SUPPORTING INFORMATION

First-principles characterization of the singlet excited state manifold in DNA/RNA nucleobases

Vishal K. Jaiswal,[a,b] Javier Segarra-Martí,[b,c,d] Marco Marazzi,[e,f,g,h] Elena Zvereva,[†e,f,i] Xavier Assfeld,[e,f] Antonio Monari,[e,f] Marco Garavelli,*[a] and Ivan Rivalta*[a,b]*

[a.] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy.*

[b.] *Univ Lyon, Ens de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie UMR 5182, F-69342, Lyon, France.*

[c.] *Molecular Sciences Research Hub, White City Campus, Imperial College London, 80 Wood Lane, W12 0BZ London, UK.*

[d.] *Instituto de Ciencia Molecular, Universitat de Valencia, P.O.Box 22085 Valencia, Spain.*

[e.] *Université de Lorraine and CNRS, LPCT UMR 7019, F-54000 Nancy, France.*

[f.] *CNRS, Laboratoire de Physique et Chimie Théoriques. Vandoeuvre-lès-Nancy, 54506 France*

[g.] *Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Ctra, Madrid-Barcelona Km. 33,600, E-28805 Alcalá de Henares (Madrid), Spain.*

[h.] *Chemical Research Institute "Andrés M. del Río" (IQAR), Universidad de Alcalá, E-28871 Alcalá de Henares (Madrid), Spain*

[i.] *A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences*

[*]E-mail: j.segarra-marti@imperial.ac.uk; marco.garavelli@unibo.it; i.rivalta@unibo.it

Table S1: Adenine $S_0 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
2 (Lb)	4.94(*0.00*)	5.56(*0.07*)	5.38(*0.04*)	5.77(*0.08*)	5.59(*0.02*)
3 (La)	5.18(*0.23*)	5.28(*0.16*)	5.09(*0.20*)	5.64(*0.18*)	5.44(*0.27*)
4	6.24(*0.15*)	-	6.22(*0.17*)	6.96(*0.42*)	6.64(*0.44*)
5	6.37(*0.00*)	6.49(*0.09*)	6.26(*0.02*)	7.21(*0.03*)	7.29(*0.01*)
6	6.38(*0.35*)	6.58(*0.14*),7.00(*0.17*)[#]	6.66(*0.10*)	7.36(*0.11*)	7.07(*0.10*)
7	6.86(*0.43*)	7.36(*0.13*)	7.08(*0.17*)	7.79(*0.16*)	7.56(*0.15*)
8	7.00(*0.17*)	7.75(*0.13*)	7.36(*0.03*)	8.51(*0.10*)	8.51(*0.00*)
9	7.39(*0.35*)	7.61(*0.11*)	7.46(*0.19*)	8.22(*0.08*)	7.97(*0.05*)
10	7.94(*0.09*)	8.87(*0.04*)	8.57(*0.00*)	9.59(*0.01*)	9.36(*0.03*)
11	8.19(*0.45*)	9.10(*0.18*)	8.37(*0.12*)	9.29(*0.13*)	9.24(*0.08*)
12	8.53(*0.13*)	9.27(*0.03*)	9.13(*0.03*)		
13	8.83(*0.02*)				

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S2: Adenine $L_a \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
4	1.06(*0.01*)	-	1.12*(0.03)*	1.32(*0.01*)	1.20(*0.00*)
5	1.19(*0.04*)	1.22(*0.06*)	1.16(*0.07*)	1.56(*0.07*)	1.85(*0.01*)
6	1.20(*0.02*)	1.30(*0.02*),1.72(*0.01*)[#]	1.57(*0.01*)	1.71(*0.01*)	1.63(*0.02*)
7	1.68(*0.00*)	2.08(*0.00*)	1.99(*0.00*)	2.14(*0.00*)	2.12(*0.00*)
8	1.82(*0.01*)	2.47(*0.01*)	2.27(*0.01*)	2.87(*0.02*)	3.07(*0.00*)
9	2.21(*0.00*)	2.33(*0.00*)	2.37(*0.00*)	2.57(*0.01*)	2.54(*0.01*)
10	2.76(*0.01*)	3.60(*0.01*)	3.48(*0.01*)	3.94(*0.03*)	3.92(*0.02*)
11	3.01(*0.02*)	3.83(*0.00*)	3.28(*0.00*)	3.65(*0.01*)	3.80(*0.00*)
12	3.35(*0.00*)	3.99(*0.01*)	4.04(*0.00*)		
13	3.65(*0.12*)				

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S3: Adenine $L_b \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
4	1.30(*0.01*)	-	*0.83(0.00)*	1.20(*0.01*)	1.05(*0.00*)
5	1.43(*0.00*)	0.93(*0.00*)	0.87(*0.00*)	1.44(*0.01*)	1.70(*0.01*)
6	1.44(*0.00*)	1.02(*0.00*),1.44(*0.00*)[#]	1.28(*0.01*)	1.59(*0.01*)	1.48(*0.01*)
7	1.92(*0.01*)	1.80(*0.01*)	1.70(*0.01*)	2.02(*0.01*)	1.96(*0.01*)
8	2.06(*0.02*)	2.19(*0.02*)	1.98(*0.01*)	2.75(*0.01*)	2.92(*0.00*)
9	2.45(*0.03*)	2.05(*0.00*)	2.08(*0.03*)	2.45(*0.02*)	2.38(*0.00*)
10	3.00(*0.00*)	3.31(*0.01*)	3.19(*0.00*)	3.82(*0.01*)	3.77(*0.00*)
11	3.25(*0.01*)	3.54(*0.00*)	2.99(*0.00*)	3.53(*0.00*)	3.64(*0.00*)
12	3.59(*0.05*)	3.71(*0.03*)	3.74(*0.03*)		
13	3.89(*0.02*)				

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S4: Guanine $S_0 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
2 (La)	4.68(*0.14*)	5.20(*0.16*)	4.99(*0.13*)	5.45(*0.18*)	5.24(*0.16*)
3 (Lb)	5.20(*0.27*)	5.52(*0.19*)	5.24(*0.26*)	5.94(*0.27*)	5.63(*0.33*)
4	6.00(*0.03*)	6.47(*0.00*)	6.11(*0.02*),6.17(0.00)[#]	7.01(*0.01*)	6.59(*0.02*)
5	6.57(*0.26*)	7.22(*0.29*)	-	7.81(*0.15*)	7.55(*0.10*)
6	6.77(*0.56*)	7.35(*0.17*)	-	7.87(*0.25*)	7.53(*0.13*)
7	6.79(*0.67*)	7.11(*0.05*)	6.86(*0.10*)	7.65(*0.30*)	7.33(*0.24*)
8	6.90(*0.01*)	7.56(*0.14*)	7.22(*0.20*)	8.06(*0.06*)	7.84(*0.10*)
9	7.32(*0.02*)	7.91(*0.10*)	7.67(*0.10*)	8.47(*0.07*)	8.13(*0.03*)
10	8.00(*0.25*)	8.20(*0.00*)	7.82(*0.00*)	9.06(*0.03*)	8.71(*0.05*)
11	8.04(*0.04*)	8.70(*0.07*)	8.27(*0.15*)	9.17(*0.03*)	8.82(*0.02*)
12	8.28(*0.01*)	8.52(*0.02*)	8.16(*0.04*)	9.79(*0.06*)	
13	8.51(*0.06*)	9.78(*0.03*)		10.38(*0.03*)	
14	8.92(*0.08*)	10.01*(0.14)*		10.87(*0.00*)	

