Supporting Information

The UV Absorption of Nucleobases: Semi-Classical *Ab Initio* Spectrum Simulations

Mario Barbatti, Adelia J. A. Aquino, and Hans Lischka

I. Features of the experimental and theoretical spectra

Base	Ref.	Phase	ΔE (eV) Sh1	Max1	Sh2	Sh3	Max2
Ade	Present work	V		5.26			6.38
	[1]	V		5.07			
	[2]	V		4.92			5.99
	[3]	W		4.78			
	[4]	W		4.78			
Gua	Present work (SVP)	V		(4.94,5.65)			7.27
	Present work (TZVP)	V		(4.81,5.49)			
	[2]	V		(4.23,4.37)			
	[3]	W		(4.50,5.07)			
	[4]	W		(4.44,4.92)			
Cyt	Present work	V		4.65		5.62	6.40
	[2]	V	4.28	~4.77			
	[3]	W		4.65			
	[4]	W		4.56	4.99	5.38	
	[5]	W		4.66	5.39	5.85	6.29
Thy	Present work	V		5.23			6.58
	[3]	W		4.70			
	[4]	W		4.61			
Ura	Present work	V		5.36			6.96
	[2]	V		5.08	6.05		6.63
	[3]	W		4.79			

Sh – Shoulder; Max – maximum; V – vapor; W – in water.

II. Vertical excitations

A. Adenine – CC2/TZVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\rightarrow\pi^*$	5.20	0.003	33a-36a	79.2
S_2	$\pi\rightarrow\pi^*$	5.29	0.070	35a-38a	44.5
				34a-36a	31.6
S_3	$\pi\rightarrow\pi^*$	5.42	0.301	35a-36a	83.1
S_4	$n\rightarrow\pi^*$	5.86	0.004	33a-38a	87.4
S_5	$n\rightarrow\pi^*$	6.26	0.007	31a-38a	87.2
S_6	$\pi\rightarrow\pi^*$	6.55	0.455	34a-36a	44.6
				35a-38a	24.6
S_7	$\pi\rightarrow R_{3s}$	6.74	0.009	35a-37a	33.4
				35a-39a	31.3
S_8	$\pi\rightarrow\pi^*$	6.83	0.074	32a-36a	57.7
S_9	$\pi\rightarrow\pi^*$	6.92	0.044	35a-40a	46.0
				35a-41a	15.2
S_{10}	$n\rightarrow\pi^*$	7.03	0.014	31a-38a	72.8

B. Adenine – CC2/TZVP-aug

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\rightarrow\pi^*$	5.11	0.003	33a-52a	19.2
				33a-50a	16.8
S_2	$\pi\rightarrow\pi^*$	5.20	0.073	35a-58a	30.5
S_3	$\pi\rightarrow\pi^*$	5.25	0.212	35a-58a	19.6
				35a-50a	11.5
S_4	$\pi\rightarrow R_{3s}$	5.47	0.009	35a-36a	45.3
S_5	$n\rightarrow\pi^*$	5.75	0.005	33a-58a	58.9
S_6	$\pi\rightarrow R_{3s}$	5.80	0.005	35a-37a	41.9
				35a-36a	22.6
S_7	$n\rightarrow R_{3s}$	6.02	0.028	33a-36a	56.2
S_9	$n\rightarrow\pi^*$	6.19	0.016	31a-52a	18.5
				31a-50a	15.7
S_9	$\pi\rightarrow R_{3s}$	6.24	0.001	35a-38a	50.1
S_{10}	$n\rightarrow R_{3s}$	6.29	0.333	33a-37a	18.2
	$\pi\rightarrow\pi^*$			35a-58a	10.2

C. Guanine – CC2/SVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$\pi\rightarrow\pi^*$	5.26	0.210	39a-40a	79.8
S_2	$n\rightarrow\pi^*$	5.64	0.002	35a-41a	32.3
				37a-41a	30.4
S_3	$\pi\rightarrow\pi^*$	5.89	0.263	39a-41a	75.0
S_4	$n\rightarrow\pi^*$	6.26	0.000	37a-40a	68.8
S_5	$n\rightarrow\pi^*$	6.48	0.000	35a-40a	72.5

