Supporting Information

The non-adiabatic deactivation of 9H-adenine: a comprehensive picture based on mixed quantum-classical dynamics

Mario Barbatti and Hans Lischka

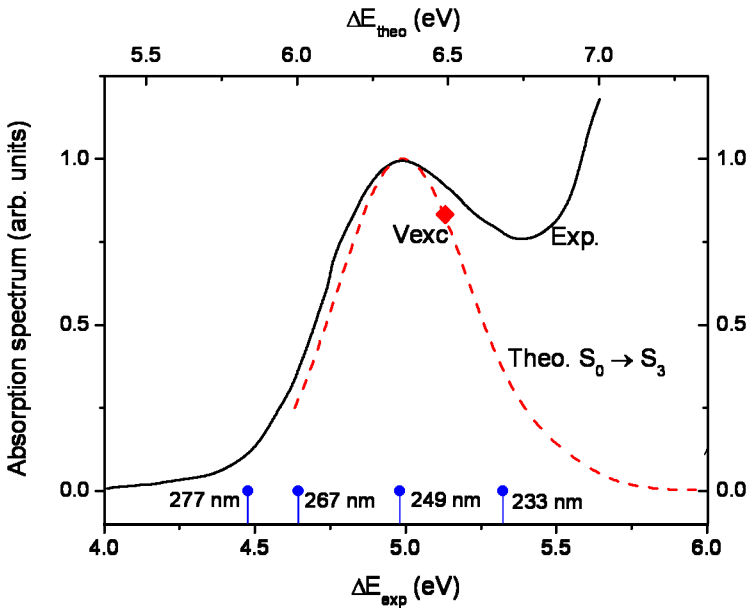

Fig. SI1 – 9H-Ade absorption spectrum in gas phase. Solid line (bottom abscissa): experimental results of Clark et al. J. Phys. Chem. 69, 3615 (1965). Dashed line (top abscissa): MR-CIS data used as initial condition for the dynamics. In the simulation a phenomenological broadening 0.2 eV of was used and only $S_0 \rightarrow S_3$ transitions were included. Transient spectra are usually measured at 277 and 267 nm. The maximum of the band is at 249 nm. Ultrafast dissociation trough N-H dissociation is estimated to occur below 233 nm. The theoretical vertical excitation is indicated as well.

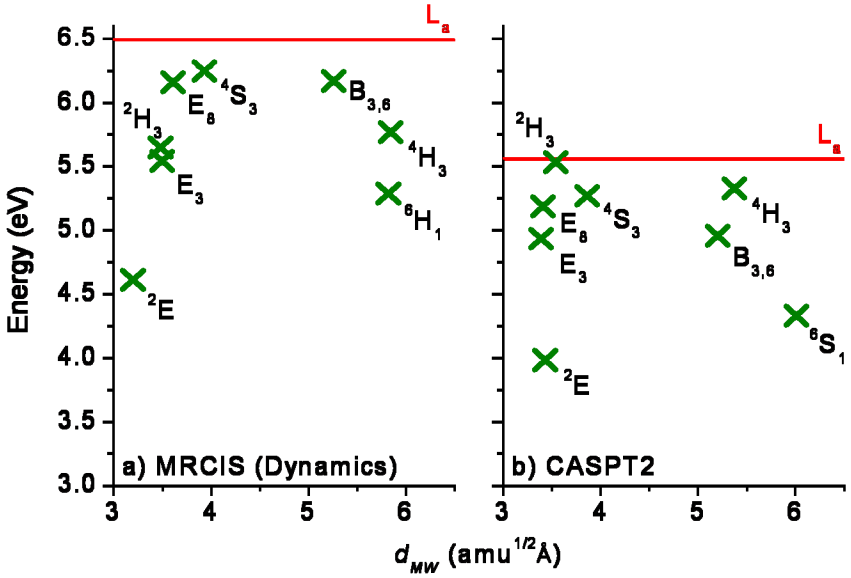

Fig. SI2 – Comparison between the vertical excitation (La) and the conical intersections in 9H-adenine computed at the a) MR-CIS(6,4)/SA-4-CASSCF(12,10)/Bmix level and at the b) CASPT2/SA-5-CASSCF(16,12)/6-31G* level. The graphs give the energy (relative to the ground state minimum) as a function of the mass-weighted distance between the conical intersection and the ground state minimum.

