Benzene

1 Theoretical Results

1.1 Bz

Table 1: Bz. EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) UV-vis excitation energies (EE) ω_i (eV), oscillator strengths f, and ionization energy (IE, eV).

	Symm.	ω_i	f
EE	B_{2u}	5.21	0.0000
	B_{3u}	6.64	0.0000
	B_{1u}	6.97	0.0591
	B_{1u}	7.04	0.0000
	B_{2u}	7.16	0.1762
	B_{3u}	7.16	0.1762
	B_{3u}	7.58	0.5302
	B_{1u}	8.37	0.0000
IP	B_{2g}	9.22	
	B_{3g}	9.22	

Table 2: Bz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge excitation energies (EE) ω_i (eV), oscillator strengths f, and core ionization energy (IE, eV).

	Symm.	ω_i	f	Assignment
EE	B_{1u}	285.97	0.30677	(A)
	B_{3u}	287.80	0.02200	(B)
	B_{2u}	287.80	0.02205	(B)
	B_{3u}	288.79	0.00177	(C)
	B_{2u}	288.79	0.00178	(C)
	B_{2u}	288.83	0.00502	(C)
	B_{3u}	288.83	0.00503	(C)
	B_{1u}	288.91	0.00543	(C)
	B_{2u}	289.35	0.00162	
	B_{3u}	289.35	0.00162	
	B_{2u}	289.40	0.00123	
	B_{3u}	289.40	0.00123	
	B_{2u}	289.46	0.00013	
	B_{3u}	289.46	0.00014	
	B_{1u}	289.66	0.00270	
	B_{3u}	289.75	0.01014	(D)
	B_{2u}	289.75	0.01045	(D)
	B_{2u}	290.12	0.00060	
	B_{3u}	290.12	0.00060	
	B_{3u}	290.14	0.00018	
	B_{2u}	290.14	0.00019	
	B_{3u}	290.21	0.00001	
	B_{1u}	290.28	0.00270	
	B_{1u}	290.83	0.00057	
	B_{1u}	291.07	0.02991	
IP	A_g	290.93		
	B_{1g}	290.93		

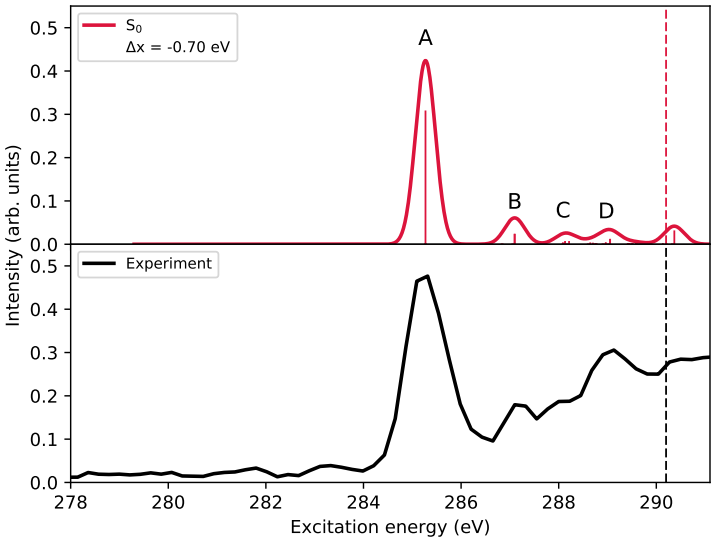
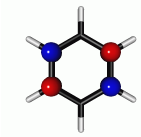
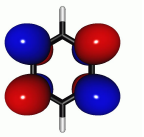
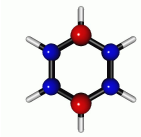
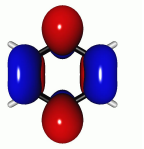
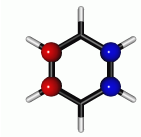
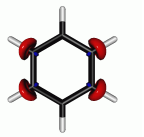
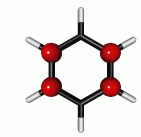
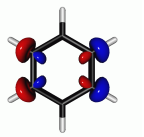
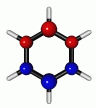
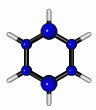
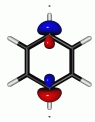


Figure 1: Bz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge X-ray absorption spectra obtained by convolution of the spectral data in Table 2 with a Gaussian function (FWHM = 0.8 eV). Dashed vertical lines correspond to the IEs. The energy shifts required to align the NEXAFS profiles with the experimental one is - 0.7 eV. The computed IE has been shifted by the same amount as used to align the NEXAFS profiles.