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S5: Guanine $L_a \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
4	1.32(0.01)	1.27(0.02)	1.11(*0.00*),1.17(*0.00*)[#]	1.57(0.02)	1.34(0.01)
5	1.89(0.01)	2.02(0.01)	-	2.36(0.01)	2.31(0.01)
6	2.09(0.03)	2.15(0.01)	-	2.42(0.02)	2.29(0.02)
7	2.11(0.01)	1.91(0.00)	1.86(0.00)	2.20(0.00)	2.09(0.00)
8	2.22(0.00)	2.36(0.00)	2.23(0.01)	2.62(0.00)	2.59(0.00)
9	2.64(0.03)	2.71(0.04)	2.68(0.04)	3.03(0.06)	2.88(0.02)
10	3.32(0.00)	3.00(0.01)	2.83(0.00)	3.61(0.01)	3.47(0.02)
11	3.36(0.02)	3.50(0.01)	3.27(0.02)	3.73(0.04)	3.58(0.02)
12	3.60(0.06)	3.32(0.01)	3.17(0.00)	4.35(0.00)	-
13	3.83(0.04)	4.58(0.00)	-	4.93(0.00)	-
14	4.24(0.01)	4.81(0.00)	-	5.42(0.05)	-

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S6: Guanine $L_b \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
4	0.80(0.03)	0.94(0.04)	0.86(*0.03*),0.92(*0.03*)[#]	1.07(0.05)	0.96(0.07)
5	1.37(0.04)	1.69(0.01)	-	1.87(0.01)	1.92(0.03)
6	1.57(0.00)	1.83(0.01)	-	1.93(0.02)	1.91(0.00)
7	1.59(0.03)	1.58(0.01)	1.61(0.01)	1.71(0.01)	1.70(0.01)
8	1.70(0.01)	2.03(0.01)	1.98(0.02)	2.12(0.02)	2.21(0.01)
9	2.12(0.00)	2.39(0.03)	2.43(0.01)	2.53(0.00)	2.50(0.00)
10	2.80(0.01)	2.67(0.03)	2.58(0.03)	3.12(0.11)	3.08(0.05)
11	2.84(0.07)	3.18(0.00)	3.02(0.00)	3.23(0.00)	3.20(0.03)
12	3.08(0.02)	2.99(0.00)	2.92(0.00)	3.85(0.01)	-
13	3.31(0.00)	4.25(0.00)	-	4.44(0.01)	-
14	3.72(0.03)	4.49(0.01)	-	4.93(0.02)	-

[#] The two values relate to the presence of two states featuring the same primary electronic excitation that associates to the corresponding state at RASPT2 reference

Table S7: Uracil $S_0 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
2	5.20(*0.17*)	5.41(*0.12*)	5.22(*0.12*)	5.70(*0.17*)	5.47(*0.18*)
3	6.18(*0.04*)	6.09(*0.04*)	5.97(*0.03*)	6.78(*0.04*)	6.63(*0.04*)
4	6.55(*0.18*)	6.85(*0.11*)	6.53(*0.12*)	7.29(*0.14*)	6.89(*0.16*)
5	7.39(*0.71*)	7.89(*0.17*)	7.52(*0.37*)	8.16(*0.41*)	7.88(*0.33*)
6	8.42(*0.05*)	9.27(*0.08*)	9.13(*0.10*)	10.01(*0.08*)	10.03(*0.05*)

Table S8: Uracil $S_1 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
4	1.35(*0.00*)	1.44(*0.01*)	1.31(*0.00*)	1.59(*0.01*)	1.42(*0.01*)
5	2.19(*0.01*)	2.39(*0.00*)	2.30(*0.00*)	2.46(*0.00*)	2.40(*0.00*)
6	3.22(*0.08*)	2.53(*0.02*)	3.91(*0.02*)	4.32(*0.05*)	4.56(*0.00*)
7	3.29(*0.00*)	3.14(*0.05*)	3.13(*0.05*)	3.47(*0.04*)	3.44(*0.07*)

Table S9: Thymine $S_0 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
2	5.00(*0.17*)	5.30(*0.12*)	5.06(*0.13*)	5.60(*0.18*)	5.33(*0.18*)
3	6.20(*0.11*)	6.36(*0.07*)	6.08(*0.05*)	6.90(*0.07*)	6.70(*0.05*)
4	6.51(*0.17*)	6.74(*0.14*)	6.46(*0.12*)	7.18(*0.18*)	6.83(*0.20*)
5	7.32(*0.89*)	7.91(*0.34*)	7.81(*0.31*)	8.27(*0.40*)	7.94(*0.23*)
6	8.06(*0.38*)	8.27(*0.06*)	8.06(*0.05*)	8.92(*0.07*)	8.70(*0.08*)

Table S10: Thymine $S_1 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
3	1.20(*0.01*)	0.96(*0.01*)	1.02(*0.01*)	1.30(*0.01*)	1.37(*0.01*)
4	1.51(*0.00*)	1.45(*0.00*)	1.40(*0.01*)	1.58(*0.01*)	1.51(*0.01*)
5	2.32(*0.00*)	2.61(*0.00*)	2.75(*0.00*)	2.67(*0.00*)	2.61(*0.00*)
6	3.06(*0.02*)	2.98(*0.09*)	3.00(*0.12*)	3.32(*0.10*)	3.37(*0.12*)

Table S11: Cytosine $S_0 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
2	4.66(*0.05*)	4.74(*0.13*)	5.65(*0.03*)	5.12(*0.05*)	5.00(*0.106*)
3	5.59(*0.10*)	5.66(*0.08*)	5.48(*0.06*)	6.15(*0.12*)	65.94(*0.11*)
4	6.46(*0.83*)	6.88(*0.23*)	6.34(*0.21*)	7.16(*0.46*)	6.70(*0.15*)
5	6.90(*0.30*)	7.10(*0.38*)	6.69(*0.33*)	7.46(*0.21*)	6.96(*0.11*)
6	8.01(*0.24*)	8.02(*0.14*)	7.87(*0.15*)	8.61(*0.18*)	8.45(*0.16*)

Table S12: Cytosine $S_1 \rightarrow S_n$ vertical transition energies (in eV) and corresponding oscillator strengths in parentheses at various levels of theory.

