
Supplementary Material

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1 Optimized cartesian geometry of adenine

C	-1.970585	-1.395137	-0.045467
N	-1.881922	-0.101178	-0.187746
C	-0.530036	0.162042	-0.075212
C	0.194518	-1.008769	0.138884
N	-0.752839	-2.003591	0.155019
H	-0.575304	-2.985001	0.288894
H	-2.887084	-1.963704	-0.076026
C	0.220821	1.350420	-0.134877
N	1.548880	1.275830	0.014725
C	2.109044	0.076787	0.214691
N	1.515353	-1.110912	0.290953
H	3.187892	0.080293	0.328711
N	-0.350021	2.556054	-0.336758
H	-1.344255	2.632817	-0.451219
H	0.231906	3.373853	-0.370895

2 Optimized cartesian geometry of thymine

C	-1.246495	0.412642	-0.003573
C	-2.507237	1.217084	-0.011848
H	-3.117873	1.004161	-0.892346
H	-2.252332	2.276314	-0.024950
H	-3.115843	1.025528	0.874939
C	-1.217630	-0.931441	0.012635
N	-0.056489	-1.654192	0.020052
C	1.197028	-1.083944	0.011743
N	1.154191	0.288466	-0.004799
C	0.033038	1.117787	-0.013561
H	2.050520	0.753906	-0.011435
O	0.171793	2.321663	-0.028248
O	2.217898	-1.730464	0.018397
H	-2.125375	-1.524102	0.020825
H	-0.070123	-2.660021	0.032219

3 Thymine Oxygen K-Edge

Table S1 Calculated and experimental thymine oxygen core excitation energies in eV are shown in the table. All computations are performed using the def2-TZVP basis set and B3LYP functional. The largest contribution to the particle orbital (ϕ_p) with reference to the ground state valence set is reported along with the hole orbital (ϕ_h) for each transition. Relative oscillator strengths (f_{rel}) are also reported

OCDFT				Experiment	
ϕ_h	ϕ_p	ω_{fi}	f_{rel}	Peak	ω_{fi}
O ₂	81.8% π_1^*	531.05	1.000	A	531.4
O ₁	64.0% π_2^*	532.08	0.968	B	532.3
O ₁	71.2% π_1^*	533.38	0.146	B'	≈ 533.8
O ₂	78.3% π_2^*	533.75	0.162		
O ₁	77.0% D ₁	534.74	0.008	C	535.7
O ₂	65.9% D ₁	534.85	0.042		
O ₂	44.1% D ₃	535.28	0.020		
O ₁	69.5% D ₃	535.46	0.098		
O ₂	60.8% D ₂	535.53	0.085		
O ₁	76.0% π_3^*	536.12	0.222		
O ₂	69.0% π_3^*	536.24	0.104		
O ₂	86.3% D ₄	536.34	0.052		
O ₁	76.3% D ₂	536.60	0.039		
O ₂	44.4% D ₆	537.02	0.024	D	537.1
O ₁	83.5% D ₄	537.10	0.047		
O ₂	63.7% D ₅	537.21	0.021		
O ₁	35.6% D ₇	537.45	0.054		
O ₂	44.0% D ₇	537.67	0.073		
O ₁	43.6% D ₅	537.72	0.036		
O ₁	70.7% D ₆	538.49	0.058		

4 Thymine Nitrogen K-Edge

Table S2 Calculated and experimental thymine nitrogen core excitation energies in eV are shown in the table. All computations are performed using the def2-TZVP basis set and B3LYP functional. The largest contribution to the particle orbital (ϕ_p) with reference to the ground state valence set is reported along with the hole orbital (ϕ_h) for each transition. Relative oscillator strengths (f_{rel}) are also reported