Table 3: Bz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states. NTO isosurface is 0.05.

Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.35	
		0.35	
(B) B_{2u}		0.50	
		0.20	
(B) B_{3u}		0.50	
		0.20	

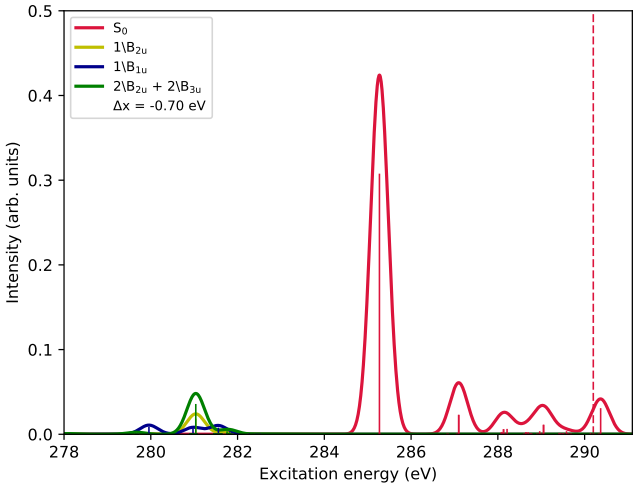


Figure 2: Bz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and excited-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 4: Bz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) TR-NEXAFS. Excitation energies (EE) ω_i (eV), oscillator strengths f, and core ionization energy (IE, eV).

	B_{1u}			B_{2u}			B_{3u}		
	Symm.	ω_i	f	Symm.	ω_i	f	Symm.	ω_i	f
EE	B_{2g}	282.30	0.000001	B_{3g}	278.80	0.000292	B_{3g}	278.80	0.000292
	B_{3g}	282.30	0.000001	B_{3g}	280.35	0.000902	B_{3g}	280.35	0.000902
	A_g	282.61	0.007834	A_g	281.61	0.000002	A_g	281.61	0.000002
	A_g	283.62	0.005864	B_{1g}	281.61	0.000002	B_{1g}	281.61	0.000002
	A_g	284.15	0.000584	A_g	281.65	0.000001	A_g	281.65	0.000001
	A_g	284.21	0.006911	B_{1g}	281.65	0.000001	B_{1g}	281.65	0.000001
				B_{3g}	281.74	0.017425	B_{3g}	281.74	0.017425
				A_g	282.25	0.000001	A_g	282.25	0.000001
				B_{1g}	282.25	0.000001	B_{1g}	282.25	0.000001
				A_g	282.26	0.000005	A_g	282.26	0.000005
				B_{3g}	282.46	0.001297	B_{3g}	282.46	0.001297
				B_{3g}	282.51	0.000814	B_{3g}	282.51	0.000814
				B_{1g}	282.94	0.000002	B_{1g}	282.94	0.000002
				B_{3g}	283.12	0.000029	B_{3g}	283.12	0.000029
				B_{3g}	283.19	0.000080	B_{3g}	283.19	0.000080

1.2 Bz^+

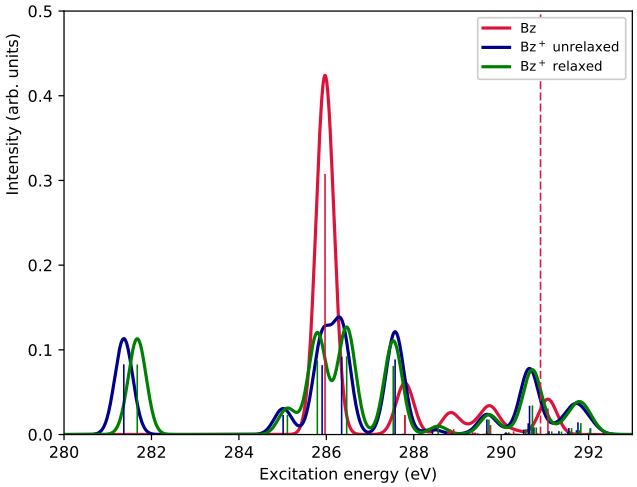


Figure 3: Bz and Bz^+. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and ionized-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory and at the EOM-CCSD/cc-pVTZ optimized geometry for the ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 5: Bz^+. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) core excitation energies (EE) ω_i (eV) and oscillator strengths f at the neutral unrelaxed geometry and the relaxed geometry