State (n+1)	RASPT2	B3LYP 6-31G**	B3LYP 6-311++G**	CAMB3LYP 6-31G**	CAMB3LYP 6-311++G**
3	0.93(*0.01*)	0.91(*0.01*)	0.82(*0.01*)	1.02(*0.01*)	0.94(*0.01*)
4	1.91(*0.00*)	2.14(*0.00*)	1.69(*0.00*)	2.04(*0.00*)	1.70(*0.00*)
5	2.24(*0.03*)	2.36(*0.01*)	2.03(*0.00*)	2.34(*0.01*)	1.96(*0.00*)
6	3.35(*0.09*)	3.28(*0.05*)	3.22(*0.05*)	3.49(*0.06*)	3.45(*0.08*)

ADENINE

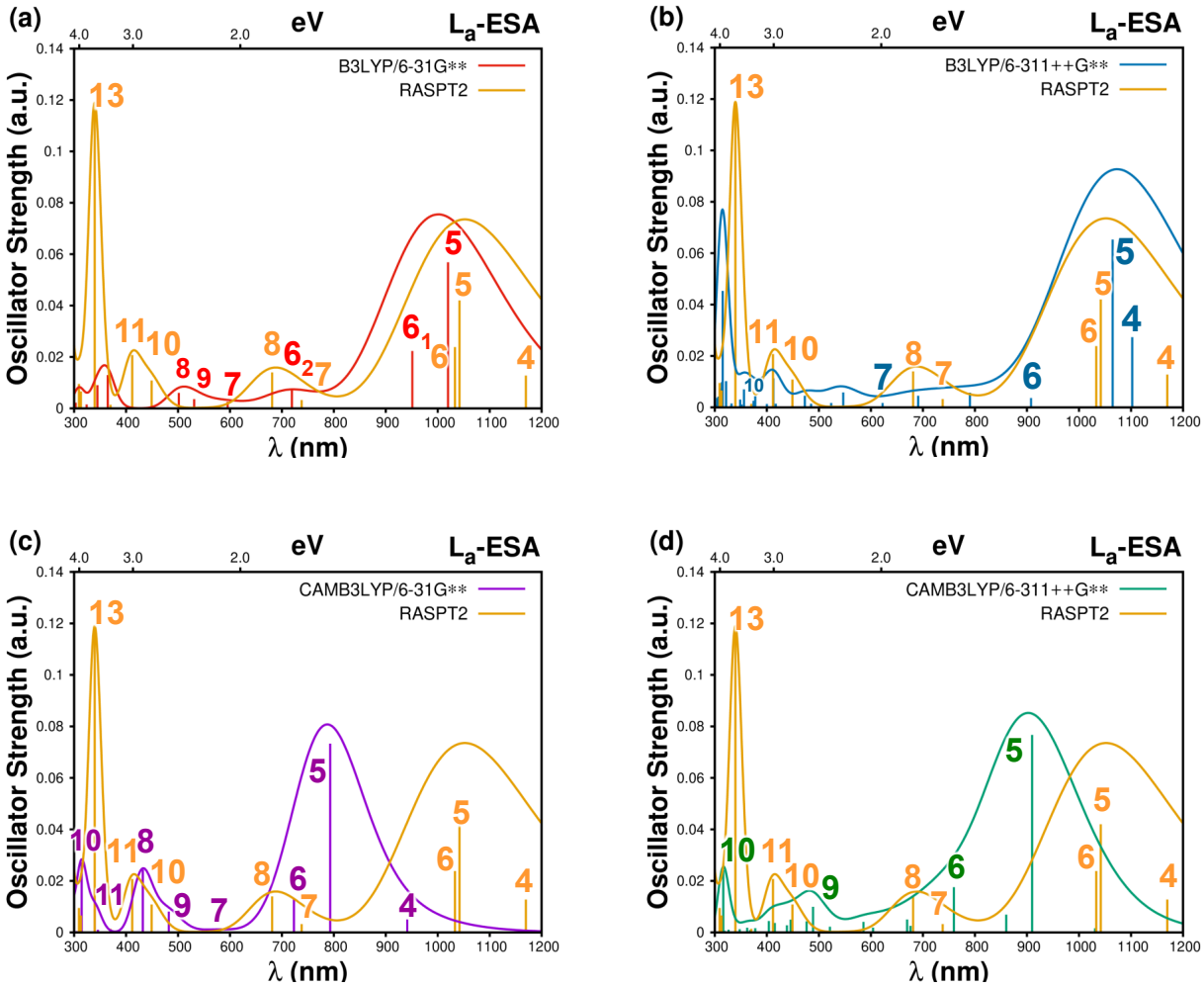

Figure S1. Computed ESAs associated to vertical $L_a \rightarrow S_m$ excitations (colored sticks) of adenine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S2)

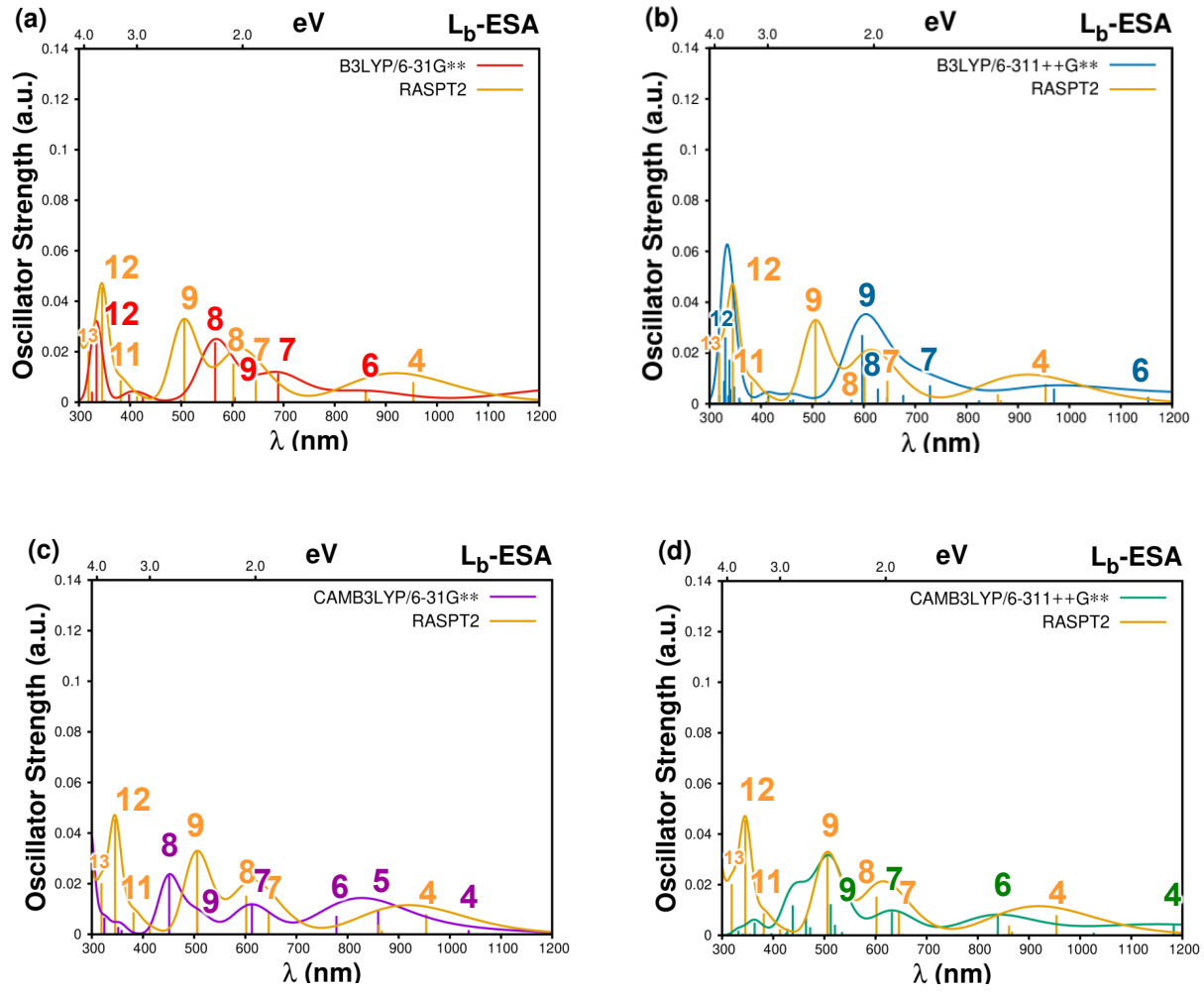

Figure S2. Computed ESAs associated to vertical $L_b \rightarrow S_m$ excitations (colored sticks) of adenine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S3)