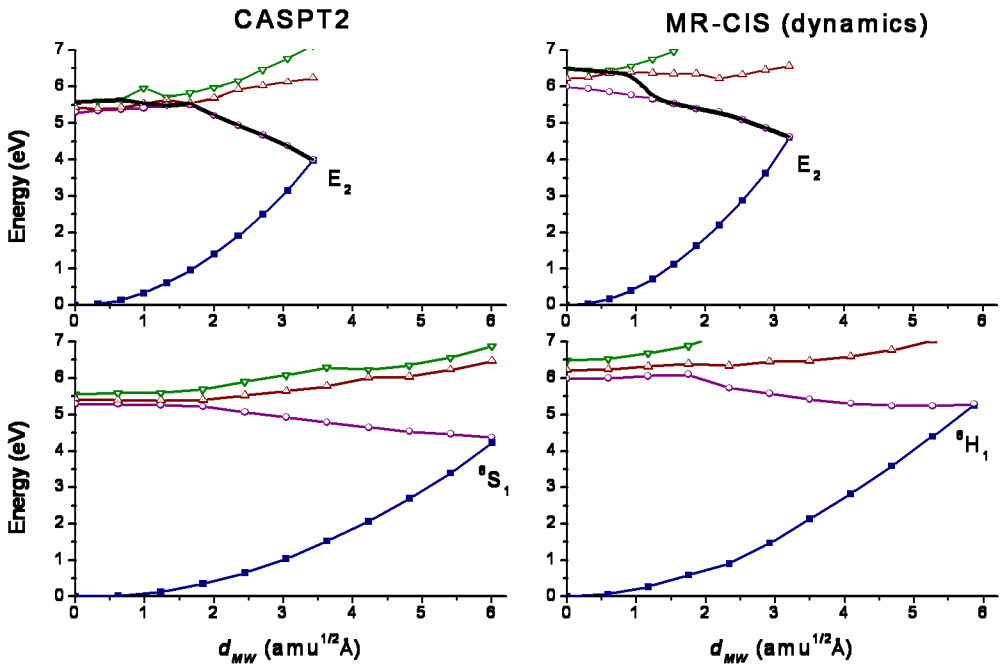

Fig. SI3 – Linearly interpolated paths between the ground state minimum (FC) and the conical intersections puckering at the C_2 atom (E_2, top) and at the C_6 atom ($^6S_1$ and $^6H_1$, bottom). The paths were calculated at the MR-CIS(6,4)/SA-4-CASSCF(12,10)/Bmix level used in the dynamics simulations (right) and at the CASPT2/SA-5-CASSCF(16,12)/6-31G* level (left). The thick lines in the FC-E2 paths show the diabatic $\pi\pi^*$ connection.

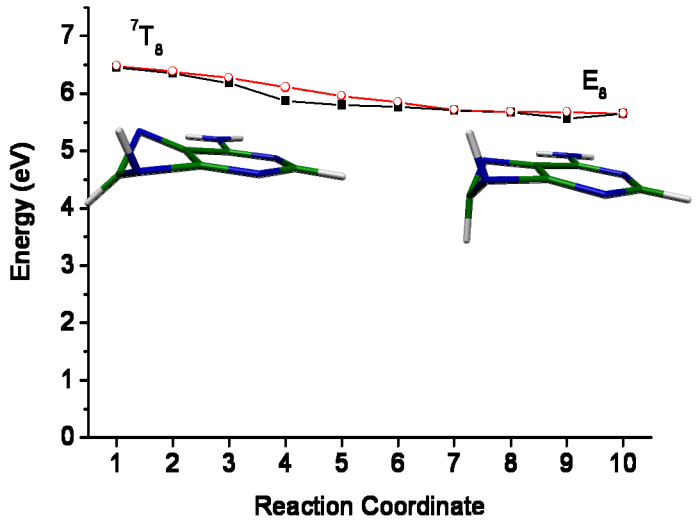

Fig. SI4 – Ground and first excited state along the path on the crossing seam connecting the $^7T_8$ and the E_8 conical intersections. CASSCF(12,10)/6-31G*.