	Unrelaxed			Relaxed		
	Symm.	ω_i	f	Symm.	ω_i	f
EE	B_{1u}	281.37	0.08195	B_{1u}	281.67	0.08184
	B_{1u}	285.01	0.02218	B_{1u}	285.11	0.02228
	B_{1u}	285.90	0.08089	B_{1u}	285.79	0.08666
	B_{1u}	286.35	0.09067	B_{1u}	286.46	0.09136
	B_{1u}	287.57	0.08774	B_{1u}	287.53	0.08007
	B_{1u}	288.43	0.00431	B_{1u}	288.56	0.00712
	B_{3u}	289.23	0.00059	B_{3u}	289.27	0.00057
	B_{3u}	289.67	0.01685	B_{3u}	289.72	0.01661
	B_{3u}	290.09	0.00076	B_{3u}	290.16	0.00071
	B_{2u}	290.11	0.00176	B_{2u}	290.18	0.00178
	B_{3u}	290.51	0.00490	B_{3u}	290.56	0.00497
	B_{3u}	290.62	0.01235	B_{3u}	290.69	0.01103
	B_{2u}	290.65	0.03291	B_{2u}	290.71	0.03329
	B_{3u}	290.75	0.00766	B_{3u}	290.80	0.00738
	B_{2u}	291.02	0.00000	B_{2u}	291.06	0.00008
	B_{2u}	291.23	0.00001	B_{2u}	291.27	0.00007
	B_{2u}	291.55	0.00685	B_{2u}	291.61	0.00670
	B_{2u}	291.76	0.00190	B_{2u}	291.73	0.00189

1.3 ClBz

Table 6: ClBz. EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) UV-vis excitation energies (EE) ω_i (eV), oscillator strengths f, and ionization energy (IE, eV).

	Symm.	ω_i	f
EE	B_1	5.10	0.0012
	B_2	6.28	0.0067
	A_1	6.38	0.0839
	A_2	6.75	0.0000
	B_2	6.76	0.0001
	A_2	6.89	0.0000
	A_1	7.06	0.0327
	B_1	7.14	0.4226
IP	B_2	9.01	
	A_2	9.57	
	B_1	11.21	
	(B_2	$\sim$ 11.8)	
	A_1	12.60	

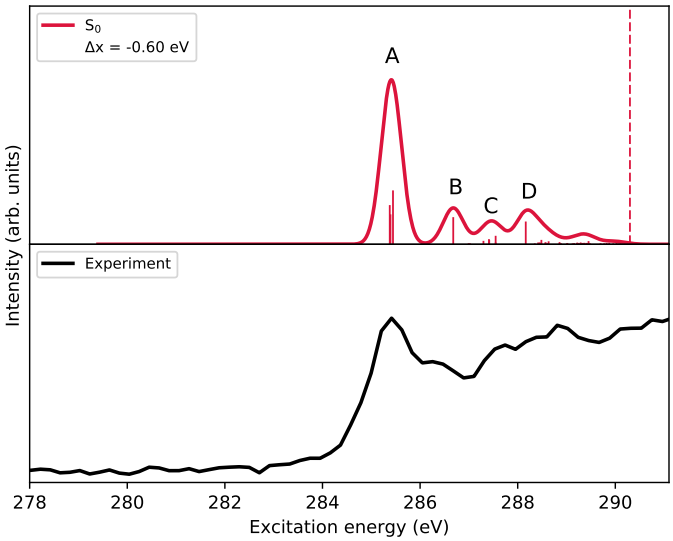
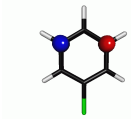
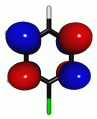
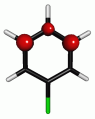
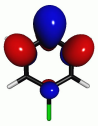
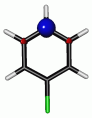
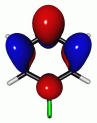
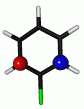
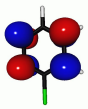
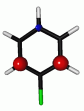
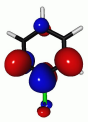
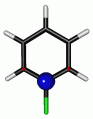
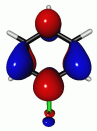
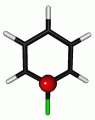