GUANINE

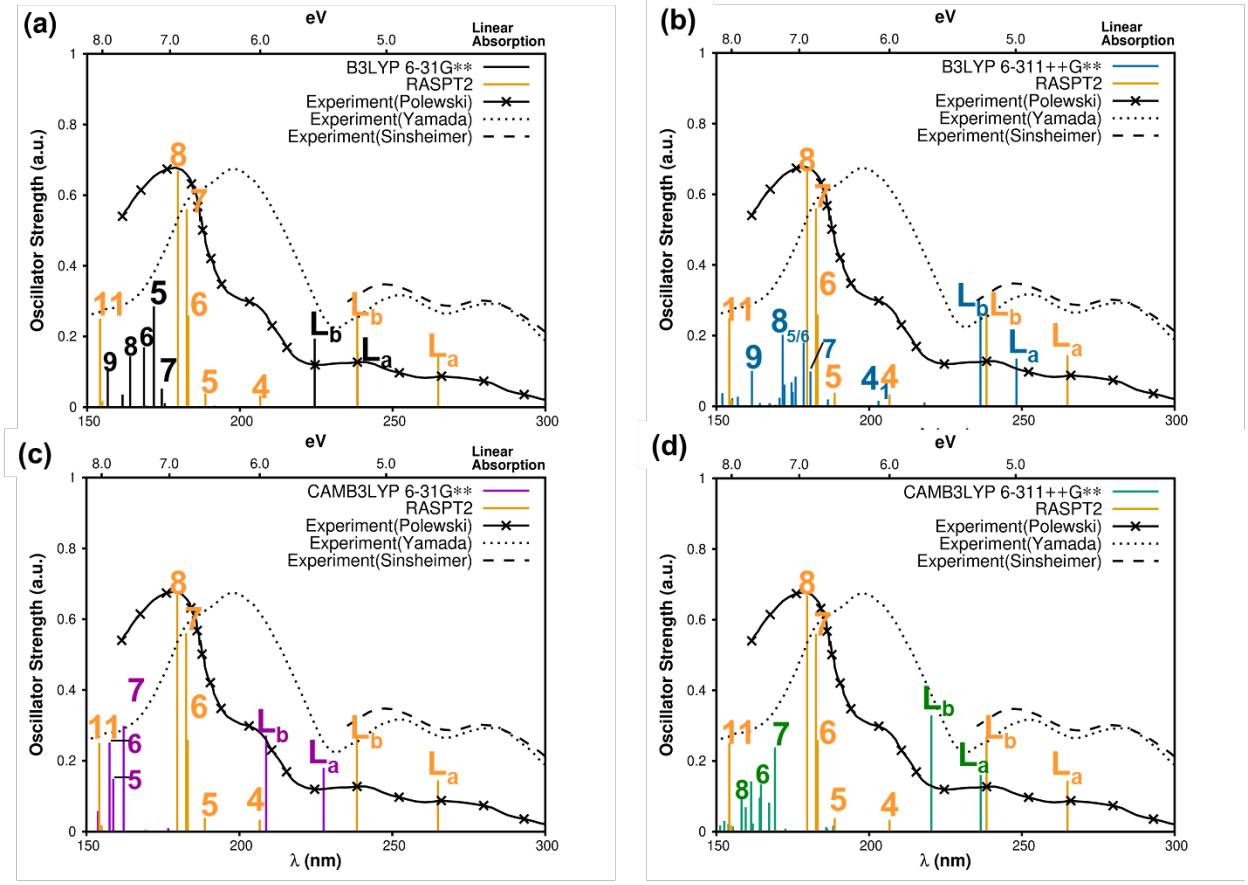

Figure S3. Computed spectra associated to vertical $S_0 \rightarrow S_n$ excitations (colored sticks) of guanine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(black sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S4)

