Simulation of X-Ray Absorption Spectra with Orthogonality Constrained Density Functional Theory

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1 Supplementary

For the sake of brevity the tables reporting the computed core excitations for adenine and thymine were condensed in the text to only display the largest contributors to the respective peak features. However, in the simulation of the NEXAS spectra of each molecule we computed 10 core excitations for each 1s core hole. These calculated transitions correspond directly with the stick spectra shown in the main text. Here we report the full unabridged tables for each k-edge in Tables 3–7.
We report the optimized geometries of adenine and thymine used in the simulation. These structures were optimized using the Psi4 *ab initio* quantum chemistry package. We optimized them at the B3LYP/def2-TZVP level of theory, we chose this level of theory after analyzing the performance of the test set and noticing that there was not a noticable difference between the triple-ζ and quadruple-ζ basis sets. So in order to save on computational cost we utilized the triple-ζ basis.

List of Tables

Table 1 Optimized cartesian geometry of adenine used for simulation of NEXAS spectra optimized at the B3LYP/def2-TZVP level of theory.

C	-1.970585664532	-1.395137524338	-0.045467117394
N	-1.881922764968	-0.101178970901	-0.187746915294
C	-0.530036651175	0.162042066892	-0.075212958513
C	0.194518534413	-1.008769908818	0.138884730519
N	-0.752839154291	-2.003591795126	0.155019478510
H	-0.575304730981	-2.985001122876	0.288894532977
H	-2.887084126393	-1.963704194624	-0.076026591074
C	0.220821847281	1.350420528553	-0.134877528376
N	1.548880751460	1.275830644080	0.014725285193
C	2.109044063853	0.076787593229	0.214691629565
N	1.515353675426	-1.110912425553	0.290953400869
H	3.187892320597	0.080293623862	0.328711091758
N	-0.350021924019	2.556054469300	-0.336758184831
H	-1.344255431781	2.632817141374	-0.451219656473
H	0.231906121724	3.373853460732	-0.370895998201

Table 2 Optimized cartesian geometry of thymine used for simulation of NEXAS spectra optimized at the B3LYP/def2-TZVP level of theory.

C	-1.246495845834	0.412642804754	-0.003573103168
C	-2.507237287316	1.217084061874	-0.011848989295
H	-3.117873132937	1.004161896948	-0.892346853646
H	-2.252332058556	2.276314275673	-0.024950360779
H	-3.115843391524	1.025528612536	0.874939447790
C	-1.217630214628	-0.931441458484	0.012635606229
N	-0.056489889005	-1.654192870252	0.020052122522
C	1.197028093408	-1.083944060777	0.011743762351
N	1.154191491462	0.288466721271	-0.004799899183
C	0.033038734047	1.117787686433	-0.013561659185
H	2.050520064174	0.753906293046	-0.011435103920
O	0.171793664591	2.321663419892	-0.028248779210
O	2.217898772608	-1.730464525441	0.018397425821
H	-2.125375374356	-1.524102636497	0.020825176486
H	-0.070123074504	-2.660021414373	0.032219688224

Table 3 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		
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	C	535.7
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		
O_1	83.5% D_4	537.10	0.047		
O_2	63.7% D_5	537.21	0.021	D	537.1
O_1	35.6% 42-A	537.45	0.054		
O_2	44.0% 42-A	537.67	0.073		
O_1	43.6% D_5	537.72	0.036		
O_1	70.7% D_6	538.49	0.058		

Table 4 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		
N_3	77.0% D_1	403.09	0.863	B	402.7
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		
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	D	405.5
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		

Table 5 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_8	97.6% π_2^*	287.33	0.171		
C_6	81.8% π_1^*	287.68	0.792	C	287.8
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		
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	D	289.4
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		
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	E	290.7
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		

Table 6 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		
N_3	63.7% π_1^*	399.28	0.926	A	399.5
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		
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	B	401.9
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		
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	C	403.0
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_4	61.7% D_6	403.67	0.007		
N_3	77.6% D_5	403.72	0.007		
N_5	61.6% D_7	403.79	0.073		
N_1	77.2% π_3^*	403.97	0.083		
N_4	37.1% D_7	404.07	0.040		
N_5	36.3% D_4	404.20	0.008		
N_4	39.8% D_7	404.24	0.022		
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		

Table 7 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_{10}	34.7% π_3^*	287.93	0.092	C′	$\approx$ 288.0
C_9	98.9% π_2^*	288.02	0.026		
C_6	74.8% π_2^*	288.78	0.008		
C_{10}	56.7% π_3^*	288.89	0.006		
C_7	78.4% D_3	288.91	0.001	D	289.0
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		
C_7	87.1% π_2^*	289.43	0.042	E	
C_7	57.1% D_6	289.66	0.329		
C_{10}	39.1% D_5	289.82	0.029		
C_9	80.2% D_2	289.98	0.266		
C_8	90.2% D_2	290.06	0.044	F	
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		
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	G	
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		