.8001909335
C         -0.4976006931      -0.1695081189       3.0951421942
H          2.6476288835       0.7071678150       3.2180292642
H          0.7210164321       0.0961674295       4.7905233510
O         -1.5597381747      -0.5074493785       3.6008802751
H         -1.9047332188      -0.5441432205       0.8400376660
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MOLPRO 40 Degrees OPT  CASSCF 6-31G*
C          0.2152512154       -0.0475525561       -3.5663800396
C          0.9622332778       -0.7660869522       -2.5580868071
C          0.5532423028       -0.7888076217       -1.2333266751
C         -0.5926576024       -0.0949439060       -0.8006076651
C         -1.2865481520        0.6763964963       -1.7801197810
C         -0.9419600879        0.6858078578       -3.0893468130
O          0.5529898434       -0.0459812340       -4.7626740265
H          1.8392518666       -1.2994027419       -2.8794670508
H          1.1282080662       -1.3320235736       -0.5075706080
H         -2.1507836622        1.2299711271       -1.4539981877
H         -1.5053310330        1.2455829906       -3.8153449624
C         -1.0281820188       -0.0559014314        0.6306952917
C         -0.1243646909        0.0712711735        1.7014949376
N          1.1802143445        0.5465598530        1.6238349046
C          1.6444362348        0.5710213044        2.8333523409
N          0.7233625708        0.1121335525        3.7559579358
C         -0.4586455549       -0.1885225188        3.0880395827
H          2.6394437631        0.8541601264        3.1121562273
H          0.8044457462        0.1270990065        4.7441790030
O         -1.4807448799       -0.5871597213        3.6327691340
H         -1.8834931621       -0.6756926786        0.8681058175
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MOLPRO 50 Degrees OPT  CASSCF 6-31G*
C          0.2129947750       -0.0435301137       -3.5453839941
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C          0.3999315666       -0.9556398637       -1.2583802532
C         -0.6330945164       -0.1122875260       -0.7918249039
C         -1.1788337143        0.8158298947       -1.7337195832
C         -0.8194364637        0.8418298562       -3.0364043037
O          0.5656848850       -0.0354527564       -4.7338501938
H          1.6077849701       -1.5775628815       -2.9225313799
H          0.8704060032       -1.6199764803       -0.5578103939
H         -1.9465784437        1.4811118567       -1.3784774778
H         -1.2723799595        1.5239379782       -3.7342159914
C         -1.0541347381       -0.0748971663        0.6357394078
C         -0.1336432825        0.0717826669        1.6922237811
N          1.1622533565        0.5658951231        1.5809627082
C          1.6549668831        0.6003819321        2.7785273822
N          0.7624540595        0.1309936064        3.7225398686
C         -0.4321549690       -0.1875955254        3.0817577074
H          2.6519577113        0.8996224452        3.0333640381
H          0.8654126165        0.1486649896        4.7086108236
O         -1.4340758349       -0.6002664340        3.6560366719
H         -1.8836073676       -0.7257804979        0.8838317154
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MOLPRO 60 Degrees OPT  CASSCF 6-31G*
C          0.2052193993       -0.0449801392       -3.5346377571
C          0.6372483826       -1.0788488734       -2.6096936262
C          0.2181219082       -1.0841739540       -1.2967563298
C         -0.6497649624       -0.0879578439       -0.7840004429
C         -1.0246295687        0.9629651292       -1.6849941427
C         -0.6570950090        0.9873196264       -2.9829021458
O          0.5599346654       -0.0462069250       -4.7199336131
H          1.2959018680       -1.8370130829       -2.9941904416
H          0.5575246900       -1.8532059832       -0.6279722169
H         -1.6632182572        1.7351120629       -1.2939717621
H         -0.9753504572        1.7704876016       -3.6479820265
C         -1.0651208548       -0.0526507675        0.6372957093
C         -0.1338235786        0.0726393880        1.6892694751
N          1.1763828653        0.5237624850        1.5582120305
C          1.6850079592        0.5482078218        2.7493599577
N          0.7894726016        0.1111675140        3.7046627624
C         -0.4232173167       -0.1733442788        3.0780722990
H          2.6935461601        0.8189604375        2.9910613897
H          0.9033418918        0.1297371399        4.6894599970