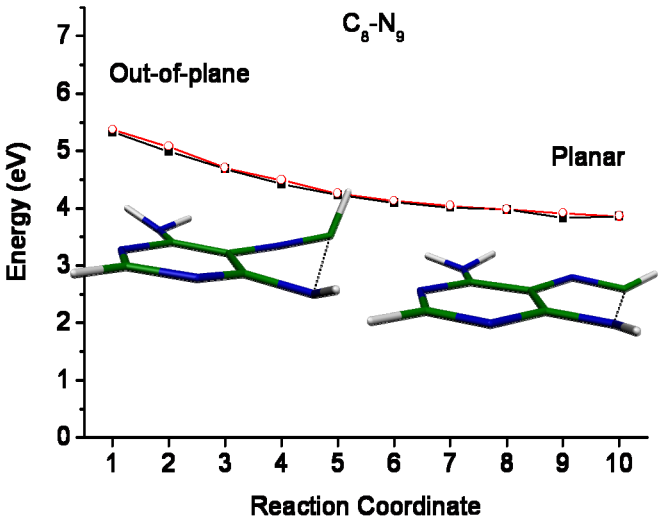

Fig. SI5 – Ground and first excited state along the path on the crossing seam connecting the out-of-plane and the planar C_8-N_9 ring-opening conical intersections. CASSCF(12,10)/6-31G*.

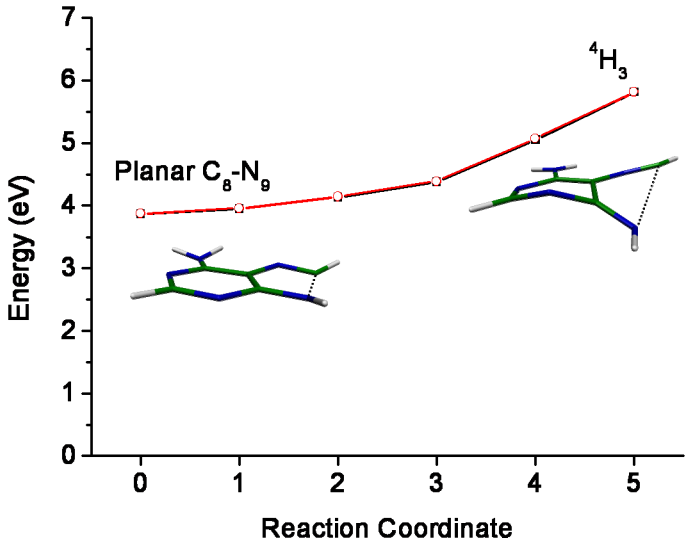

Fig. SI6 – Ground and first excited state along the path on the crossing seam connecting the $^4H_3$ and the planar C_8-N_9 ring-opening conical intersections. CASSCF(12,10)/6-31G*.

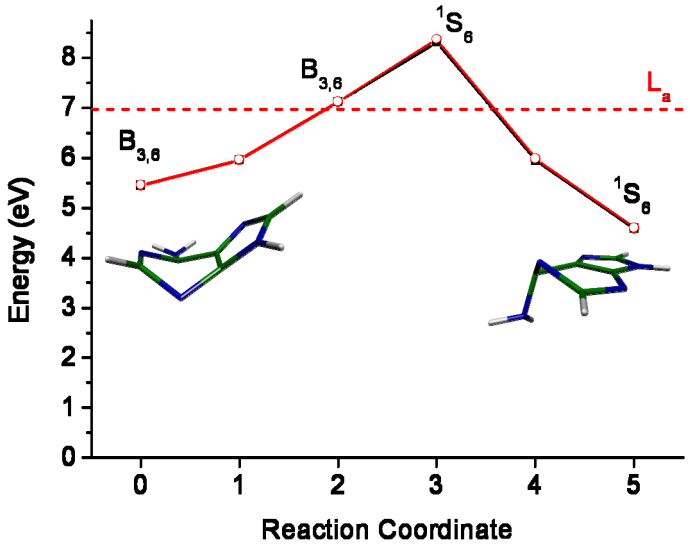

Fig. SI7 – Ground and first excited state along the path on the crossing seam connecting the $B_{3,6}$ and $^1S_6$ MXSs. The dashed line shows the Vertical excitation energy into the $\pi\pi^*$-L_a state at the same level. CASSCF(12,10)/6-31G*.