Figure 4: ClBz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge X-ray absorption spectra obtained by convolution of the spectral data in Table 7 with a Gaussian function (FWHM = 0.8 eV). Dashed vertical lines correspond to the IEs. The energy shifts required to align the NEXAFS profiles with the experimental one is - 0.6 eV. The computed IE has been shifted by the same amount as used to align the NEXAFS profiles.

Table 7: ClBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge excitation energies (EE) ω_i (eV), oscillator strengths f, and core ionization energy (IE, eV).

	Symm.	ω_i	f	Assignment
EE	B_2	285.98	0.08103	(A)
	B_2	285.99	0.06054	(A)
	B_2	286.04	0.11106	(A)
	B_2	287.28	0.05506	(B)
	B_2	287.59	0.00023	
	B_2	287.62	0.00001	
	A_1	287.90	0.00530	(C)
	B_1	288.01	0.00895	(C)
	A_1	288.02	0.00687	(C)
	A_1	288.15	0.00171	
	B_1	288.15	0.01595	(C)
	A_1	288.76	0.04590	(D)
	B_1	288.95	0.00004	
	A_1	289.02	0.00189	
	B_2	289.05	0.00030	
	B_1	289.05	0.00061	
	A_1	289.05	0.00209	
	A_1	289.08	0.00012	
	B_1	289.09	0.00740	
	A_1	289.17	0.00033	
	B_2	289.17	0.00166	
	B_1	289.17	0.00230	
	B_1	289.22	0.00009	
	A_1	289.22	0.00030	
	B_2	289.23	0.00440	
	A_1	289.46	0.00055	
	B_1	289.46	0.00271	
	A_1	289.49	0.00012	
	B_1	289.61	0.00085	
	A_1	289.62	0.00009	
	B_1	289.73	0.00009	
	A_1	289.76	0.00000	
	B_1	289.76	0.00021	
	A_1	289.81	0.00060	
	B_1	289.82	0.00157	
	A_1	289.83	0.00097	
	A_1	289.85	0.00011	
	B_1	289.85	0.00040	
	A_1	289.89	0.00196	
	B_2	289.92	0.00062	
	B_2	289.93	0.00094	
	B_1	289.94	0.00067	
	A_1	289.95	0.00002	
	B_2	289.96	0.00121	
	B_1	290.01	0.00032	
	A_1	290.01	0.00098	
	B_2	290.04	0.00029	
	A_1	290.05	0.00098	
	B_1	290.05	0.00481	
	B_2	290.08	0.00000	
	B_1	290.30	0.00019	
IP	A_1	291.21		
	B_1	291.29		

Table 8: ClBz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states. NTO isosurface is 0.05.

Excitation	Hole	σ_K^2	Particle
(A) B_2		0.55	
		0.25	
(A) B_2		0.71	
(A) B_2		0.55	
		0.25	
(B) B_2		0.79	
(D) A_1		0.82	

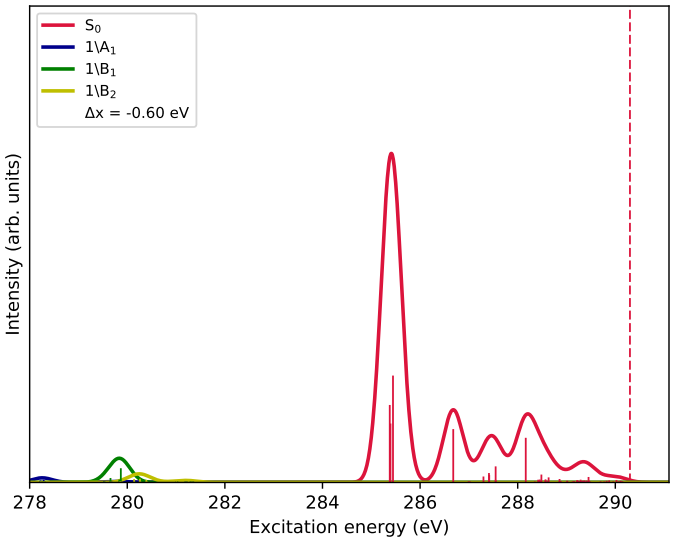


Figure 5: ClBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and excited-state core absorption spectra at the Franck-Condon geometry optimized at the level of theory. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 9: ClBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) TR-NEXAFS. Excitation energies (EE) ω_i (eV), oscillator strengths f.

