Supporting informations

Surface hopping investigation of benzophenone excited state dynamics.

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Table S1: Target values used in the reparameterization and semiempirical results obtained with the optimized parameters. Energies in eV, distances in Å, angles in degrees, frequencies in cm^{-1}. For the numbering of atoms see the main text.

	target value	semiemp. value	weight
S_0 geom., $\Delta E(S_1 - S_0)$	3.61	3.53	2.5
S_0 geom., $\Delta E(S_2 - S_0)$	4.40	4.56	2.2
S_0 geom., $\Delta E(S_3 - S_0)$	4.40	4.57	2.2
S_0 geom., $\Delta E(S_4 - S_0)$	5.01	4.76	2.5
S_0 geom., $\Delta E(S_5 - S_0)$	5.01	5.05	0.3
S_0 geom., $\Delta E(T_2 - S_0)$	3.61	3.51	1.3
S_0 geom., $\Delta E(S_1 - T_1)$	0.27	0.27	1.3
S_1 geom., $\Delta E(S_1 - S_0)$	2.95	2.93	1.0
S_1 geom., $\Delta E(T_1 - S_0)$	2.78	2.73	1.0
$\Delta E(S_1 - S_0)$, adiabatic	3.25	3.30	1.2
$\Delta E(T_1 - S_0)$, adiabatic	3.00	3.09	1.2
$\Delta E(T_2 - T_1)$, adiabatic	0.25	0.25	0.2
S_0 geom., R(CO)	1.23	1.23	1.2
S_0 geom., R(CC_1)	1.49	1.45	3.8
S_0 geom., angle OCC_1	119.2	119.5	0.7
S_0 geom., dihed. OCC_1C_2	147.0	150.4	0.6
S_0 geom., freq. CO stretch	1682	1738	1.0
S_1 geom., R(CO)	1.32	1.33	0.7
S_1 geom., R(CC_1)	1.45	1.41	2.7
S_1 geom., angle OCC_1	128.1	113.7	0.5
S_1 geom., dihed. OCC_1C_2	156.6	159.2	0.5
T_1 geom., R(CO)	1.33	1.31	0.5
T_1 geom., R(CC_1)	1.44	1.42	2.7
T_1 geom., angle OCC_1	115.5	114.5	0.4
T_1 geom., dihed. OCC_1C_2	153.6	156.9	0.5

Table S2: Optimized semiempirical parameters (AM1 Hamiltonian). The names of the parameters are those used in the MOPAC 2002 documentation [1]. Note that different parameters are used for carbonyl and phenyl C atoms.

	units	C (phenyl)	C (CO)	O	H
U_{ss}	eV	-49.6687239029	-51.5926064181	-89.0096523334	-10.8491535539
U_{pp}	eV	-39.4813823220	-39.1437309074	-77.8379181410	
β_s	eV	-16.1116257628	-15.2814454696	-26.5060604145	-6.3376982810
β_p	eV	-8.3845965271	-7.2293910728	-28.7179596479	
ζ_s	bohr^{-1}	1.6569306913	1.9117163234	3.2500086920	1.2530447780
ζ_p	bohr^{-1}	1.6551097550	1.5066165958	2.5701260986	
α	Å^{-1}	2.7268920403	2.6970289946	4.8641229413	3.0516601405
g_{ss}	eV	12.2719459805	11.7417627149	5.7214695341	12.7862091987
g_{sp}	eV	11.9324870503	11.6321710371	14.7170663247	
g_{pp}	eV	11.3601849803	11.5241312615	14.1552702814	
g_{p2}	eV	10.1373025627	10.0097524401	12.5185353113	
h_{sp}	eV	2.5377929671	2.4791208390	4.1404905520	
K_1		0.0116442026	0.0113409756	0.2805746085	0.1228093162
K_2		0.0459575575	0.0459132653	0.0814799447	0.0050787568
K_3		-0.0200528574	-0.0201275231		-0.0183256794
K_4		-0.0012600880	-0.0012597132		
L_1	Å^{-1}	5.0367158876	4.9870025958	5.0018065393	4.9997012140
L_2	Å^{-1}	5.0074531553	5.0003839163	7.0018495184	5.0013957709
L_3	Å^{-1}	4.9996150387	4.9914903143		2.0001017670
L_4	Å^{-1}	5.0346091244	5.0224265554		
M_1	Å	1.6017218027	1.6010185123	0.8482873880	1.2000291535
M_2	Å	1.8499416727	1.8512004187	1.4205195400	1.7917419639
M_3	Å	2.0513647895	2.0501383394		2.1018835858
M_4	Å	2.6473006889	2.6501071193		