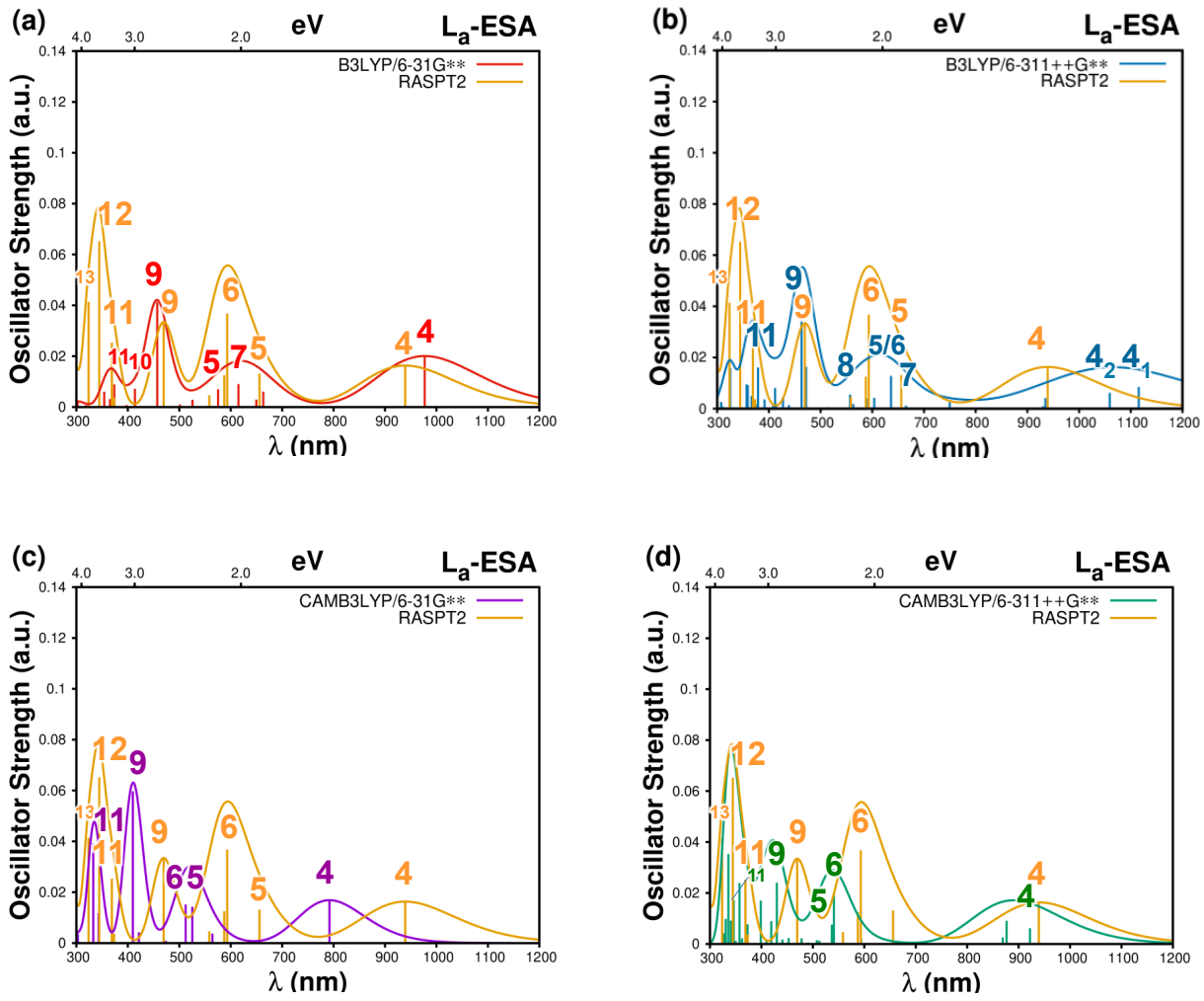

Figure S4. Computed ESAs associated to vertical $L_a \rightarrow S_m$ excitations (colored sticks) of guanine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S5)

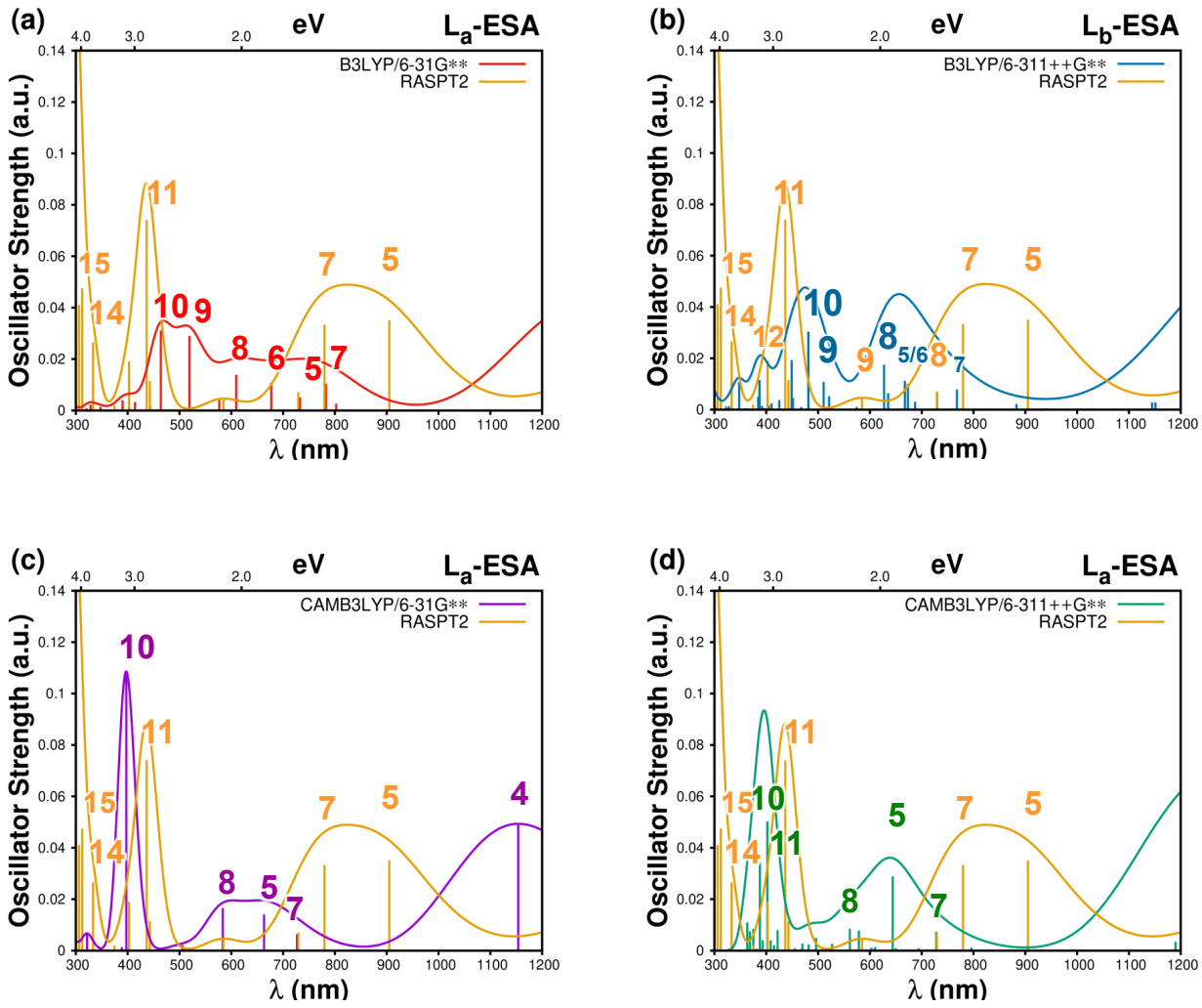

Figure S5. Computed ESAs associated to vertical $L_b \rightarrow S_m$ excitations (colored sticks) of guanine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S6)