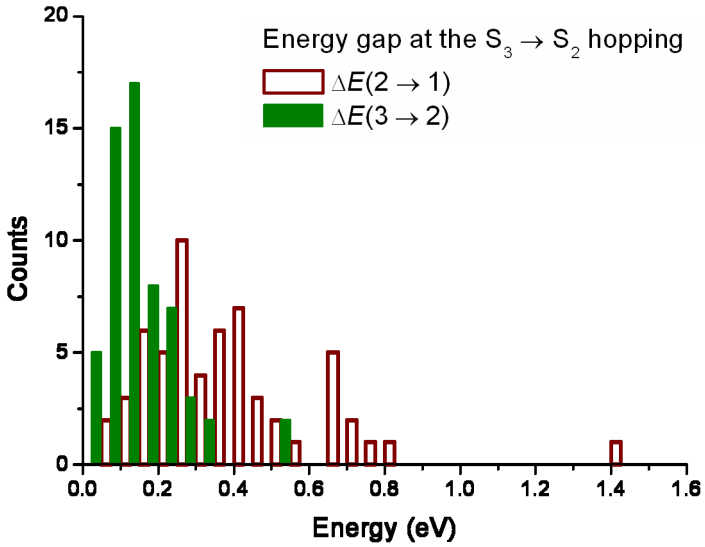

Fig. SI8 – ΔE_{32} and ΔE_{21} energy gaps at the time of the $S_3 \rightarrow S_2$ hopping.

Complete Reference 43:

Lischka, H.; Shepard, R.; Shavitt, I.; Pitzer, R. M.; Dallos, M.; Müller, T.; Szalay, P. G.; Brown, F. B.; Ahlrichs, R.; Boehm, H. J.; Chang, A.; Comeau, D. C.; Gdanitz, R.; Dachsel, H.; Ehrhardt, C.; Ernzerhof, M.; Höchtl, P.; Irle, S.; Kedziora, G.; Kovar, T.; Parasuk, V.; Pepper, M. J. M.; Scharf, P.; Schiffer, H.; Schindler, M.; Schüler, M.; Seth, M.; Stahlberg, E. A.; Zhao, J.-G.; Yabushita, S.; Zhang, Z.; Barbatti, M.; Matsika, S.; Schuurmann, M.; Yarkony, D. R.; Brozell, S. R.; Beck, E. V.; Blaudeau, J.-P., *COLUMBUS, an ab initio electronic structure program, release 5.9.1* **2006**, www.univie.ac.at/columbus.

Cartesian coordinates of stationary points, minima on the crossing seam (MXS), and conical intersections (CI)

XYZ format in Å, optimized at MR-CIS(6,5)/SA-3-CAS(12,10)/6-31G* level.

```
Min S0
15

      c         0.003655         0.009274         0.009595
      c         0.019378         0.007606         1.404115
      c         1.253576         0.001270         2.019365
      c         2.303871        -0.009405         0.081367
      c        -0.380028        -0.007102         3.467938
      n         2.427424        -0.004203         1.416316
      n         1.166079        -0.006981        -0.638883
      n        -0.997950        -0.001044         2.351559
      n        -1.160567         0.069664        -0.718103
      n         0.975779        -0.005188         3.365713
      h         3.217211        -0.020271        -0.483742
      h        -1.073712        -0.234700        -1.663218
      h        -1.980488        -0.252050        -0.251784
      h        -0.859423        -0.014483         4.427176
      h         1.637891        -0.007301         4.107052

MXS E2
15

      c         0.021620         0.110338        -0.050811
      c        -0.017251         0.157621         1.395123
      c         1.258887         0.041230         2.050771
      c         1.998482         0.895267         0.340471
      c        -0.419710        -0.553596         3.323523
      n         2.432330         0.134619         1.430693
      n         1.180094         0.345863        -0.632878
      n        -1.010523        -0.243657         2.250113
      n        -1.085478        -0.248953        -0.771369
      n         0.923318        -0.428648         3.310557
      h         1.931976         1.968958         0.483541
      h        -0.892384        -0.566833        -1.696861
      h        -1.773067        -0.777670        -0.279872
      h        -0.922334        -0.897072         4.208706
      h         1.551205        -0.640614         4.051951

MXS 6S1
15

      C         0.451383        -1.904027         0.415445
      C        -0.501572        -0.740463         0.348144
      C         0.031704         0.414361        -0.035734
      C         2.182798        -0.350969        -0.038890
      C        -2.120320         0.577030         0.100860
      N         1.369309         0.668954        -0.305899
      N         1.762965        -1.343733         0.827645
      N        -1.866606        -0.655851         0.400459
      N         0.547614        -2.558834        -0.841733
      N        -1.015799         1.289397        -0.175026
```

H	3.233626	-0.226497	-0.222495
H	0.983497	-3.456713	-0.765824
H	-0.351989	-2.671003	-1.263724
H	-3.097435	1.014676	0.078202
H	-0.966360	2.253097	-0.414056