	A_1			B_1			B_2		
	Symm.	ω_i	f	Symm.	ω_i	f	Symm.	ω_i	f
EE	B_2	278.8208	0.001107	A_2	278.8160	0.000012	A_1	280.7405	0.002615
	B_2	278.8353	0.000678	A_2	278.8823	0.000032	A_1	280.8604	0.002936
	B_2	278.8869	0.001757	A_2	280.2561	0.003739	A_1	280.9908	0.001709
	B_2	280.1211	0.000419	A_2	280.4368	0.002036	A_1	281.6067	0.000601
	B_2	280.4400	0.000594	A_2	280.4681	0.013979	A_1	281.8610	0.001218
	A_1	280.7405	0.000061	B_1	280.8532	0.000003			
	B_1	280.8532	0.000054	B_1	280.9907	0.000002			
	A_1	280.8604	0.000011						
	B_1	280.9907	0.000041						
	A_1	280.9908	0.000026						
	A_1	281.6067	0.000106						
	A_1	281.8610	0.000016						
	B_1	281.8963	0.000024						

1.3.1 ClBz$^+$

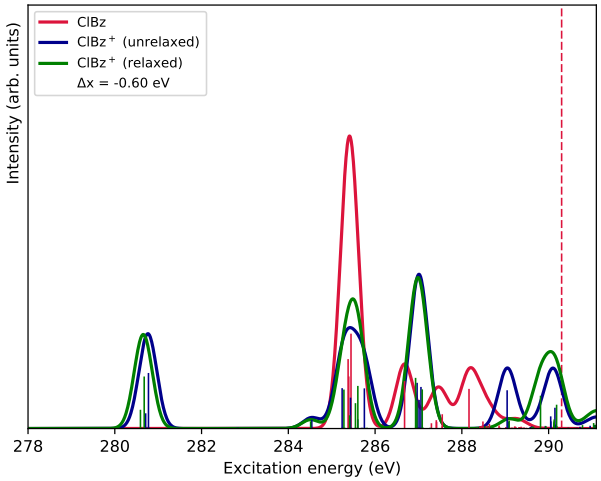


Figure 6: ClBz and ClBz$^+$. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and ionized-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory and at the EOM-CCSD/cc-pVTZ optimized geometry for the ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 10: $ClBz^+$. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) core excitation energies (EE) ω_i (eV) and oscillator strengths f at the neutral unrelaxed geometry and the relaxed geometry.