OCDFT				Experiment	
ϕ_h	ϕ_p	ω_{fi}	f_{rel}	Peak	ω_{fi}
N ₄	81.8% π_1^*	401.18	1.000	A	401.7
N ₃	64.0% π_2^*	401.76	0.805		
N ₄	78.3% π_2^*	402.50	0.087	B	402.7
N ₃	77.0% D ₁	403.09	0.863		
N ₄	65.9% D ₁	403.33	0.765		
N ₄	44.1% D ₃	404.17	0.912	C	404.1
N ₄	60.8% D ₂	404.94	0.144	D	405.5
N ₃	69.5% D ₃	405.09	0.374		
N ₄	86.3% D ₄	405.31	0.864		
N ₃	76.0% π_3^*	405.41	0.333		
N ₄	69.0% π_3^*	405.62	0.183		
N ₃	71.2% π_1^*	405.67	0.490		
N ₃	76.3% D ₂	405.76	0.177		

5 Thymine Carbon K-Edge

Table S3 Calculated and experimental thymine carbon core excitation energies in eV are shown in the table. All computations are performed using the def2-TZVP basis set and B3LYP functional. The largest contribution to the particle orbital (ϕ_p) with reference to the ground state valence set is reported along with the hole orbital (ϕ_h) for each transition. Relative oscillator strengths (f_{rel}) are also reported

OCDFT				Experiment	
ϕ_h	ϕ_p	ω_{fi}	f_{rel}	Peak	ω_{fi}
C ₈	92.1% π_1^*	284.90	0.372	A	284.9
C ₇	95.9% π_1^*	285.98	0.698	B	285.9
C ₉	75.4% π_2^*	286.56	0.036	C	287.8
C ₈	97.6% π_2^*	287.33	0.171		
C ₆	81.8% π_1^*	287.68	0.792		
C ₉	89.9% π_1^*	287.92	0.117		
C ₈	48.1% D ₃	288.19	0.006		
C ₉	87.7% D ₁	288.46	0.229	D	289.4
C ₈	53.9% D ₁	288.94	0.037		
C ₉	85.1% D ₃	289.01	0.158		
C ₇	94.2% π_2^*	289.06	0.289		
C ₅	64.0% π_2^*	289.14	1.000		
C ₈	32.5% D ₃	289.17	0.017		
C ₇	90.3% D ₁	289.22	0.001		
C ₉	63.1% π_3^*	289.26	0.333		
C ₉	49.5% D ₂	289.31	0.375		
C ₈	67.1% D ₂	289.67	0.082		
C ₈	77.0% D ₄	289.68	0.105	E	290.7
C ₆	78.3% π_2^*	289.94	0.135		
C ₉	75.4% D ₄	290.14	0.023		
C ₈	33.3% D ₅	290.31	0.119		
C ₅	71.2% π_1^*	290.33	0.029		
C ₉	30.5% D ₅	290.43	0.047		
C ₇	71.6% D ₃	290.44	0.050		
C ₇	41.5% D ₂	290.54	0.041		
C ₈	38.1% D ₆	290.80	0.093		
C ₉	24.4% D ₆	291.12	0.076		
C ₈	61.2% D ₇	291.13	0.024		
C ₇	45.5% π_3^*	291.42	0.018		
C ₇	83.1% D ₄	291.44	0.001		
C ₉	24.8% D ₅	291.45	0.289		
C ₆	65.9% D ₁	291.59	0.036		
C ₇	44.3% D ₅	291.83	0.055		

6 Adenine Nitrogen K-Edge

Table S4 Calculated and experimental adenine nitrogen core excitation energies in eV are shown in the table. All computations are performed using the def2-TZVP basis set and B3LYP functional. The largest contribution to the particle orbital (ϕ_p) with reference to the ground state valence set is reported along with the hole orbital (ϕ_h) for each transition. Relative oscillator strengths (f_{rel}) are also reported

