SUPPORTING INFORMATION

Site-Specific Photo-Oxidation of the Isolated Adenosine-5´-Triphosphate Dianion Determined by Photoelectron Imaging

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Contents

Section S.1 Computational details

S.1.1 $[ATP–H_2]^{2–}$ ground state optimization and excited states calculation

S.1.2 Repulsive Coulomb Barrier calculations

S.1.3 Ab initio molecular dynamics

References

Section S.1 Computational details

Section S.1.1 $[ATP–H_2]^{2–}$ ground state optimization and excited states calculation

Methods

An initial conformational space sampling of $[ATP–H_2]^{2–}$ was done using the OPLS_2005 force field [1] and MACROMODEL 11.5. [2] with the Monte Carlo method. The resulting minimum energy conformer was optimized with the Møller-Plesset second order perturbation theory using the resolution of identity approximation (RI-MP2)[3] and the def2-TZVP [4] basis set. The ground state energy was then redefined at the def2-QZVP level of theory to be compatible with the five lowest-lying excitation energies calculated with the Algebraic Diagrammatic Construction scheme for the polarization propagator at the second order (ADC(2)) [5] method and def2-QZVP[4] basis set. Scaled opposite spin was used with a scaling factor of 1.3 [6]. The energies are reported in Table S1. All the quantum chemical calculations were performed with the TURBOMOLE suite, v. 7.0 [7].

Data

Table S1: energy and oscillator strength (fos) for the first five singlet excited states of $[ATP–H_2]^{2–}$

State	Energy (eV)	fos
S_1	5.048	0.055
S_2	5.330	0.212
S_3	5.538	0.001

S_4	6.072	0.003
S_5	6.269	0.099

Table S2: relevant information about S_2 transition: orbitals and transition dipole moment

Occupied orbital	Virtual orbital	coefficient
130	133	0.7033
TDM component	Left/right moment	Transition moment
x	0.545	0.298
y	0.071	0.005
z	1.149	1.320

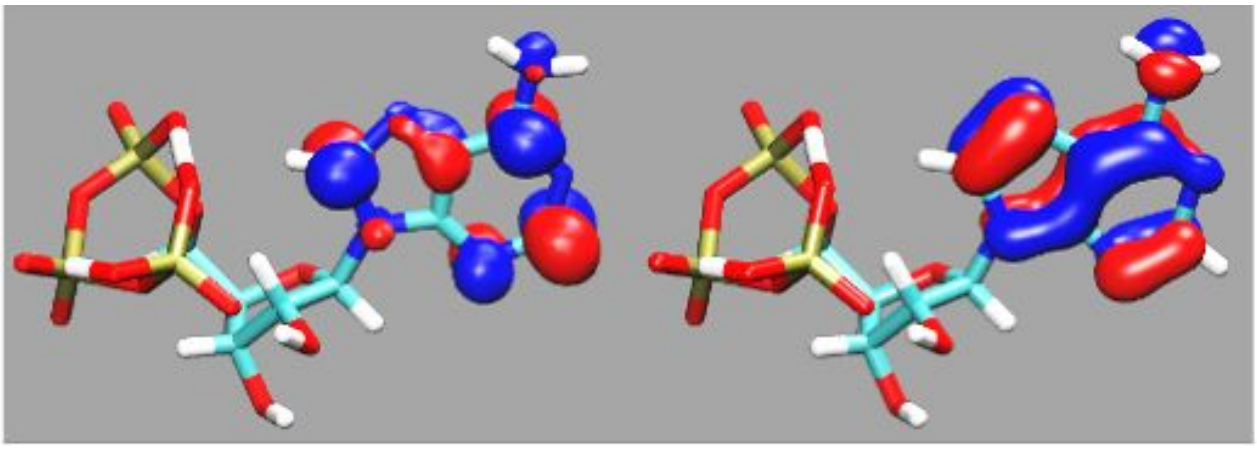

Figure S1: natural transition orbitals for the S_2 $^1\pi\pi^*$ state (isovalue = 0.046)

Cartesian coordinate of $[ATP–H_2]^{2–}$ optimized geometry at RI-MP2/def2-TZVP level of theory in the xyz format (Å).

