

**Supporting Information for:**

**Solvent Effects on De-Excitation Channels in *p*-Coumaric Acid Methyl Ester Anion, an Analogue of the Photoactive Yellow Protein Chromophore (PYP)**

*Francisco F. García-Prieto<sup>1</sup>, Aurora Muñoz-Losa<sup>2</sup>, M. L. Sánchez<sup>1</sup>, M. Elena Martín<sup>1</sup> and Manuel A. Aguilar<sup>1</sup>*

Correspondence to: M. A. Aguilar (e-mail: maguilar@unex.es)

<sup>1</sup>*Área de Química Física, University of Extremadura, Avda. Elvas s/n, Edif. José M<sup>a</sup> Viguera Lobo 3<sup>a</sup>, planta Badajoz, 06006, (Spain)*

<sup>2</sup>*Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Str. 17, A-1090 Vienna (Austria)*

**Gas phase structures**

**SO**

O	4.992590	-0.374243	-0.000377
C	3.775220	-0.182754	-0.000234
C	2.808628	-1.272815	-0.000194
H	3.208561	-2.280677	-0.000298
C	1.452661	-1.057673	-0.000035
H	0.792965	-1.918098	-0.000015
C	0.881790	0.252682	0.000104
C	1.818218	1.330301	0.000067
H	1.430046	2.344942	0.000170
C	3.179303	1.142548	-0.000090
H	3.856782	1.988914	-0.000113
C	-0.510831	0.517105	0.000282
H	-0.781285	1.568966	0.000349
C	-1.578749	-0.348056	0.000400
H	-1.462482	-1.421365	0.000369
C	-2.940068	0.147066	0.000635
O	-3.316952	1.291430	0.000671
O	-3.842922	-0.868774	0.000868
C	-5.193994	-0.503397	0.001385
H	-5.763099	-1.432174	0.001237
H	-5.451384	0.082010	0.885300

H -5.451928 0.082641 -0.881941

**S1<sup>P</sup>**

O 4.96782 -0.50571 -0.00023  
C 3.74476 -0.27200 -0.00014  
C 2.73313 -1.29829 0.00001  
H 3.07008 -2.32744 0.00004  
C 1.36675 -0.99822 0.00011  
H 0.65469 -1.80894 0.00022  
C 0.89462 0.35339 0.00006  
C 1.87799 1.37915 -0.00009  
H 1.55085 2.41223 -0.00013  
C 3.23846 1.09414 -0.00018  
H 3.97323 1.88986 -0.00029  
C -0.52701 0.70649 0.00015  
H -0.78469 1.75594 0.00010  
C -1.57338 -0.24020 0.00032  
H -1.38238 -1.30086 0.00040  
C -2.94216 0.15704 0.00041  
O -3.39850 1.28815 0.00037  
O -3.80136 -0.91882 0.00056  
C -5.16165 -0.61781 0.00150  
H -5.69129 -1.57170 0.00034  
H -5.45310 -0.04522 0.88503  
H -5.45379 -0.04260 -0.88002

**S1<sup>α</sup>**

O 4.94745 -0.40429 -0.23802  
C 3.73265 -0.19592 -0.13665  
C 3.19021 1.15136 -0.06326  
H 3.89658 1.97050 -0.10497  
C 1.83418 1.36423 0.05438  
H 1.44951 2.37382 0.10541  
C 0.88779 0.29188 0.11458  
C 1.42114 -1.03405 0.03386  
H 0.72082 -1.85756 0.06921  
C 2.77053 -1.28514 -0.08389  
H 3.16225 -2.29260 -0.14115  
C -0.56245 0.54076 0.25181  
H -0.97400 0.60283 1.25132  
C -1.41184 0.69719 -0.87169  
H -1.00499 0.63584 -1.87315  
C -2.79232 0.93410 -0.75962

O -3.48219 1.04417 0.24653  
O -3.41559 1.05250 -2.00105  
C -4.78308 1.28777 -1.97143  
H -5.11386 1.35396 -3.01126  
H -5.33259 0.48377 -1.47410  
H -5.03347 2.22058 -1.45869

### **S1<sup>β</sup>**

O 4.53536 -1.09859 0.21666  
C 3.42504 -0.55060 0.09283  
C 2.22140 -1.27389 -0.26786  
H 2.31830 -2.34253 -0.42925  
C 0.99724 -0.66376 -0.40734  
H 0.14453 -1.27773 -0.68053  
C 0.79644 0.74130 -0.21246  
C 1.98142 1.46683 0.14922  
H 1.89761 2.53717 0.31515  
C 3.21080 0.86271 0.29137  
H 4.07838 1.45531 0.56464  
C -0.44946 1.38403 -0.35918  
H -0.49334 2.46169 -0.23635  
C -1.68106 0.72171 -0.80278  
H -1.93779 0.63035 -1.85459  
C -2.67152 0.15364 0.10610  
O -2.65090 0.19067 1.30662  
O -3.68884 -0.44446 -0.56172  
C -4.69052 -1.03158 0.22446  
H -5.41004 -1.46340 -0.46886  
H -4.28492 -1.81407 0.86657  
H -5.18702 -0.29278 0.85513