S_6	$n\rightarrow\pi^*$	6.72	0.004	35a-41a	37.5
				37a-41a	36.0
S_7	$\pi\rightarrow\pi^*/R_{3s}$	6.84	0.006	39a-42a	55.1
S_8	$\pi\rightarrow\pi^*$	6.97	0.019	39a-45a	43.2
	$\pi\rightarrow\pi^*/R_{3s}$			39a-44a	20.5
S_9	$\pi\rightarrow R_{3s}$	7.34	0.002	39a-43a	95.5
S_{10}	$n\rightarrow\pi^*$	7.42	0.119	33a-40a	32.2
				37a-45a	12.5
S_{11}	$\pi\rightarrow\pi^*$	7.45	0.083	38a-41a	43.2
				36a-40a	29.3
S_{12}	$\pi\rightarrow\pi^*$	7.50	0.377	38a-41a	22.0
				36a-41a	18.3
				36a-40a	15.9
S_{13}	$\pi\rightarrow\pi^*$	7.51	0.363	38a-40a	57.9
S_{14}	$\pi\rightarrow\pi^*$	7.90	0.005	36a-41a	24.4
	$n\rightarrow\pi^*/R_{3s}$			37a-42a	12.7
S_{15}	$\pi\rightarrow \pi^*/R_{3s}$	7.97	0.011	39a-44a	40.3
S_{16}	$n\rightarrow\pi^*$	8.01	0.009	33a-40a	39.7
				37a-45a	18.9
S_{17}	$\pi\rightarrow\pi^*$	8.10	0.103	36a-41a	22.0
	$n\rightarrow\pi^*/R_{3s}$			37a-42a	20.3
S_{18}	$\pi\rightarrow\pi^*$	8.20	0.013	34a-40a	40.9
				39a-45a	11.2
S_{19}	$n\rightarrow R_{3s}$	8.42	0.011	37a-43a	72.8
S_{20}	$\pi\rightarrow\pi^*/R_{3s}$	8.45	0.018	36a-42a	29.6
				39a-44a	18.4

D. Guanine – CC2/TZVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$\pi\rightarrow\pi^*$	5.13	0.194	39a-41a	67.6
S_2	$n\rightarrow\pi^*$	5.56	0.003	35a-43a	26.7
				37a-43a	22.4
S_3	$\pi\rightarrow\pi^*$	5.67	0.286	39a-43a	83.2
S_4	$\pi\rightarrow R_{3s}$	6.03	0.005	39a-40a	67.0
S_5	$n\rightarrow\pi^*$	6.21	0.00	37a-41a	50.2
S_6	$n\rightarrow\pi^*$	6.36	0.00	35a-41a	54.7
S_7	$\pi\rightarrow\pi_R^*$	6.57	0.001	39a-42a	79.6
S_8	$n\rightarrow\pi^*$	6.61	0.003	37a-43a	39.8
S_9	$\pi\rightarrow\pi^*$	6.70	0.02	39a-46a	64.4
S_{10}	$n\rightarrow R_{3s}$	7.13	0.034	35a-40a	22.9
				37a-40a	21.9
S_{11}	$\pi\rightarrow\pi^*$	7.21	0.215	38a-43a	33.5
				36a-41a	17.0
S_{12}	$\pi\rightarrow\pi^*$	7.22	0.254	38a-43a	19.4
				34a-40a	11.8
S_{13}	$\pi\rightarrow\pi^*$	7.31	0.178	38a-41a	33
				38a-43a	14.9
S_{14}	$\pi\rightarrow R_{3s}$	7.33	0.02	39a-45a	58.8
S_{15}	$\pi\rightarrow R_{3s}$	7.36	0.228	39a-44a	30.3
	$\pi\rightarrow\pi^*$			36a-41a	18.7