45

$[ATP-H_2]^{2-}$

O	-0.3181870	-1.2406154	-7.3746486
C	-1.4599304	-2.0884473	-7.4606841
H	-1.1733859	-3.1065930	-7.1805698
H	-1.8715451	-2.0758802	-8.4756371
C	-2.5003129	-1.5540728	-6.4974069
H	-3.3837408	-2.2008788	-6.5354468
O	-1.9892416	-1.5840671	-5.1409899
C	-1.8431705	-0.2561629	-4.6714926
H	-2.6348058	-0.0030107	-3.9594463
N	-0.6039278	-0.1513380	-3.9258059
C	0.6816484	-0.1759440	-4.4077936
H	0.8899289	-0.2572101	-5.4664305
N	1.6065407	-0.1038108	-3.4566580
C	0.8737721	-0.0300463	-2.3029117
C	1.2519355	0.0981189	-0.9627561
N	2.5785931	0.0993505	-0.5940390
H	2.7532239	0.5610243	0.2865291
H	3.2055120	0.3512720	-1.3464607
N	0.3126745	0.1785309	-0.0182617
C	-0.9792366	0.1208615	-0.4121159
N	-1.4739853	0.0025322	-1.6419745
C	-0.5024709	-0.0607779	-2.5623005
C	-2.8959137	-0.1153181	-6.7603570
H	-2.8337256	0.1443776	-7.8175679
C	-1.9087309	0.6598212	-5.8897669
H	-0.9384563	0.6936984	-6.3806660
O	-2.3587640	1.9433955	-5.5450522
H	-1.8747739	2.5573965	-6.1757128
O	-4.2096896	0.1105214	-6.2429546
P	0.8861805	-1.3158286	-8.4439069
O	1.3797817	-2.6848327	-8.6731501
P	-0.9089972	0.3840356	-10.1429143
O	-2.1511015	-0.4176477	-10.2574986
P	-0.1406236	2.5675946	-8.3276243
O	1.2177706	2.0520405	-7.9002494
H	-4.1779658	1.0489607	-5.9830598
O	0.3260587	-0.6498065	-9.7715730

O	-1.0199776	1.2671310	-8.7803469
O	-0.0363970	3.4001405	-9.6807404
O	-0.9477792	3.3117375	-7.3114358
O	-0.3873211	1.2754942	-11.2274697
O	1.8913781	-0.3116061	-7.8236158
H	1.5960120	0.7166469	-7.8838971
H	-0.0563997	2.7338907	-10.4288747
H	-1.7081754	0.1851238	0.3904611

Section S.1.2 Repulsive Coulomb Barrier (RCB) calculations

Methods

The RCB maps were calculated using the Local Static Approximation model [8] employing the $[ATP–H_2]^{2–}$ minimum energy geometry and calculating the energy for the monoanion plus an electron, located as a point charge along the two planes of interest, with an interval of 0.5 Å. These two planes pass through the transition dipole moment of the S_2 state. The plane showed in the main text (xz) is the one passing through the adenine ring, while in figure S1 is reported the RCB map along the plane orthogonal to it (yz). The coordinates of the planes (Å), which refer to the optimized geometry mentioned above, are given in the following (bottom left BL, top left TL, top right TR and bottom right BR). All the calculations are performed at MP2/def2-SVP[4] level of theory with the TURBOMOLE suite, v. 7.0 [7].