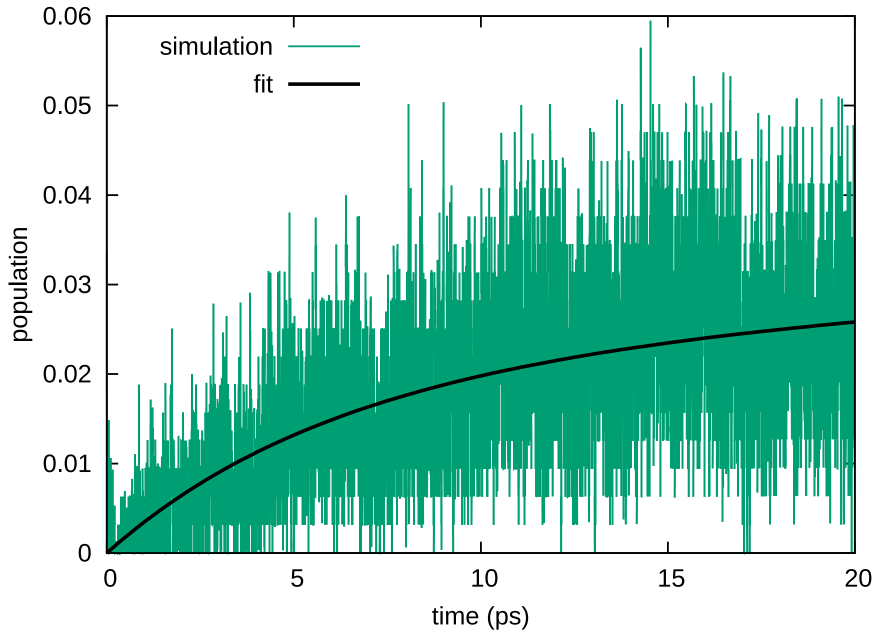

Figure S1: T_3 population. Green curve, simulation; black curve, fit with biexponential decay of S_1.

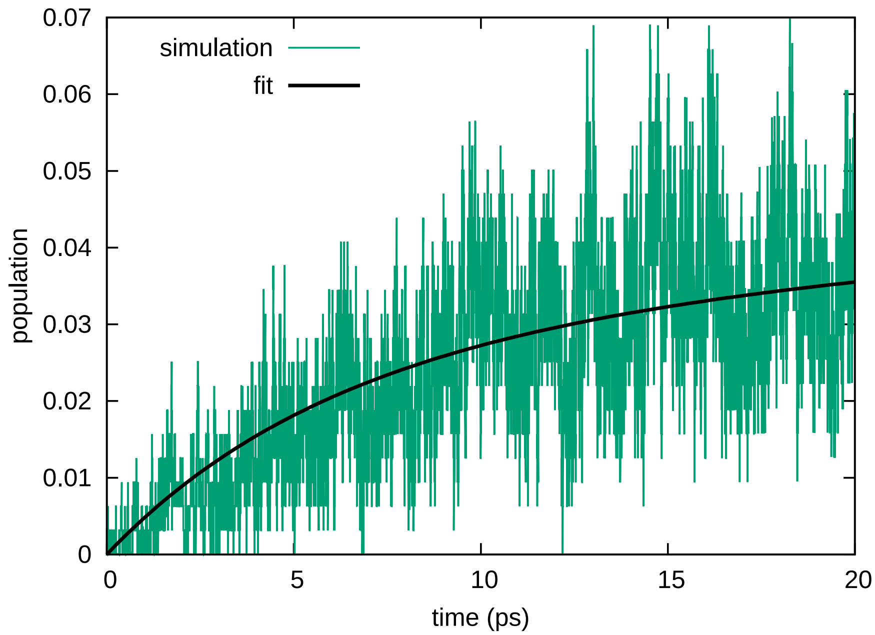

Figure S2: Sum of the populations of T_4 and higher triplets. Green curve, simulation; black curve, fit with biexponential decay of S_1.

Table S3: Radiationless transition rates $\overline{R}_{KL}$ (ps^{-1}) and rate constants $\overline{T}_{KL}$ between spin-diabatic states (or groups of states), averaged over time intervals $[t_1, t_2]$. Some of the rate constants cannot be reliably determined, because in the given time interval very few hops took place, starting from a state with a small population.

