Hofmeister Salt Effects on the Photocycle Dynamics of Photoactive Yellow Protein

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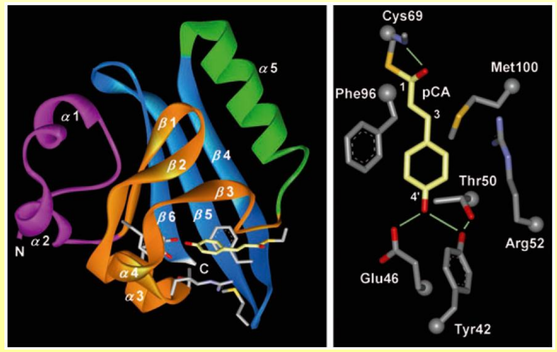
Photoactive yellow protein (PYP) is a water-soluble photosensor protein in purple photosynthetic bacteria. Light excitation of PYP initiates a photocycle with chromophore (*p*-coumaric acid) isomerization, transient protonation and conformational changes. The formation and decay of the consecutive photocycle intermediates were followed with time-resolved UV-vis multichannel absorption spectroscopy. The effect of Hofmeister salts on protein stability was investigated through the salt dependence of the molecular rate constants.

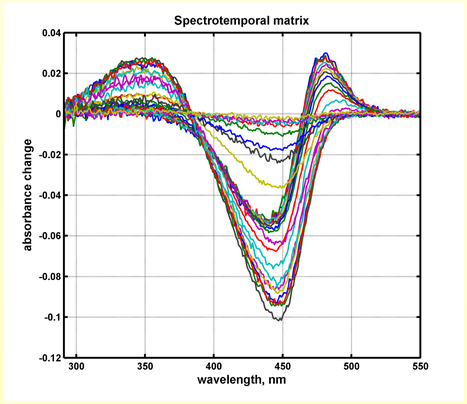


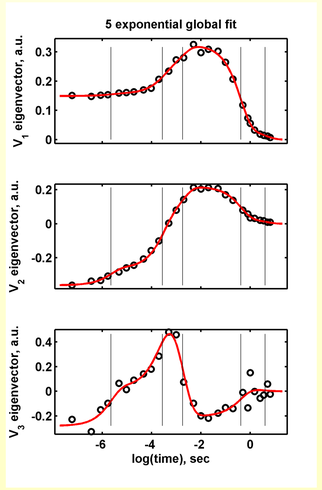
PYP from *Halorhodospira halophila*
Imamoto and Kataoka, Photochem. Photobiol. 83:40–49, 2007

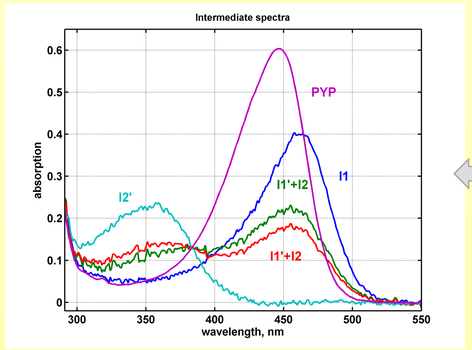
Rate constants, sec^{-1}

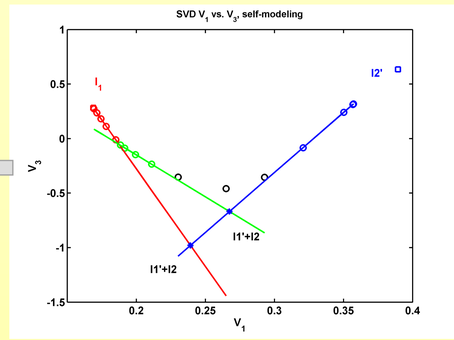
	NaF	NaCl	$NaClO_4$	
I1 to I1'+I2	6.89e+004	1.08e+005	1.28e+005	→
reverse	3.51e+005	3.03e+005	1.07e+005	→
I1'+I2 to I1'+I2	1.7e+004	1.44e+004	2.07e+004	~
reverse	-	-	-	
I1'+I2 to I2'	184	385	1.39e+003	↗
reverse	83	122	158	→
I2' to PYP'	5.66	2.89	1.33	→
reverse	0.602	0.266	0.492	~
PYP' to PYP	0.608	0.301	0.709	~

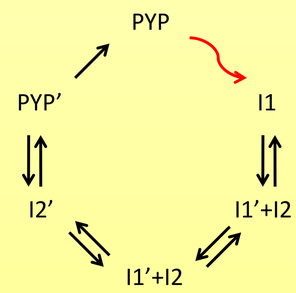
0.66 M NaCl, pH 8.2, 22 °C

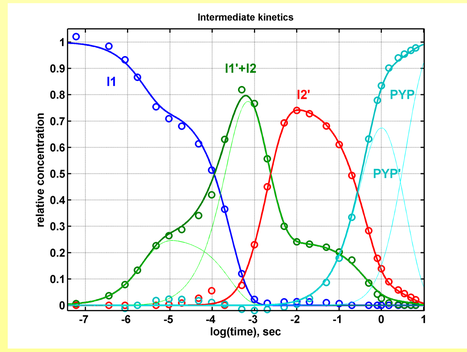




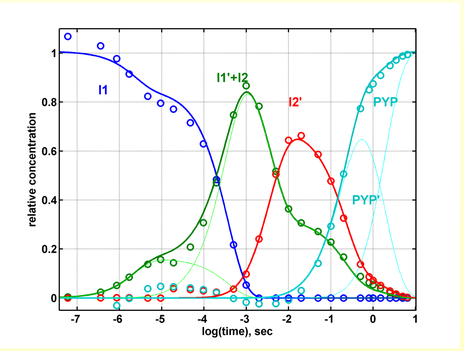




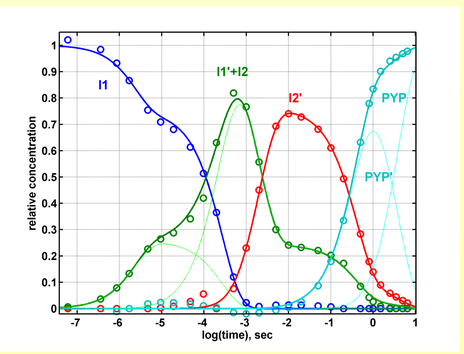




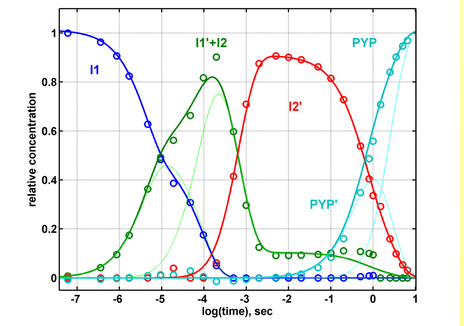
NaF



NaCl



$NaClO_4$



Summary: SVD-EFASM[1] has been successfully applied to obtain the spectra and kinetics of the photocycle intermediates. Fit by the photocycle scheme yielded rate constants with various Hofmeister salt dependences. The forward and reverse rates of the previously established large conformational change (I2 -> I2') both accelerate with increasingly chaotropic salts, in accordance with the fluctuation model of the Hofmeister effect on protein dynamics[2].

[1] Zimányi, L. 2004. J. Phys. Chem. B 108:4199-4209.
[2] Neagu, A., Neagu, M. and Dér, A. 2001. Biophys. J. 81:1285-1294.