URACIL

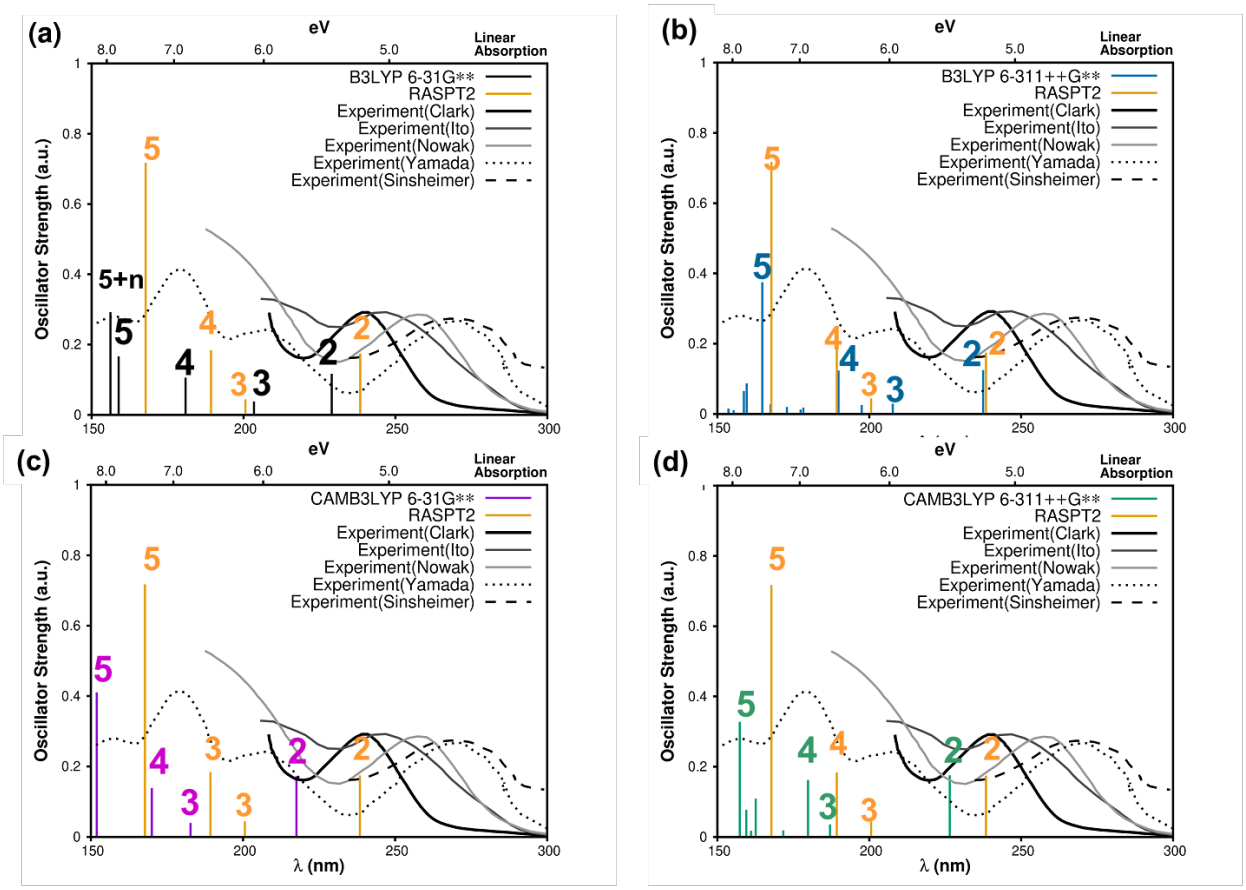

Figure S6. Computed spectra associated to vertical $S_0 \rightarrow S_n$ excitations (colored sticks) of uracil in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(black sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S7)

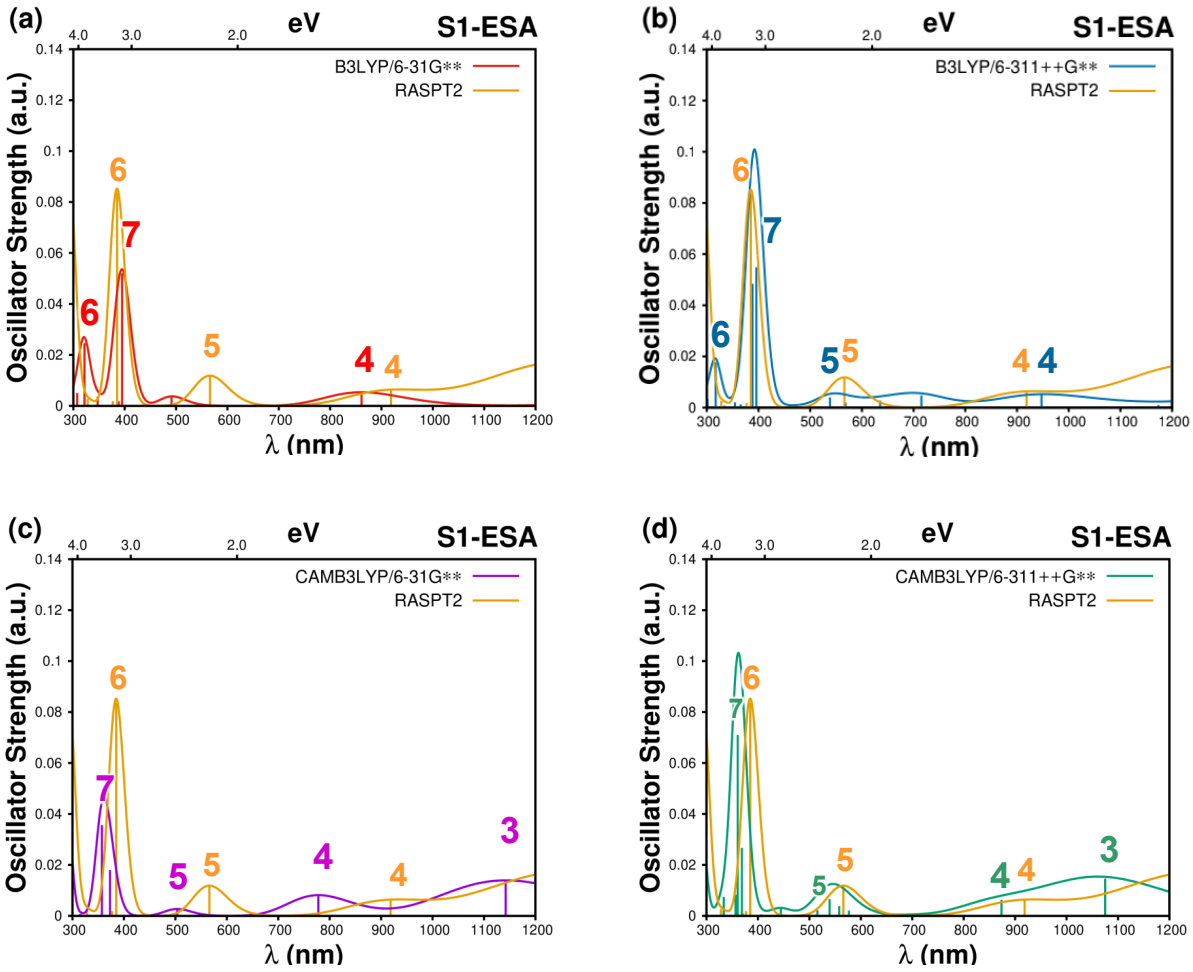

Figure S7. Computed ESAs associated to vertical $S_1 \rightarrow S_m$ excitations (colored sticks) of uracil in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S8)

