Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting informations

Dynamics of acetone photodissociation: a surface hopping study.

Lucilla Favero, Giovanni Granucci, Maurizio Persico

We show in Tables S1–S6 the state averaged CASSCF (6 electrons/5 MOs) optimized geometries for acetone. Four states (S_0, S_1, T_0, T_1) are averaged with equal weights. Basis set: cc-pVTZ for C and O, cc-pVDZ for H. The cartesian coordinates are given in Å.

Table S1: Minimum of the S_0 state.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.509732
O	1.047142	0.000000	2.145328
C	-1.339319	0.000000	2.206521
H	1.016055	0.000000	-0.373413
H	-1.201640	0.000000	3.280229
H	-0.524143	-0.875814	-0.374261
H	-1.913244	-0.875814	1.914275
H	-0.524143	0.875814	-0.374261
H	-1.913244	0.875814	1.914275

Table S2: Minimum of the S_1 state.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.496859
O	1.293753	0.000000	2.023355
C	-0.925745	-0.882245	2.274822
H	0.650393	0.779401	-0.385914
H	-0.864661	-0.664463	3.337011
H	0.346819	-0.956526	-0.394606
H	-0.680832	-1.935890	2.130630
H	-1.004092	0.178987	-0.370797
H	-1.949378	-0.721881	1.952042

Table S3: Minimum of the T_1 state.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.500306
O	1.274332	0.000000	2.023051
C	-0.927925	-0.899776	2.262065
H	0.674359	0.757513	-0.387729
H	-0.850825	-0.721403	3.330316
H	0.309102	-0.967399	-0.399209
H	-0.706158	-1.951860	2.075758
H	-0.998909	0.215869	-0.365254
H	-1.952412	-0.708708	1.959165

Table S4: Minimum of the T_2 state.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.489920
O	1.369919	0.000000	2.047719
C	-0.922538	-0.875762	2.265695
H	0.572278	0.839873	-0.381177
H	-0.931571	-0.587727	3.312183
H	0.460873	-0.914474	-0.381734
H	-0.595358	-1.917152	2.212303
H	-1.012440	0.055062	-0.388361
H	-1.933369	-0.819174	1.873383

Table S5: S_0/S_1 MXS.

C	0.326304	0.289794	0.155477
C	-0.770697	-0.065336	1.065682
C	-1.582579	-0.022191	-2.208091
O	1.165995	0.731873	-0.551023
H	-0.445844	-0.044718	2.104299
H	-0.871717	-0.711913	-2.624400
H	-1.630185	0.588337	0.950530
H	-1.413521	1.030558	-2.337395
H	-1.079709	-1.076297	0.825137
H	-2.576337	-0.368677	-1.986532

Table S6: S_1/T_1 MXS.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.480999
O	1.536945	0.000000	2.198341
C	-1.135175	-0.000023	2.432175
H	0.524650	0.875314	-0.378449
H	-1.088302	0.875281	3.077388
H	0.524671	-0.875302	-0.378449
H	-1.088276	-0.875335	3.077377
H	-1.005209	-0.000021	-0.405151
H	-2.091319	-0.000043	1.921899

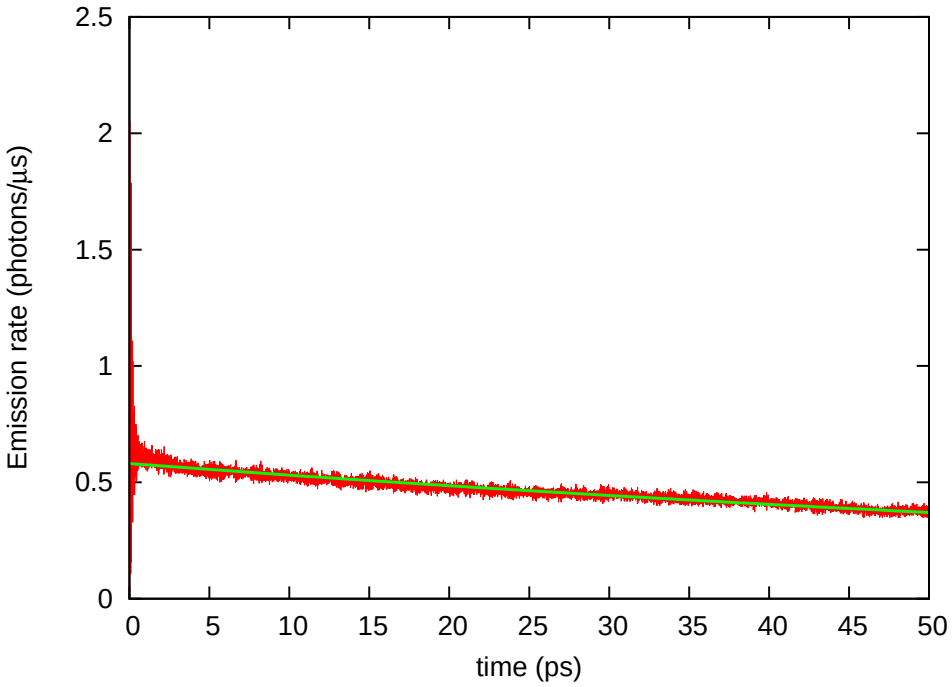

Figure S1: Decay of the fluorescence emission rate $I_F(t)$, evaluated according to Ref. [2]. The green line is a fit with a single exponential: $I_F(t) = K_F e^{-t/\tau_{S_1}}$, with $K_F = 0.58$ μs^{-1} and $\tau_{S_1} = 111$ ps.

Table S7: Semiempirical parameters used in this work (AM1 Hamiltonian). The names of the parameters are those used in the MOPAC 2002 documentation [1]. For the definition of β^{SCF} and β^{CI} see the text.

	units	C	O	H
U_{ss}	eV	-51.8909383808	-97.5139998672	-10.4039536311
U_{pp}	eV	-36.5021722573	-75.9645125304	
β_s^{SCF}	eV			-20.0
β_s^{CI}	eV	-13.5453111948	-28.0752048501	-9.8210776144
β_p	eV	-9.9978260863	-30.6875748839	
ζ_s	bohr^{-1}	1.6943036758	2.6628908640	1.3643861791
ζ_p	bohr^{-1}	1.6866127180	2.6641911805	
g_{ss}	eV	16.3147894450	15.6700451123	15.6659286338
g_{sp}	eV	12.2040592656	14.1791912178	
g_{pp}	eV	9.9440840041	14.5073141904	
g_{p2}	eV	8.9564330097	12.6854923108	
h_{sp}	eV	4.7177809393	3.1245676837	
α	Å^{-1}	2.4952475932	5.4104606534	2.2109546744
K_1		0.0116041336	0.2843623279	0.1179309540
K_2		0.0469381536	0.0963386154	0.0048378260
K_3		-0.0147366125		-0.0205229755
K_4		-0.0015357049		
L_1	Å^{-1}	4.1679997332	4.4460925961	5.0839087501
L_2	Å^{-1}	4.7910101173	6.9519187545	4.7537837140
L_3	Å^{-1}	5.0247436997		1.8492052033
L_4	Å^{-1}	4.8846966670		
M_1	Å	1.6837983391	0.8583319670	1.1606126823
M_2	Å	1.7810685354	1.4286432756	2.3600161003
M_3	Å	2.0756825494		2.4017376334
M_4	Å	2.7856321837		

References

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

[2] T. Cusati, G. Granucci and M. Persico, *J. Am. Chem. Soc.*, 2011, **133**, 5109-5123.