E. Guanine – CC2/TZVP-aug

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$\pi \rightarrow R_{3s}$	4.90	0.064	39a-40a	45.2
	$\pi \rightarrow \pi^*$			39a-60a	12.4
S_2	$\pi \rightarrow \pi^*$	4.97	0.099	39a-60a	34.4
	$\pi \rightarrow R_{3s}$			39a-40a	18.4
S_3	$\pi \rightarrow R_{3s}$	5.30	0.013	39a-41a	71.4
S_4	$\pi \rightarrow \pi^*$	5.40	0.269	39a-64a	22.5
				39a-61a	17.7
S_5	$n \rightarrow \pi^*$	5.42	0.026	37a-60a	18.7
				35a-60a	17.2
S_6	$\pi \rightarrow R_{3s}$	5.84	0.005	39a-42a	55.4
S_7	$\pi \rightarrow R_{3s}$	5.95	0.001	39a-45a	33.5
				39a-42a	13.2
S_8	$\pi \rightarrow R_{3s}$	5.99	0.009	39a-43a	35.1
	$\pi \rightarrow R_{3px}$			39a-44a	27.4
S_9	$n \rightarrow R_{3s}$	6.03	0.010	37a-40a	28.7
				35a-40a	14.5
S_{10}	$n \rightarrow \pi^*$	6.09	0.006	37a-60a	17.2
				37a-64a	15.3
S_{11}	$\pi \rightarrow R_{3px}$	6.21	0.001	39a-44a	39.2
	$\pi \rightarrow R_{3s}$			39a-43a	32.8
S_{12}	$n \rightarrow \pi^*$	6.23	0.001	35a-60a	26.8
				35a-64a	12.6
S_{13}	$\pi \rightarrow \pi^*$	6.33	0.015	39a-77a	21.0
	$\pi \rightarrow R_{3s}$			39a-46a	15.0
S_{14}	$n \rightarrow R_{3s}$	6.37	0.002	37a-41a	20.8
				37a-40a	10.3
S_{15}	$n \rightarrow \pi^*$	6.39	0.001	35a-61a	11.7
				37a-60a	9.3

F. Cytosine –CC2/TZVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$\pi \rightarrow \pi^*$	4.71	0.051	29a-30a	81.6
S_2	$n \rightarrow \pi^*$	4.95	0.007	27a-30a	83.7
S_3	$n \rightarrow \pi^*$	5.35	0.009	26a-30a	81.5
S_4	$\pi \rightarrow \pi^*$	5.77	0.155	28a-30a	84.2
S_5	$n \rightarrow \pi^*$	5.94	0.003	27a-33a	52.3
S_6	$\pi \rightarrow R_{3s}$	6.54	0.311	29a-31a	51.1
	$\pi \rightarrow \pi^*$			29a-33a	29.8
S_7	$\pi \rightarrow \pi^*$	6.66	0.303	29a-33a	40.8
	$\pi \rightarrow R_{3s}$			29a-32a	21.1
S_8	$n \rightarrow \pi^*$	6.76	0.009	26a-33a	38.8
				27a-33a	21.5
S_9	$\pi \rightarrow R_{3s}$	6.93	0.067	28a-31a	31.7
	$\pi \rightarrow \pi^*$			28a-33a	20.4
S_{10}	$n \rightarrow R_{3s}$	7.13	0.026	27a-31a	46.4
				26a-31a	14.5

G. Cytosine – CC2/TZVP-aug

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$\pi\to\pi^*$	4.61	0.052	29a-41a	25.9
				29a-42a	20.2
S_2	$n\to\pi^*$	4.87	0.007	27a-41a	26.7
				27a-42a	20.3
S_3	$n\to\pi^*$	5.27	0.01	26a-41a	24.6
				26a-42a	19.5
S_4	$\pi\to R_{3s}$	5.44	0.006	29a-30a	64.3
S_5	$\pi\to\pi^*$	5.64	0.127	28a-41a	24.8
				28a-42a	20.3
S_6	$n\to\pi^*$	5.79	0.006	27a-53a	22.4
				27a-54a	17.3
S_7	$n\to R_{3s}$	5.92	0.051	27a-30a	38.2
S_8	$\pi\to R_{3s}$	6.00	0.026	29a-31a	43.9
S_9	$\pi\to R_{3s}$	6.04	0.002	28a-30a	32.7
				29a-31a	17.5
S_{10}	$\pi\to\pi^*$	6.28	0.388	29a-53a	19.8
				29a-54a	15.8
S_{11}	$\pi\to R_{3s}$	6.32	0.003	29a-32a	34.1
				29a-35a	10.2
S_{12}	$n\to R_{3s}$	6.39	0.075	27a-31a	17.8
				26a-30a	15.3
S_{13}	$\pi\to R_{3px}$	6.52	0.021	29a-34a	55.1
S_{14}	$n\to R_{3s}$	6.53	0.033	27a-31a	30.5
				26a-30a	18.0
S_{15}	$n\to\pi^*$	6.59	0.025	26a-53a	11.2
				26a-54a	7.9
S_{16}	$\pi\to R_{3s}$	6.66	0.03	28a-31a	33.7
S_{17}	$\pi\to R_{3s}$	6.74	0.01	29a-35a	22.0
S_{18}	$n\to R_{3s}$	6.75	0.10	27a-32a	29.8
S_{19}	$\pi\to\pi^*$	6.76	0.07	28a-53a	10
				28a-54a	8.2
S_{20}	$n\to R_{3s}$	6.91	0.00	26a-31a	31.9
S_{21}	$n\to R_{3px}$	6.94	0.00	27a-34a	42.3
S_{22}	$\pi\to R_{3s}$	6.98	0.00	29a-33a	38.8
S_{23}	$\pi\to R_{3s}$	7.05	0.00	28a-32a	39.9
S_{24}	$n\to R_{3s}$	7.14	0.00	27a-35a	18.5
S_{25}	$n\to R_{3s}$	7.24	0.02	27a-32a	15.0
				26a-32a	14.7