THYMIME

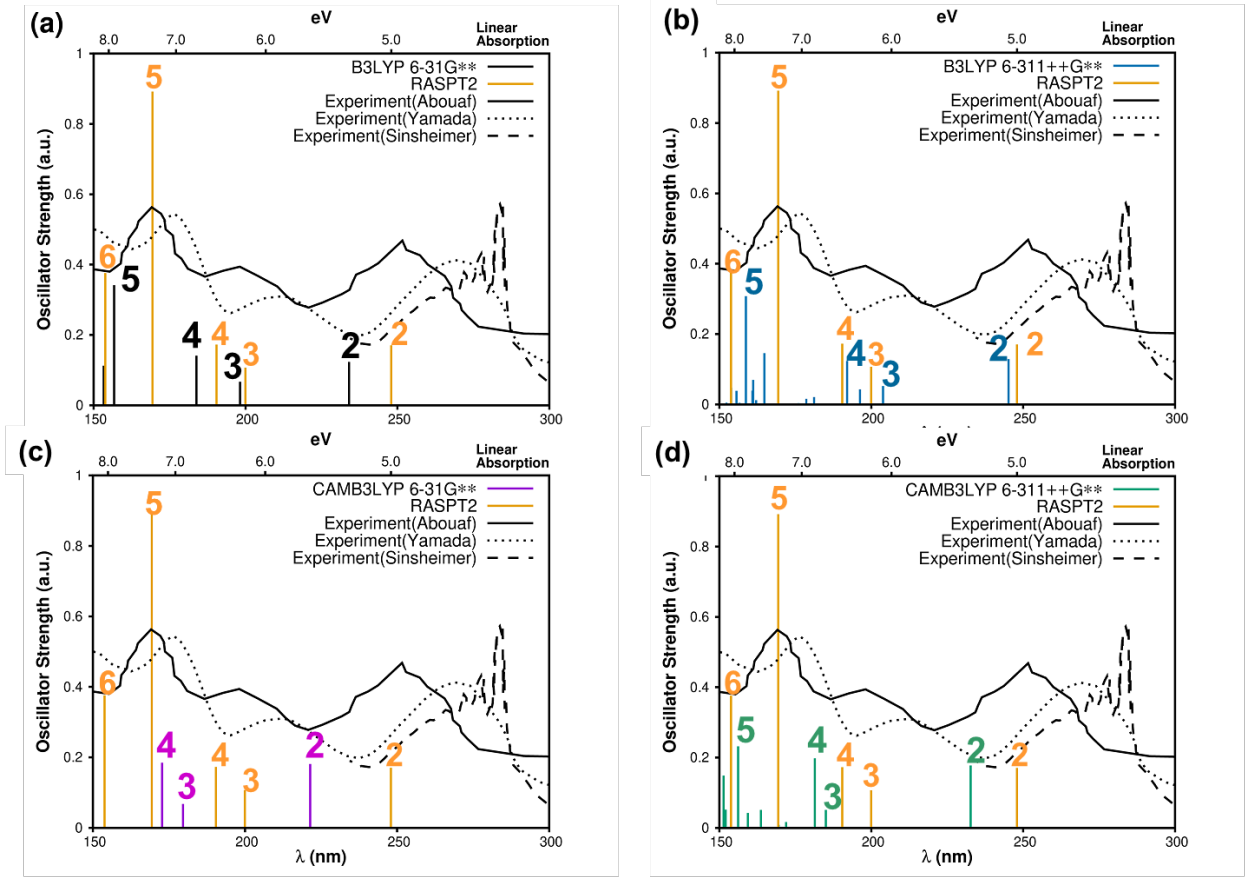

Figure S8. Computed spectra associated to vertical $S_0 \rightarrow S_n$ excitations (colored sticks) of thymine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(black sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S9)

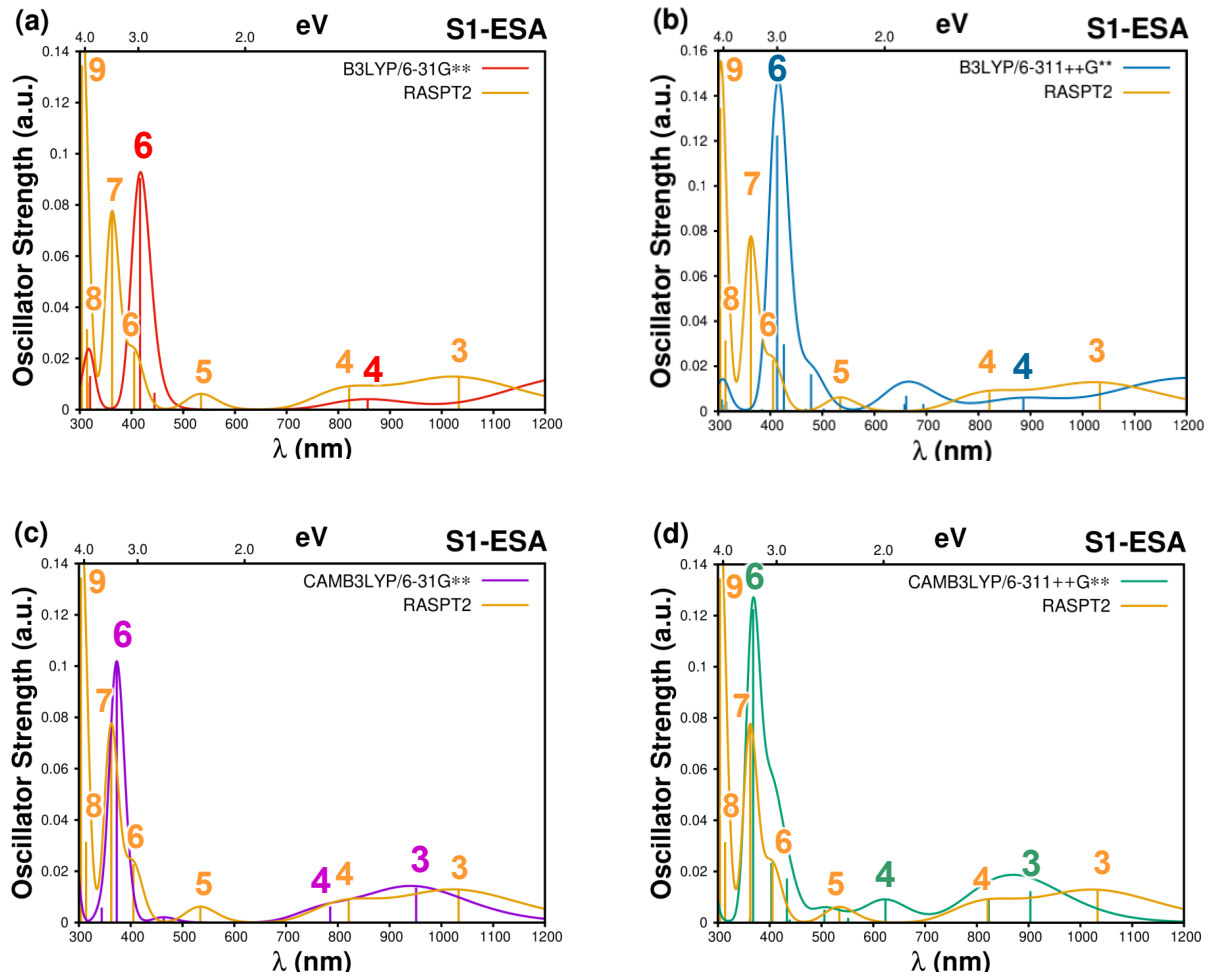

Figure S9. Computed ESAs associated to vertical $S_1 \rightarrow S_m$ excitations (colored sticks) of thymine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S10)

