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Supplementary Material

New Insights into the State Trapping of UV-Excited Thymine

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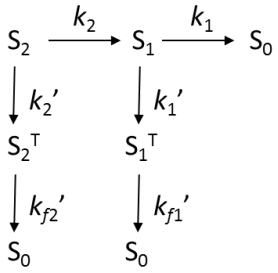
Kinetic model for occupation fitting

Consider the set of reactions in the scheme below.



Part of S_2 population relaxes to S_1 with rate k_2, while another part is trapped in S_2^T, until it later relaxes to S_0 with k_{f2}'. By construction, k_{f2}' << k_2 and k_2'. The same is valid for S_1, with rates k_1 << k_1' and k_{f1}'. Rewriting $k_2' = (\alpha - 1)k_2$ and $k_1' = (\beta - 1)k_1$, the kinetic equations for this set of reactions have as solution the equations SI-1.

$$
\begin{aligned}
S_2(t) &= S_{20}\exp(-\alpha k_2 t) \\
S_2^T(t) &= \frac{(\alpha-1)}{\alpha} S_{20}\left[1-\exp(-\alpha k_2 t)\right] \\
S_1(t) &= \frac{k_2 S_{20}}{\beta k_1 - \alpha k_2}\left[\exp(-\alpha k_2 t) - \exp(-\beta k_1 t)\right] \\
S_1^T(t) &= \frac{k_1(\beta-1)k_2 S_{20}}{\beta k_1 - \alpha k_2}\left[\frac{1-\exp(-\alpha k_2 t)}{\alpha k_2} - \frac{1-\exp(-\beta k_1 t)}{\beta k_1}\right] \\
S_0(t) &= \frac{k_2 k_1}{\beta k_1 - \alpha k_2}\left[\frac{1-\exp(-\alpha k_2 t)}{\alpha k_2} - \frac{1-\exp(-\beta k_1 t)}{\beta k_1}\right]
\end{aligned}
\qquad \text{(SI-1)}
$$

Asymptotically, the population trapped in S_2 is $(1-1/\alpha)$ and in S_1 is $(\beta-1)/\alpha\beta$ ($S_{20} = 1$). The time constant for the fast decay from S_2 to S_1 is $1/k_2$. The time constant for the fast decay from S_1 to S_0 is $1/k_1$.

Asymptotic populations and time constants were obtained by fitting the S_2 state occupation with the function $S_2(t) + S_2^T(t)$ and the S_1 state occupation with $S_1(t) + S_1^T(t)$.

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Cartesian coordinates

Cartesian coordinates of minima and intersection points optimized with ADC(2)/(aug-)cc-pVDZ (in Å).

S0 min

N	-3.757921	0.391909	-0.457421
C	-2.955367	-0.721660	-0.672991
N	-1.599944	-0.434009	-0.563253
C	-0.990970	0.802030	-0.271308
C	-1.928450	1.912081	-0.061501
C	-3.265663	1.653150	-0.164921
O	-3.401520	-1.837122	-0.932248
O	0.237798	0.893292	-0.208360
C	-1.365380	3.269833	0.255801
H	-4.756137	0.224830	-0.528884
H	-0.971100	-1.221558	-0.713817
H	-4.022615	2.429164	-0.021755
H	-2.172402	4.009748	0.370491
H	-0.685924	3.602328	-0.544247
H	-0.776189	3.236749	1.185509

S1 min

N	-3.749358	0.340197	-0.303378
C	-2.950857	-0.721762	-0.667756
N	-1.581449	-0.423846	-0.637897
C	-1.112995	0.866668	-0.382220
C	-1.901943	1.913089	-0.050927
C	-3.312746	1.636664	0.006639
O	-3.370156	-1.838220	-0.980590
O	0.311020	0.871753	-0.502860
C	-1.351272	3.284322	0.251723
H	-4.741649	0.122680	-0.306485
H	-0.963579	-1.140341	-1.010360
H	-4.074116	2.374324	0.263236
H	-1.749343	4.035453	-0.448920
H	-0.251840	3.291133	0.165842
H	-1.611502	3.598649	1.275047

S2 min

N	-3.746974	0.367199	-0.306531
C	-2.952425	-0.732122	-0.655535
N	-1.603630	-0.405055	-0.697130
C	-1.111272	0.867492	-0.411555
C	-1.850471	1.901685	-0.049262
C	-3.335441	1.630815	0.037271
O	-3.417754	-1.845691	-0.899421
O	0.361895	0.829995	-0.548825
C	-1.343547	3.275823	0.279002
H	-4.741293	0.139764	-0.297041
H	-0.931388	-1.125187	-0.954763
H	-4.092843	2.418849	0.083351
H	-1.788478	4.029300	-0.393251

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H	-0.249054	3.306305	0.171019
H	-1.609102	3.551588	1.313768

X10 pp*/S0

N	-6.472869	0.415164	-0.054546
C	-7.676460	1.083781	0.424943
N	-7.515171	2.450152	0.601444
C	-6.660789	3.235047	-0.284851
C	-5.535512	2.494450	-0.730766
C	-5.342296	1.150553	-0.051520
O	-8.663297	0.427524	0.721114
O	-7.082789	4.331444	-0.690862
C	-5.226347	2.504643	-2.212824
H	-6.477878	-0.580395	0.185573
H	-8.394352	2.921515	0.823404
H	-4.449496	0.803497	0.483144
H	-4.155421	2.696060	-2.406538
H	-5.818679	3.299262	-2.693194
H	-5.478564	1.530834	-2.677541

X10 np*/S0

N	-3.734396	0.337524	-0.272188
C	-2.934778	-0.716795	-0.640752
N	-1.541435	-0.488071	-0.498846
C	-1.176345	0.867257	-0.322312
C	-1.865359	1.901915	0.006483
C	-3.355496	1.598381	0.241963
O	-3.358960	-1.803751	-1.044581
O	0.324714	0.800016	-0.525806
C	-1.342894	3.289332	0.250024
H	-4.722158	0.094920	-0.310527
H	-1.021322	-1.042711	-1.180291
H	-4.071546	2.405623	0.023747
H	-1.776499	4.001943	-0.470916
H	-0.243661	3.332008	0.146860
H	-1.591655	3.633161	1.268223

X21 pp*/np*

N	-3.696326	0.430982	0.030353
C	-2.857771	-0.686754	-0.309832
N	-1.660106	-0.300695	-0.893176
C	-1.051456	0.938355	-0.481788
C	-1.834791	1.955446	-0.132858
C	-3.355149	1.691555	-0.336062
O	-3.252097	-1.837558	-0.158375
O	0.290048	0.826474	-0.304954
C	-1.435356	3.082637	0.776127
H	-4.670513	0.147567	0.168662
H	-1.007186	-1.072701	-1.023189
H	-4.056672	2.317383	-0.908713
H	-1.601300	4.067821	0.307413
H	-0.369466	2.982077	1.044713

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H -2.038288 3.057581 1.703737