H. Thymine – CC2/TZVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\to\pi^*$	4.93	0.000	31a-34a	84.6
S_2	$\pi\to\pi^*$	5.37	0.197	33a-34a	87.4
S_3	$n\to\pi^*$	6.32	0.000	31a-38a	37.9
	$n\to\pi^*$			30a-34a	36.5
S_4	$\pi\to\pi^*$	6.44	0.082	32a-34a	93.7
S_5	$\pi\to R_{3s}$	6.68	0.000	33a-35a	69.5
S_6	$n\to\pi^*$	6.73	0.000	30a-34a	43.1

				31a-38a	25.7
S_7	$\pi\rightarrow\pi^*$	6.79	0.250	33a-38a	89.9
S_8	$n\rightarrow\pi^*$	7.18	0.000	30a-38a	67.1
S_9	$n\rightarrow R_{3s}$	7.53	0.019	31a-35a	61.8
S_{10}	$\pi\rightarrow R_{3s}$	7.67	0.000	33a-37a	55.0

I. Thymine – CC2/TZVP-aug

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\rightarrow\pi^*$	4.83	0.000	31a-45a	44.8
S_2	$\pi\rightarrow\pi^*$	5.18	0.178	33a-45a	42.2
S_3	$\pi\rightarrow R_{3s}$	5.60	0.000	33a-34a	67.1
S_4	$n\rightarrow\pi^*$	6.16	0.000	30a-45a	18.3
				31a-61a	17.0
S_5	$\pi\rightarrow\pi^*$	6.22	0.016	32a-45a	30.1
	$n\rightarrow R_{3s}$			31a-34a	18.3
S_6	$n\rightarrow R_{3s}$	6.30	0.082	31a-34a	42.3
S_7	$\pi\rightarrow R_{3s}$	6.34	0.001	33a-35a	38.6
S_8	$\pi\rightarrow\pi^*$	6.45	0.147	33a-59a	36.7
S_9	$\pi\rightarrow R_{3s}$	6.49	0.000	33a-36a	42.2
S_{10}	$n\rightarrow\pi^*$	6.55	0.001	30a-45a	25.5
S_{11}	$\pi\rightarrow R_{3px}$	6.71	0.012	33a-37a	48.5
S_{12}	$n\rightarrow R_{3s}$	6.78	0.098	31a-36a	20.3
				31a-34a	15.1
S_{13}	$n\rightarrow R_{3s}$	6.94	0.014	30a-34a	24.2
				31a-35a	18.9
S_{14}	$n\rightarrow\pi^*$	7.00	0.000	30a-61a	30.4
S_{15}	$\pi\rightarrow R_{3s}$	7.02	0.000	32a-34a	38.6

J. Uracil – CC2/TZVP

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\rightarrow\pi^*$	4.89	0.0000	27a-30a	85.1
S_2	$\pi\rightarrow\pi^*$	5.50	0.1987	29a-30a	86.7
S_3	$n\rightarrow\pi^*$	6.25	0.0000	27a-33a	42.6
				26a-30a	32.9
S_4	$\pi\rightarrow\pi^*$	6.41	0.0595	28a-30a	94.5
S_5	$n\rightarrow\pi^*$	6.72	0.0002	26a-30a	57.2
				27a-33a	37.4
S_6	$\pi\rightarrow R_{3s}$	6.92	0.0002	29a-31a	90.3
S_7	$\pi\rightarrow\pi^*$	6.96	0.1871	29a-33a	89.0
S_8	$n\rightarrow\pi^*$	7.12	0.0000	26a-33a	75.1
S_9	$n\rightarrow R_{3s}$	7.53	0.0580	27a-31a	54.4
	$\pi\rightarrow\pi^*$			28a-33a	21.3
S_{10}	$\pi\rightarrow\pi^*$	7.66	0.5351	28a-33a	56.9
	$n\rightarrow R_{3s}$			27a-31a	27.3