CYTOSINE

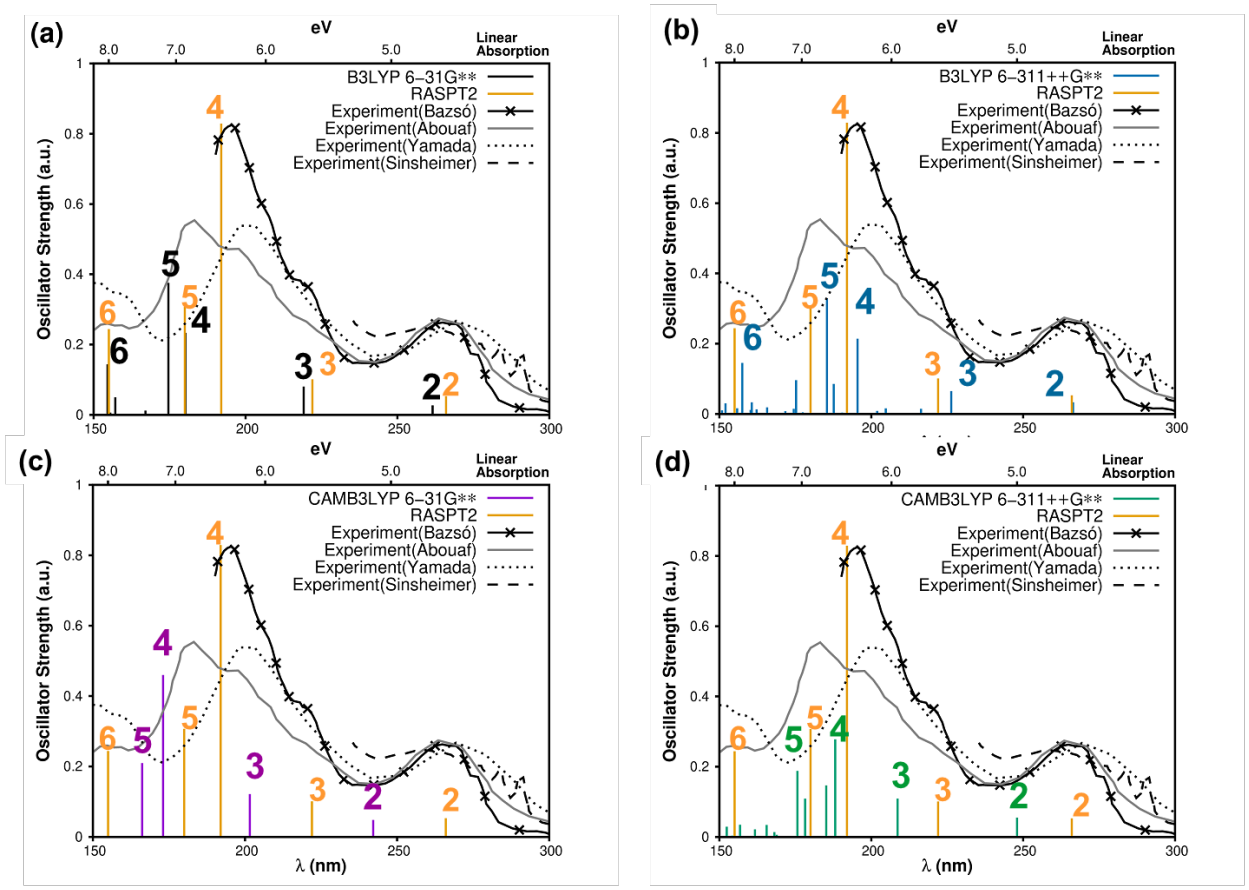

Figure S10. Computed spectra associated to vertical $S_0 \rightarrow S_n$ excitations (colored sticks) of cytosine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(black sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S11)

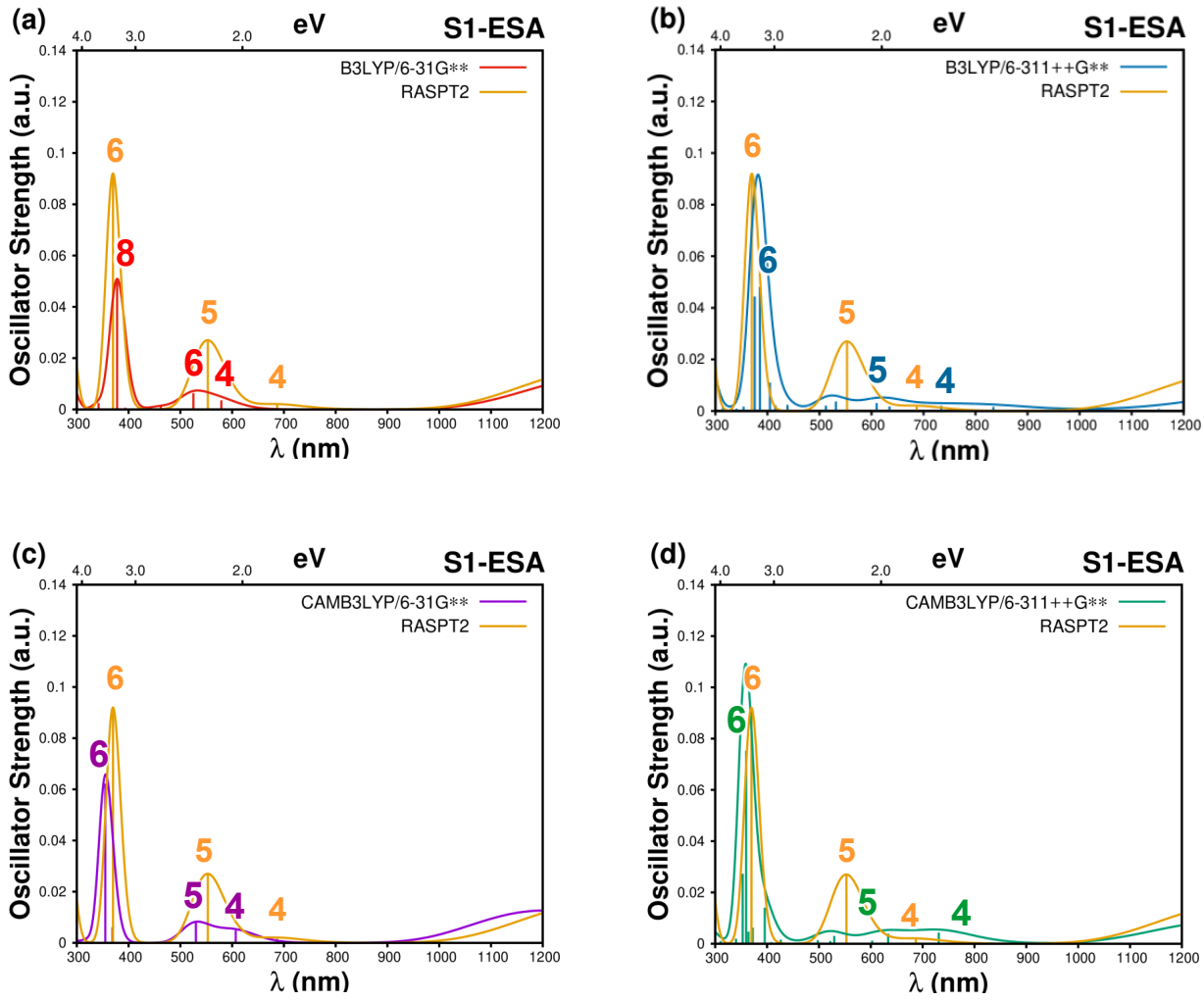

Figure S11. Computed ESAs associated to vertical $S_1 \rightarrow S_m$ excitations (colored sticks) of cytosine in gas-phase. Reference theoretical values at RASPT2 (yellow sticks) are compared with B3LYP/6-31G**(red sticks), B3LYP/6-311++G** (blue sticks), CAMB3LYP/6-31G**(violet sticks) and CAMB3LYP/6-311++G** (green sticks) and corresponding convoluted spectra (colored lines). Only ππ* states are labeled, according to root numbers in the reference RASPT2 computations (Table S12)