Data

XZ plane coordinates:
BL: (-16.69, 0.38, 27.28); TL: (-24.83, 0.24, -8.81); TR: (18.48, -0.36, -21.01); BR: (26.62, -0.24, 15-09)

YZ plane coordinates:

BL: (-3.43, -6.14, -14.82); TL: (1.41, -6.07, 6.64); TR: (1.52, 6.93, 6.55); BR: (-3.26, 6.85, -14.90);

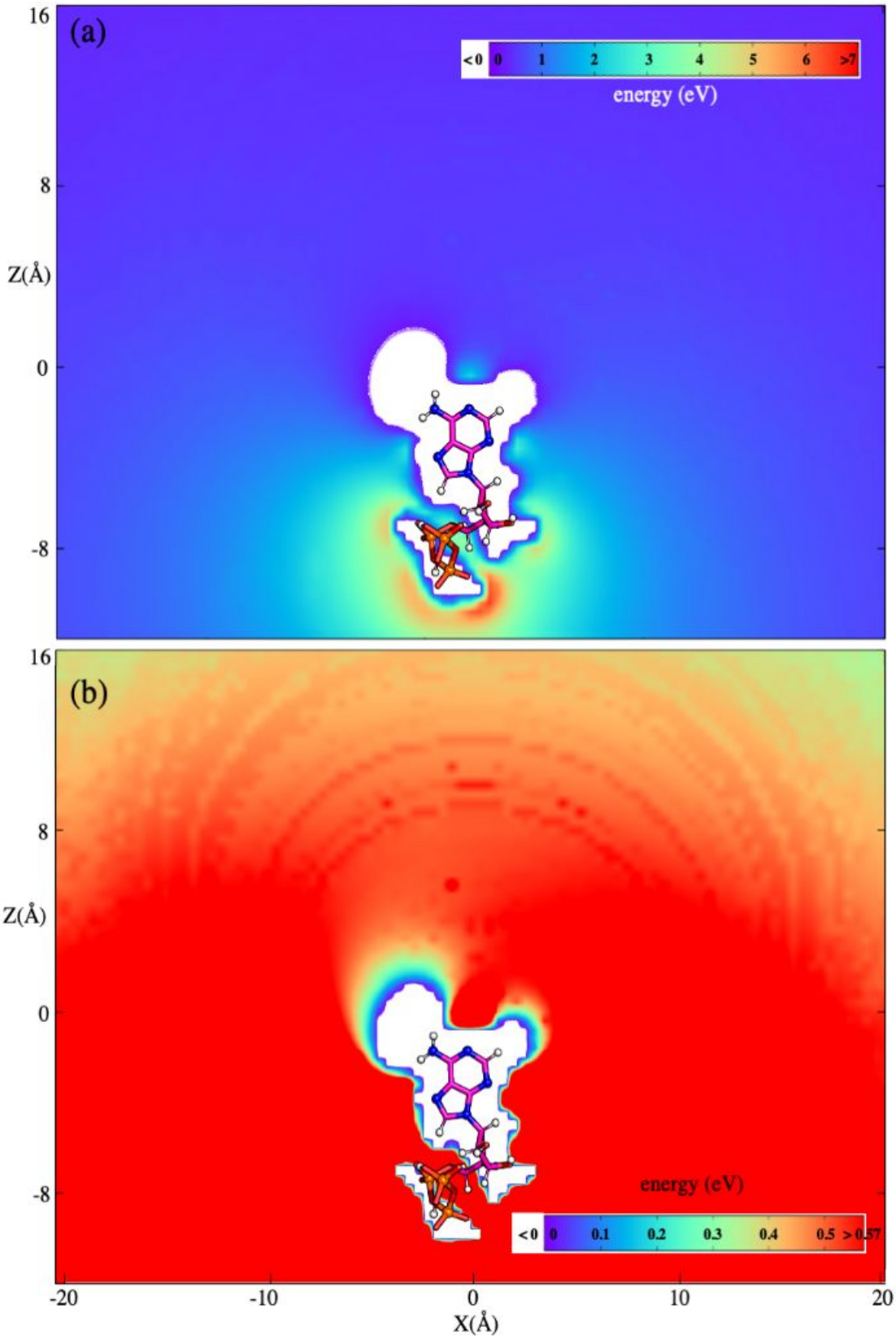

Figure S.2 Extended RCB map for the plane xz. Comparing with fig. 2 of the main text, this wider investigation of the RCB does not show any long range effect on the barrier.