### **Water solution structures for the last ASEP/MD cycle**

#### **S0**

O 5.002043 -0.413778 0.018645  
C 3.727143 -0.194604 0.003954  
C 2.786153 -1.261043 -0.006059  
H 3.160872 -2.276358 -0.006416  
C 1.417694 -1.035028 -0.009904  
H 0.750053 -1.885520 -0.015192  
C 0.894816 0.273710 -0.007715  
C 1.811659 1.338781 -0.006394

H	1.444024	2.358690	-0.006070
C	3.186158	1.114434	-0.002706
H	3.870191	1.953255	0.002016
C	-0.537077	0.563641	-0.008981
H	-0.795211	1.614414	-0.017508
C	-1.550463	-0.326080	-0.004042
H	-1.403391	-1.394619	-0.003615
C	-2.946739	0.134653	0.000466
O	-3.293597	1.288733	0.008128
O	-3.808593	-0.866675	-0.002023
C	-5.186208	-0.533281	0.009271
H	-5.721526	-1.475680	0.007702
H	-5.434539	0.035137	0.902788
H	-5.446015	0.045503	-0.873958

### ***S1<sup>P</sup>***

O	4.956046	-0.492293	0.000909
C	3.723451	-0.253410	0.002062
C	2.735559	-1.293360	0.005935
H	3.082830	-2.317479	0.009460
C	1.375489	-1.008077	0.001420
H	0.676129	-1.828763	0.000356
C	0.901355	0.346972	-0.004340
C	1.874487	1.389025	-0.005283
H	1.540121	2.417296	-0.008128
C	3.230032	1.110197	-0.001524
H	3.960782	1.906764	-0.000928
C	-0.511166	0.683505	-0.006098
H	-0.776616	1.729356	-0.008239
C	-1.552590	-0.283575	-0.002254
H	-1.354018	-1.343791	0.001856
C	-2.919373	0.116457	0.002656
O	-3.325851	1.276243	0.012480
O	-3.798820	-0.905797	-0.005375
C	-5.173262	-0.567218	-0.002362
H	-5.715914	-1.507180	-0.003248
H	-5.431968	0.004584	0.886099
H	-5.433462	0.009481	-0.887781

### ***Cl<sup>α</sup>***

O	4.801542	0.376024	-0.544366
C	3.612802	0.181128	-0.262178

C	3.040496	-1.145749	-0.386528
H	3.686480	-1.931844	-0.747981
C	1.728872	-1.363196	-0.026132
H	1.302339	-2.348990	-0.092377
C	0.909530	-0.313588	0.476039
C	1.463529	1.011899	0.548811
H	0.833465	1.810500	0.901202
C	2.765766	1.265156	0.206282
H	3.208096	2.248084	0.275526
C	-0.530790	-0.572479	0.880699
H	-0.725179	-0.271061	1.905615
C	-1.450857	-0.015553	-0.172471
H	-1.139139	0.022205	-1.210356
C	-2.818070	0.039671	0.088923
O	-3.377422	-0.073542	1.188978
O	-3.634504	0.230902	-1.006145
C	-5.019464	0.194631	-0.773531
H	-5.498623	0.347842	-1.738298
H	-5.333711	-0.767886	-0.372286
H	-5.336353	0.980266	-0.089605

***CI<sup>β</sup>***

O	4.117876	-1.330038	-0.269580
C	3.086668	-0.643549	-0.079505
C	1.930512	-1.202451	0.567327
H	1.984516	-2.231227	0.898713
C	0.799756	-0.460991	0.738623
H	-0.069937	-0.868009	1.230251
C	0.732028	0.911830	0.287889
C	1.905622	1.483835	-0.340502
H	1.877663	2.514772	-0.666358
C	3.036191	0.741474	-0.507217
H	3.922792	1.149356	-0.973567
C	-0.462196	1.579639	0.382131
H	-0.469809	2.608116	0.016541
C	-1.653654	0.891352	0.857256
H	-1.885614	0.858776	1.909818
C	-2.413596	0.196525	-0.078582
O	-2.236013	0.191021	-1.301518
O	-3.492994	-0.434720	0.446527
C	-4.167117	-1.339948	-0.384606
H	-4.940955	-1.795455	0.228782
H	-3.496151	-2.118821	-0.748777
H	-4.625888	-0.844623	-1.237064

Table S1. PME parameters used during the molecular dynamics simulations.

rvdw	1.4 nm
rlist	1.3 nm
rcoulomb	1.3 nm
fourierspacing	0.12 nm
pme-order	6

Table S2. Forward and backward free energy values (kcal/mol) in water solution corresponding to the  $\Delta G_{\text{int}}$  free energy values showed in Table 8 of the main manuscript.

	Forward	Backward	Average value	std
$S1^p$	-	-	-	-
$CI^\alpha$	-18.58	-18.68	-18.63	0.07
$CI^\beta$	-30.77	-31.10	-30.93	0.23