	Unrelaxed			Relaxed		
	Symm.	ω_i	f	Symm.	ω_i	f
EE	A_2	281.31	0.00000	A_2	281.19	0.00000
	B_2	281.31	0.01705	B_2	281.19	0.02122
	A_2	281.37	0.00000	A_2	281.27	0.00000
	B_2	281.38	0.06466	B_2	281.28	0.06050
	A_2	282.06	0.00000	A_2	281.92	0.00000
	A_2	283.42	0.00000	A_2	283.40	0.00000
	B_2	285.14	0.00938	B_2	285.11	0.00756
	A_2	285.84	0.00000	A_2	285.88	0.00000
	B_2	285.84	0.04675	B_2	285.88	0.04510
	A_2	286.03	0.00000	B_2	286.01	0.01469
	B_2	286.03	0.03550	A_2	286.15	0.00000
	B_2	286.20	0.01002	B_2	286.15	0.02902
	A_2	286.29	0.00000	B_2	286.20	0.04940
	B_2	286.35	0.04651	A_2	286.39	0.00000
	A_2	287.57	0.00000	A_2	287.53	0.00000
	B_2	287.57	0.05305	B_2	287.53	0.05890
	A_2	287.61	0.00000	B_2	287.56	0.03213
	B_2	287.61	0.03291	A_2	287.68	0.00000
	B_2	287.66	0.04819	B_2	287.69	0.04530
	A_2	287.67	0.00000	A_2	287.87	0.00000
	A_1	288.38	0.00010	A_1	289.18	0.00011
	A_1	289.25	0.00021	A_1	289.27	0.00016
	A_1	289.64	0.04426	A_1	289.69	0.00827
	A_1	289.68	0.00749	A_1	290.21	0.00036
	A_1	290.18	0.00075	B_1	290.21	0.00075
	B_1	290.18	0.00083	A_1	290.25	0.00013
	A_1	290.21	0.00005	B_1	290.25	0.00129
	B_1	290.21	0.00162	A_1	290.41	0.03774
	A_1	290.53	0.00217	A_1	290.53	0.00196
	A_1	290.65	0.00756	A_1	290.72	0.00526
	B_1	290.65	0.01344	B_1	290.73	0.00738
	A_1	290.74	0.00300	A_1	290.73	0.00982
	A_1	290.75	0.00374	B_1	290.78	0.02720
	B_1	290.75	0.02362	A_1	290.79	0.00199
	B_1	291.06	0.00000	B_1	291.04	0.00002
	B_1	291.24	0.00000	B_1	291.19	0.00000
	B_1	291.32	0.00115	B_1	291.38	0.00309
	B_1	291.56	0.00237	B_1	291.64	0.00555
	B_1	291.65	0.00329	B_1	291.68	0.00353
	B_1	291.83	0.00574	B_1	291.84	0.00716

1.4 BrBz

Table 11: BrBz. EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) UV-vis excitation energies (EE) ω_i (eV), oscillator strengths f, and ionization energy (IE, eV).

	Symm.	ω_i	f
EE	B_1	5.08	0.0005
	B_2	5.96	0.0010
	A_1	6.27	0.1420
	B_2	6.32	0.0163
	A_2	6.70	0.0000
	A_2	6.84	0.0000
	B_1	6.98	0.0096
	A_1	7.00	0.0248
	B_2	8.91	
	A_2	9.56	
	B_1	10.51	
	(B_2	$\sim$ 11.2)	
	A_1	12.26	

Table 12: BrBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge excitation energies (EE) ω_i (eV), oscillator strengths f, and core ionization energy (IE, eV).

	Symm.	ω_i	f	Assignment
EE	B_2	287.10	0.05188	(A)
	A_1	287.81	0.04541	(B)
	A_1	289.61	0.00054	
	B_1	290.17	0.00000	
	B_2	290.32	0.00000	
	A_1	290.33	0.00049	
	A_1	290.58	0.00001	
	B_1	290.84	0.00008	
	A_1	290.84	0.00029	
	B_2	290.97	0.00003	
	A_1	291.17	0.00024	
	B_1	291.35	0.00013	
	A_1	291.37	0.00018	
	B_2	291.43	0.00022	
	A_1	291.51	0.00004	
	B_1	291.51	0.00016	
	B_2	291.59	0.00030	
	A_1	291.78	0.00000	
	B_1	291.80	0.00001	
	A_1	291.90	0.00001	
	A_1	292.03	0.00074	
	B_1	292.04	0.00003	
	B_1	292.09	0.00001	
	B_2	292.13	0.00017	
	A_1	292.24	0.00024	
	B_1	292.65	0.00103	
	A_1	292.73	0.00074	
	B_2	292.78	0.00081	
IP	A_1	292.58		

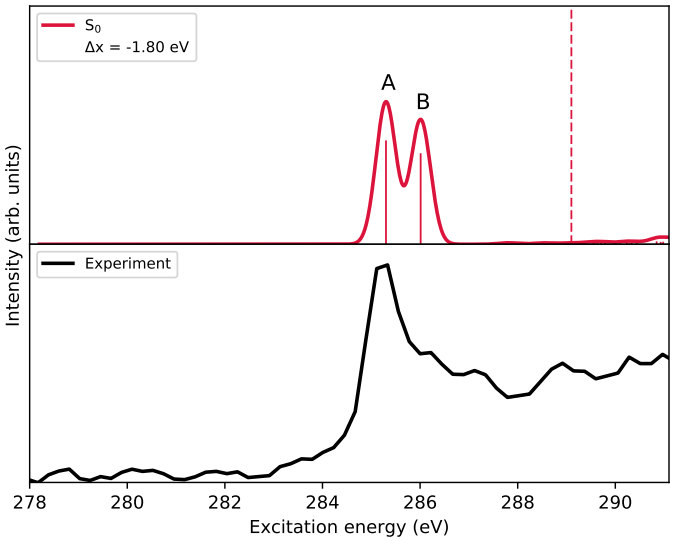
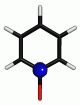
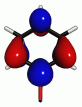
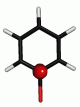