K. Uracil – CC2/TZVP-aug

State	Assignment	ΔE (eV)	f	Main contribution	%
S_1	$n\rightarrow\pi^*$	4.80	0.000	27a-40a	44.3
				27a-36a	26.7
S_2	$\pi\rightarrow\pi^*$	5.32	0.178	29a-40a	41.5
				29a-36a	29.9
S_3	$\pi\rightarrow\pi^*$	5.87	0.002	29a-30a	68.0
S_4	$n\rightarrow\pi^*$	6.09	0.000	27a-51a	34.8
				26a-40a	15.5
S_5	$n\rightarrow\pi^*$	6.21	0.024	28a-40a	41.2
				28a-36a	24.6

III. Optimized geometries at CC2/TZVP level

Cartesian coordinates in Angstrom

A. Adenine

c	0.745129	0.565905	-0.645930
n	0.325563	1.364241	-1.687309
c	-1.047993	1.421215	-1.613009
n	-1.555190	0.728173	-0.608244
c	-0.433260	0.205710	0.016994
n	1.995382	0.195446	-0.335480
c	1.993246	-0.644740	0.711057
n	0.944664	-1.129118	1.409221
c	-0.290307	-0.735573	1.049506
n	-1.355307	-1.177352	1.779989
h	-1.626123	1.990750	-2.324268
h	-1.186126	-2.015987	2.316742
h	-2.259700	-1.097843	1.337886
h	2.965898	-0.994081	1.037655
h	0.924784	1.822429	-2.359759

B. Guanine

c	-1.461583	-0.214045	0.001053
c	-0.464999	0.832910	-0.011600
c	0.892214	0.479185	0.005837
n	1.460020	-0.756240	-0.002765
c	0.561252	-1.715261	0.009299
n	-0.792873	-1.486910	0.015486
n	-0.623077	2.201134	-0.019781
c	0.609433	2.670838	-0.012843
n	1.564227	1.674524	0.000725
n	0.963528	-3.033336	0.090837
o	-2.684451	-0.165242	0.009897
h	-1.430291	-2.276917	0.101457
h	0.409282	-3.699532	-0.438500
h	1.960561	-3.130026	-0.076709
h	0.886808	3.724843	-0.016307
h	2.573723	1.779999	0.008434

C. Cytosine

c	-0.566632	0.750028	-0.004958
n	-1.322989	-0.333549	-0.026840
c	-0.730789	-1.578165	-0.007719
n	0.688364	-1.595305	-0.149899
c	1.458042	-0.480625	-0.050254
c	0.866728	0.741316	0.026443
o	-1.329044	-2.645002	0.090897
n	-1.211573	1.956484	-0.108186
h	1.107704	-2.515561	-0.110852
h	2.530739	-0.624282	-0.064958
h	1.451878	1.647854	0.070739

h	-0.738093	2.767326	0.259317
h	-2.204335	1.909482	0.076270

D. Thymine

o	-0.666471	2.323277	0.000002
c	-0.581012	1.094123	0.000001
c	0.667876	0.336986	0.000000
c	0.603301	-1.016224	-0.000001
n	-0.592498	-1.702682	0.000005
c	-1.838662	-1.089767	0.000000
n	-1.741135	0.294692	-0.000003
c	1.952972	1.103054	-0.000000
h	1.490338	-1.637930	0.000000
h	-0.609410	-2.712767	-0.000002
o	-2.896673	-1.707792	0.000000
h	-2.624718	0.793653	-0.000000
h	2.807985	0.425890	-0.000000
h	2.014054	1.747743	-0.877838
h	2.014054	1.747743	0.877837

E. Uracil

c	0.012104	1.423618	-0.000000
c	-1.159748	0.747608	-0.000000
n	-1.205123	-0.626645	0.000001
c	-0.072891	-1.438985	-0.000000
n	1.103963	-0.706227	0.000000
c	1.271907	0.698194	-0.000000
o	-0.127201	-2.662098	-0.000000
o	2.398575	1.190369	0.000000
h	1.956937	-1.255649	-0.000000
h	-2.086869	-1.119597	-0.000000
h	0.038981	2.502077	-0.000000
h	-2.121487	1.244113	0.000000

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