OCDFT				Experiment	
ϕ_h	ϕ_p	ω_{fi}	f_{rel}	Peak	ω_{fi}
N ₄	81.0% π_1^*	399.14	0.851	A	399.5
N ₃	63.7% π_1^*	399.28	0.926		
N ₅	92.6% π_2^*	399.42	1.000		
N ₅	92.4% π_1^*	399.69	0.002	A'	≈ 400.4
N ₄	98.9% π_2^*	400.39	0.022		
N ₃	81.6% π_2^*	401.21	0.109	B'	401.3
N ₂	82.1% π_1^*	401.43	0.364	B	401.9
N ₃	66.2% π_3^*	401.79	0.145		
N ₁	69.3% π_1^*	401.81	0.594		
N ₄	77.4% π_3^*	401.95	0.184		
N ₅	56.7% π_3^*	402.10	0.017		
N ₅	34.7% π_3^*	402.15	0.013		
N ₂	78.4% D ₃	402.27	0.204		
N ₄	80.2% D ₂	402.36	0.003	C	403.0
N ₃	90.2% D ₂	402.42	0.012		
N ₄	83.4% D ₃	402.73	0.038		
N ₃	69.0% D ₃	402.80	0.008		
N ₅	36.4% D ₃	402.80	0.049		
N ₁	74.8% π_2^*	403.08	0.122		
N ₅	39.1% D ₅	403.18	0.030		
N ₄	48.5% D ₄	403.22	0.033		
N ₁	87.2% D ₂	403.25	0.418		
N ₃	80.4% D ₄	403.32	0.074		
N ₂	57.1% D ₆	403.34	0.918		
N ₅	91.1% D ₆	403.38	0.052		
N ₂	94.8% π_3^*	404.33	0.038		
N ₃	42.3% D ₈	404.44	0.023		
N ₂	87.1% π_2^*	404.55	0.011		
N ₃	59.8% D ₆	404.71	0.059		
N ₅	29.0% D ₅	404.73	0.031		
N ₄	91.9% D ₁₀	404.79	0.253		
N ₂	56.6% D ₂	404.97	0.115		

7 Adenine Carbon K-Edge

Table S5 Calculated and experimental adenine carbon core excitation energies in eV are shown in the table. All computations are performed using the def2-TZVP basis set and B3LYP functional. The largest contribution to the particle orbital (ϕ_p) with reference to the ground state valence set is reported along with the hole orbital (ϕ_h) for each transition. Relative oscillator strengths (f_{rel}) are also reported

OCDFT				Experiment	
ϕ_h	ϕ_p	ω_{fi}	f_{rel}	Peak	ω_{fi}
C ₁₀	92.6% π_2^*	286.32	0.298	A	286.4
C ₉	81.0% π_1^*	286.46	0.936		
C ₁₀	92.4% π_1^*	286.71	0.260	B	286.8
C ₇	82.1% π_1^*	286.86	0.893		
C ₆	69.3% π_1^*	287.27	1.000	C	287.4
C ₈	63.7% π_1^*	287.41	0.961		
C ₈	81.6% π_2^*	287.86	0.000	C'	≈ 288.0
C ₁₀	34.7% π_3^*	287.93	0.092		
C ₉	98.9% π_2^*	288.02	0.026		
C ₆	74.8% π_2^*	288.78	0.008	D	289.0
C ₁₀	56.7% π_3^*	288.89	0.006		
C ₇	78.4% D ₃	288.91	0.001		
C ₁₀	36.4% D ₃	289.16	0.038		
C ₈	66.2% π_3^*	289.21	0.014		
C ₉	77.4% π_3^*	289.41	0.016	E	
C ₇	87.1% π_2^*	289.43	0.042		
C ₇	57.1% D ₆	289.66	0.329		
C ₁₀	39.1% D ₅	289.82	0.029	F	
C ₉	80.2% D ₂	289.98	0.266		
C ₈	90.2% D ₂	290.06	0.044		
C ₉	83.4% D ₃	290.14	0.166		
C ₆	87.2% D ₂	290.15	0.035		
C ₇	94.8% π_3^*	290.36	0.086	G	
C ₁₀	91.1% D ₆	290.37	0.020		
C ₁₀	61.6% D ₇	290.42	0.031		
C ₉	48.5% D ₄	290.45	0.014		
C ₈	69.0% D ₃	290.61	0.010		
C ₆	77.2% π_3^*	290.66	0.060		
C ₇	56.6% D ₂	290.77	0.064		
C ₉	61.7% D ₆	290.94	0.018		