O         -1.4299434303       -0.5529455323        3.6702408626
H         -1.9243887639       -0.6627313042        0.8825223076
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MOLPRO 70 Degrees OPT  CASSCF 6-31G*
C          0.1894854871       -0.0499562051       -3.5382619409
C          0.3923424909       -1.1956755856       -2.6655717251
C         -0.0059274109       -1.1671644414       -1.3484299026
C         -0.6370573630       -0.0297218637       -0.7787282906
C         -0.7997647757        1.1120686113       -1.6360659137
C         -0.4351082609        1.1168347304       -2.9330915840
O          0.5323341310       -0.0733024387       -4.7252372935
H          0.8700062841       -2.0588475284       -3.0935334282
H          0.1627799013       -2.0197147209       -0.7168974000
H         -1.2602176601        1.9820210614       -1.2033999926
H         -0.5816958202        1.9772906679       -3.5615026261
C         -1.0552507794        0.0142723288        0.6355978962
C         -0.1235807232        0.0719393935        1.6931504292
N          1.2223863467        0.3996474977        1.5579530481
C          1.7308852138        0.3918059856        2.7496683329
N          0.7986291301        0.0476609902        3.7069743338
C         -0.4343491852       -0.1360022858        3.0803097357
H          2.7588514510        0.5769202960        2.9905346134
H          0.9118531705        0.0673616850        4.6917911115
O         -1.4715691720       -0.4187603730        3.6769365228
H         -1.9961439732       -0.4603713319        0.8703438709
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  21
MOLPRO 80 Degrees OPT  CASSCF 6-31G*
C          0.1717209341       -0.0399179849       -3.5523045871
C          0.1305824442       -1.2466963533       -2.7407890160
C         -0.2365894894       -1.2005012261       -1.4156478965
C         -0.6049098790        0.0147191210       -0.7773721424
C         -0.5458498433        1.2063733667       -1.5826045374
C         -0.1917848711        1.2002777928       -2.8814685100
O          0.4948650716       -0.0738408602       -4.7438580972
H          0.4085469638       -2.1685140644       -3.2196973182
H         -0.2507197187       -2.1010156184       -0.8297630213
H         -0.8116101550        2.1301731936       -1.1013310894
H         -0.1605622133        2.1022260390       -3.4665125930
C         -1.0249866028        0.0656479005        0.6320820258
C         -0.1079575991        0.0540681880        1.7011014789
N          1.2699126104        0.2016345919        1.5713551218
C          1.7638827684        0.1696880064        2.7691772764
N          0.7876226728       -0.0204480209        3.7249167187
C         -0.4534359750       -0.0712906790        3.0888737743
H          2.8046090265        0.2365353126        3.0169816991
H          0.8938862288        0.0179035853        4.7099384092
O         -1.5235187627       -0.2012209285        3.6819566794
H         -2.0481952332       -0.1846636436        0.8569184663
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MOLPRO 90 Degrees OPT  CASSCF 6-31G*
C          0.1632101605        0.0154634352       -3.5632276045
C          0.0176229201       -1.2317572675       -2.8290119601
C         -0.3320963668       -1.2370592379       -1.4978455231
C         -0.5839736217       -0.0382006434       -0.7788227006
C         -0.4299462137        1.1937293801       -1.5120466928
C         -0.0850391613        1.2384627377       -2.8118206833
O          0.4756933070        0.0291277873       -4.7578244747
H          0.2071572880       -2.1425322434       -3.3683433625
H         -0.4252993392       -2.1681405997       -0.9698703590
H         -0.6097184625        2.1055721206       -0.9717502040
H          0.0229813446        2.1691868678       -3.3399657424
C         -1.0033106886       -0.0436401210        0.6294832507
C         -0.0992066190       -0.0111336016        1.7065287002
N          1.2862550786        0.0264929487        1.5835145488
C          1.7681407330        0.0517960638        2.7869033895
N          0.7736217219        0.0084530523        3.7413734771
C         -0.4629531046       -0.0065429546        3.0955097534
H          2.8089648172        0.0707163110        3.0422221070
H          0.8754290677        0.1087671675        4.7224636046
O         -1.5444799220       -0.0127189258        3.6825847896
H         -2.0560383150       -0.0688289421        0.8493285299
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