CI E3
15

c	0.057052	-0.074694	-0.068806
c	0.038330	-0.263431	1.399915
c	1.248012	-0.193094	2.035017
c	2.253357	0.003527	0.095828
c	-0.376431	0.187496	3.443288
n	2.179226	-0.785982	1.188404
n	1.159592	0.071231	-0.756825
n	-0.978044	-0.025760	2.293829
n	-1.117298	0.119717	-0.658168
n	1.006745	0.091668	3.319586
h	2.728240	0.990376	0.173208
h	-1.151710	0.217868	-1.647486
h	-1.959391	0.036237	-0.135875
h	-0.849627	0.368529	4.384914
h	1.669950	0.118734	4.060088

MXS B3,6
15

c	0.017188	0.221239	-0.104768
c	0.008153	0.098504	1.371783
c	1.235309	0.061330	1.879945
c	2.086223	-0.670916	-0.132927
c	-0.163158	-0.824046	3.259297
n	2.192583	0.382446	0.883347
n	0.965197	-0.628416	-0.772318
n	-0.882167	-0.469612	2.259697
n	-1.149465	0.482537	-0.814353
n	1.171001	-0.588263	3.067679
h	2.907511	-1.329102	-0.336101
h	-1.188296	-0.005683	-1.685366
h	-1.987766	0.359431	-0.283851
h	-0.523810	-1.238860	4.178311
h	1.888654	-0.692915	3.747868

MXS E8
15

C	-0.048937	0.050093	-0.040562
C	-0.114402	0.059943	1.391787
C	1.149968	0.067539	2.062705
C	2.247982	-0.036360	0.161953
C	-0.334820	-0.589430	3.199514
N	2.327772	-0.028925	1.461348
N	1.120840	0.012366	-0.604825
N	-1.164375	0.020224	2.269164
N	-1.180810	0.116095	-0.768584
N	0.861466	0.112649	3.490075

```
      H         3.165315        -0.088998        -0.394300
      H        -1.114971        -0.042035        -1.748782
      H        -2.048951        -0.068399        -0.319318
      H        -0.260430        -1.668256         3.236810
      H         0.662571         1.062843         3.760180

MXS 4S3
15

      C         0.878305         2.977597        -0.132284
      C         0.901886         1.725729         0.481594
      C         0.033417         1.367850         1.671559
      C        -1.188560         3.014294         0.569769
      C         1.297137        -0.340315         0.894382
      N        -1.035620         1.650146         0.843657
      N        -0.235829         3.747334         0.083401
      N         1.627856         0.590129         0.081867
      N         1.785567         3.388988        -1.079558
      N         0.349365        -0.007745         1.834887
      H        -2.169752         3.416217         0.733215
      H         1.712626         4.357408        -1.304917
      H         2.722965         3.076756        -0.951177
      H         1.696634        -1.334468         0.846805
      H         0.213799        -0.503292         2.683606

MXS 4H3
15

      C        -0.533933         3.729612         0.099730
      C         0.674988         3.118804        -0.109529
      C         0.668211         1.656561        -0.382919
      C        -1.632684         1.743658         0.209698
      C         2.992347         3.703228        -0.156371
      N        -0.425168         1.119303         0.306085
      N        -1.722970         3.021776         0.196326
      N         1.798177         3.947897        -0.233670
      N        -0.694566         5.068706         0.225581
      N         1.513082         1.023532        -1.079996
      H        -2.509557         1.128865         0.289493
      H        -1.606220         5.435313         0.358408
      H         0.076966         5.678867         0.097438
      H         3.790325         4.431460        -0.204163
      H         1.322391         0.039936        -1.122751

CI 2H3
15

      c        -0.033337        -0.043572         0.058035
      c        -0.080430        -0.202746         1.437488
      c         1.203891        -0.127968         1.984189
      c         2.242611         0.640841         0.139225
      c        -0.383379         0.112152         3.513706
      n         2.249722        -0.357093         1.195006
      n         1.181947         0.091117        -0.588364
      n        -1.068604         0.006887         2.410550
      n        -1.094674         0.092007        -0.721288
      n         1.014698         0.048866         3.297065
```

h	3.156063	0.812310	-0.396199
h	-0.974241	0.158365	-1.706444
h	-2.010141	-0.021050	-0.349035
h	-0.788960	0.246231	4.494806
h	1.725880	0.117172	3.988889