Figure 7: BrBz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) K-edge X-ray absorption spectra obtained by convolution of the spectral data in Table 7 with a Gaussian function (FWHM = 0.8 eV). Dashed vertical lines correspond to the IEs. The energy shifts required to align the NEXAFS profiles with the experimental one is - 0.6 eV. The computed IE has been shifted by the same amount as used to align the NEXAFS profiles.

Table 13: BrBz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states. NTO isosurface is 0.05.

Excitation	Hole	σ_K^2	Particle
(A)		0.79	
(B)		0.81	

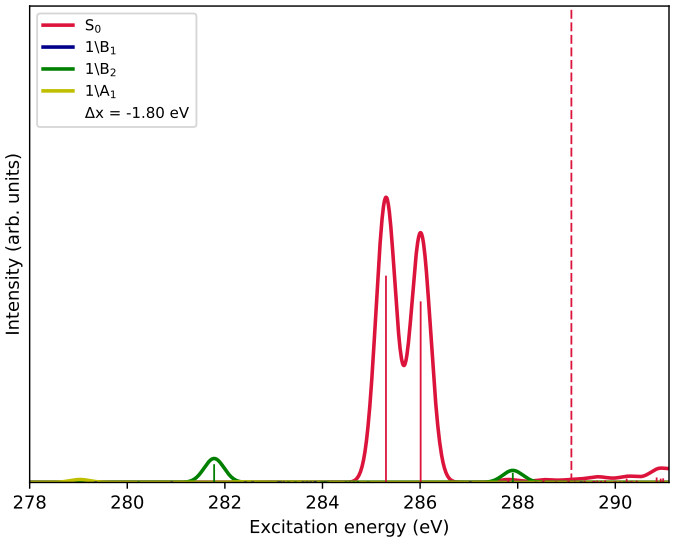


Figure 8: BrBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and excited-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 14: BrBz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) TR-NEXAFS. Excitation energies (EE) ω_i (eV), oscillator strengths f.

	A_1			B_2		
	Symm.	ω_i	f	Symm.	ω_i	f
EE	B_2	280.8307	0.000537	A_2	283.5799	0.004367
	B_2	284.0461	0.000099	A_2	286.5233	0.000003
	B_1	284.5742	0.000001	A_2	289.6995	0.002197
	B_2	284.6992	0.000022			
	B_1	285.0810	0.000001			
	B_1	285.2401	0.000003			
	B_2	285.3245	0.000053			

1.4.1 $BrBz^+$

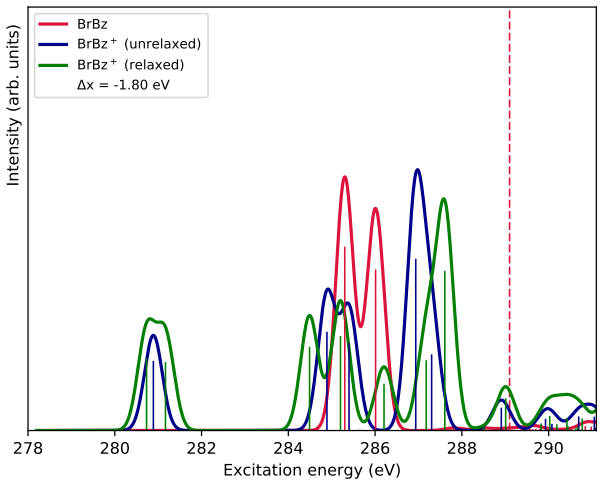


Figure 9: BrBz and $BrBz^+$. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and ionized-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory and at the EOM-CCSD/cc-pVTZ optimized geometry for the ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.