state K	state(s) L	t_1, t_2	$\overline{R}_{K\to L}$	$\overline{R}_{L\to K}$	$\Delta\overline{R}_{K\to L}$	$\overline{T}_{K\to L}$	$\overline{T}_{L\to K}$
S_1	T_1	0, 5	0.038	0.005	0.033	0.045	0.051
S_1	T_1	5,10	0.036	0.007	0.029	0.061	0.022
S_1	T_1	10,15	0.027	0.012	0.015	0.058	0.029
S_1	T_1	15,20	0.015	0.014	0.001	0.038	0.030
S_1	T_1	0,20	0.029	0.009	0.019	0.051	0.033
S_1	T_2	0, 5	0.103	0.085	0.019	0.125	1.376
S_1	T_2	5,10	0.080	0.077	0.003	0.136	1.421
S_1	T_2	10,15	0.075	0.073	0.002	0.163	1.034
S_1	T_2	15,20	0.068	0.065	0.003	0.173	0.816
S_1	T_2	0,20	0.082	0.075	0.007	0.149	1.162
S_1	T_3	0, 5	0.004	0.006	-0.002	0.005	—
S_1	T_3	5,10	0.004	0.004	-0.001	0.007	—
S_1	T_3	10,15	0.006	0.007	-0.001	0.014	0.307
S_1	T_3	15,20	0.007	0.006	0.001	0.018	0.227
S_1	T_3	0,20	0.005	0.006	0.000	0.011	0.133
S_1	$T_4 - T_{10}$	0, 5	0.008	0.003	0.005	0.009	—
S_1	$T_4 - T_{10}$	5,10	0.010	0.003	0.007	0.017	—
S_1	$T_4 - T_{10}$	10,15	0.004	0.004	0.000	0.008	—
S_1	$T_4 - T_{10}$	15,20	0.008	0.006	0.002	0.019	—
S_1	$T_4 - T_{10}$	0,20	0.007	0.004	0.003	0.013	—

Table S3 continued.

state K	state(s) L	t_1, t_2	$\overline{R}_{K\to L}$	$\overline{R}_{L\to K}$	$\Delta\overline{R}_{K\to L}$	$\overline{T}_{K\to L}$	$\overline{T}_{L\to K}$
T_1	T_2	0, 5	1.066	1.008	0.059	7.555	25.4
T_1	T_2	5,10	2.567	2.438	0.129	8.165	44.6
T_1	T_2	10,15	3.453	3.271	0.182	8.475	46.1
T_1	T_2	15,20	3.832	3.599	0.233	8.300	44.8
T_1	T_2	0,20	2.730	2.579	0.151	8.124	40.2
T_1	T_3	0, 5	0.225	0.260	-0.034	1.443	—
T_1	T_3	5,10	0.581	0.605	-0.024	1.859	—
T_1	T_3	10,15	0.810	0.853	-0.043	1.985	37.2
T_1	T_3	15,20	0.866	0.937	-0.071	1.876	38.0
T_1	T_3	0,20	0.621	0.664	-0.043	1.791	18.8
T_1	$T_4 - T_{10}$	0, 5	0.162	0.201	-0.039	1.059	—
T_1	$T_4 - T_{10}$	5,10	0.376	0.480	-0.103	1.183	—
T_1	$T_4 - T_{10}$	10,15	0.535	0.670	-0.135	1.313	—
T_1	$T_4 - T_{10}$	15,20	0.540	0.704	-0.164	1.172	—
T_1	$T_4 - T_{10}$	0,20	0.403	0.514	-0.111	1.182	—
T_2	T_3	0, 5	0.191	0.157	0.033	4.997	—
T_2	T_3	5,10	0.445	0.401	0.043	8.185	—
T_2	T_3	10,15	0.634	0.569	0.065	8.934	24.8
T_2	T_3	15,20	0.691	0.590	0.101	8.604	23.9
T_2	T_3	0,20	0.490	0.429	0.061	7.680	12.2
T_2	$T_4 - T_{10}$	0, 5	0.087	0.046	0.040	2.004	—
T_2	$T_4 - T_{10}$	5,10	0.208	0.128	0.080	3.735	—
T_2	$T_4 - T_{10}$	10,15	0.318	0.195	0.123	4.475	—
T_2	$T_4 - T_{10}$	15,20	0.326	0.196	0.130	4.057	—
T_2	$T_4 - T_{10}$	0,20	0.235	0.141	0.093	3.568	—
T_3	$T_4 - T_{10}$	0, 5	0.060	0.063	-0.003	—	—
T_3	$T_4 - T_{10}$	5,10	0.169	0.151	0.018	—	—
T_3	$T_4 - T_{10}$	10,15	0.266	0.247	0.019	11.7	—
T_3	$T_4 - T_{10}$	15,20	0.250	0.218	0.032	10.1	—
T_3	$T_4 - T_{10}$	0,20	0.186	0.170	0.016	5.45	—

References

[1] J. J. P Stewart, *MOPAC 2002*, Fujitsu Limited, Tokio, Japan.