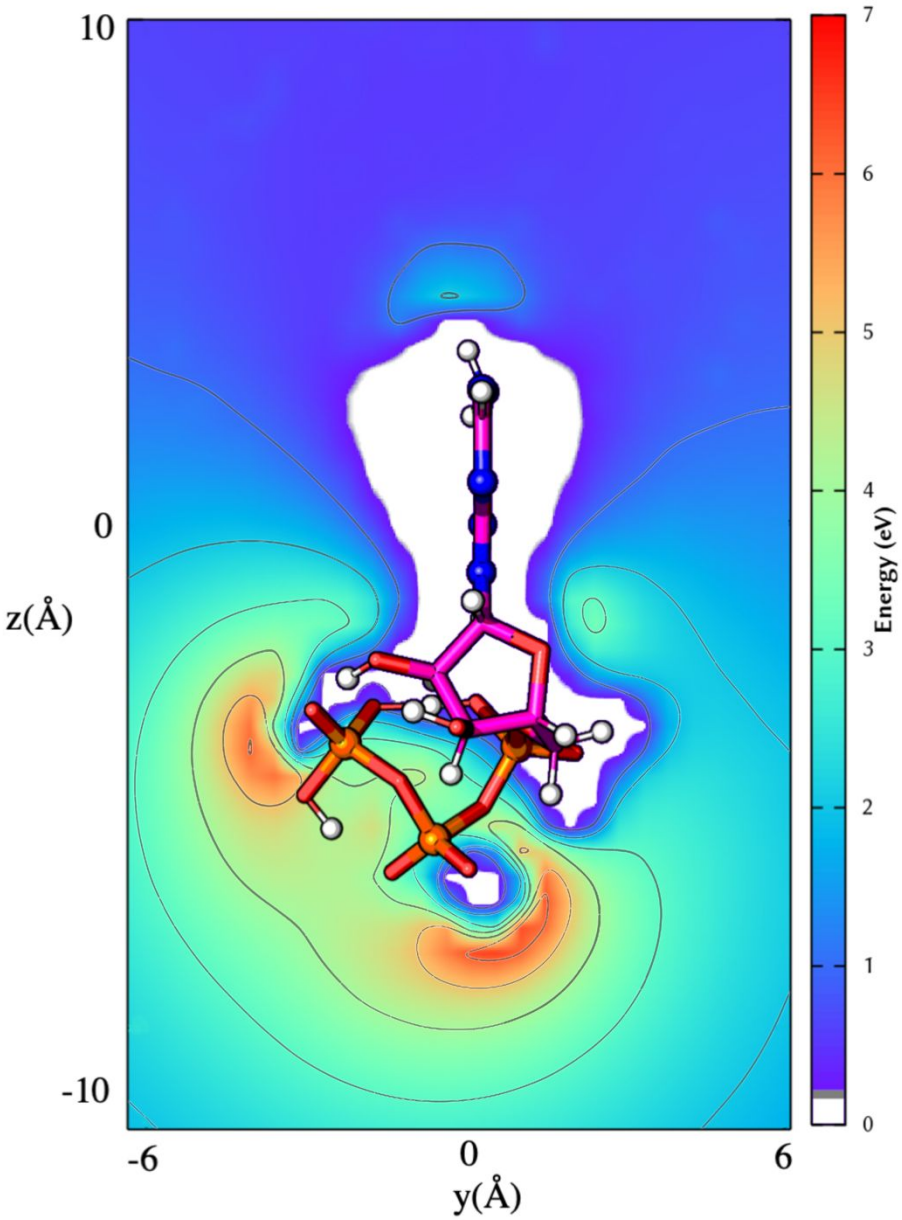

Figure S.3 RCB map for the plane yz. Each contour line represents an increment of 1 eV. The calculated high of the RCB in this plane is 0.65 eV

Section S.1.3 Ab initio molecular dynamics

Methods

Picosecond long ab initio molecular dynamics was run, starting from the [ATP–H_2]$^{2-}$ minimized geometry, at B3LYP[9]/aug-cc-pVDZ[10] level of theory. The simulation time was 4ps, time step 0.2 fs, and T=300K using Langevin thermostat. The dynamics was running with Terachem suite [11].

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