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

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Supplementary Materials

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Table 1 Optimized cartesian geometry of adenine used for simulation of NEXAS spectra optimized at the B3LYP/def2-TZVP level of theory using the PSI4 *ab initio* quantum chemistry package.

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 using the PSI4 *ab initio* quantum chemistry package.

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% 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		

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		