

Benzene

1 Theoretical Results

1.1 Bz IEs and MOs

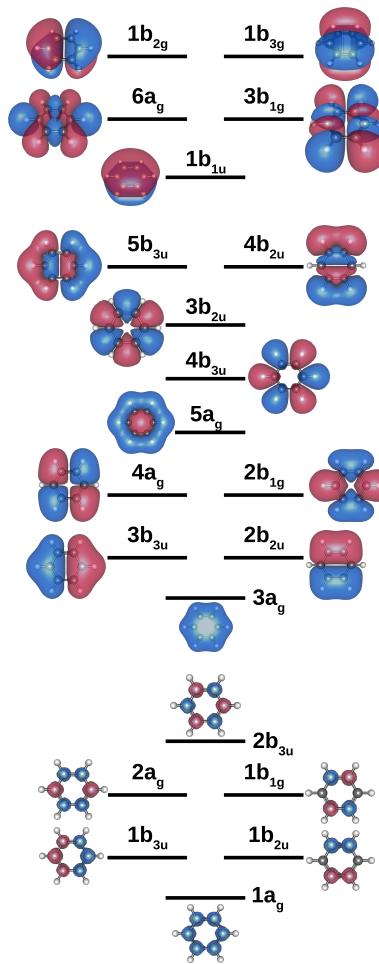


Figure 1: Occupied molecular orbitals diagram for benzene.

Table 1: Valence and core ionization energies (eV) of benzene, EOM-IP-CCSD and CVS-EOM-IP-CCSD with 6-311(2+,+)G**(uC)

MO	IE
$1a_g$	290.992
$1b_{2u}/1b_{3u}$	290.975
$1b_{1g}/2a_g$	290.934
$2b_{3u}$	290.914
$3a_g$	22.963
$2b_{2u}/3b_{3u}$	21.000
$2b_{1g}/4a_g$	19.598
$5a_g$	17.365
$4b_{3u}$	15.818
$3b_{2u}$	14.802
$4b_{2u}/5b_{3u}$	14.402
$1b_{1u}$	12.547
$3b_{1g}/6a_g$	12.108
$1b_{2g}/1b_{3g}$	9.224

Note that the numbering of MOs is opposite from the numbering of the EOM-IP states.

1.2 Bz

Table 2: 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 3: Bz. CCSD and CCSDR(3) /6-311++G** UV-vis ionization energy (IE, eV).

	Symm.	ω_i	f
CCSD	B_{2g}	9.22403	
	B_{3g}	9.22403	
CCSDR(3)	B_{2g}	9.21589	
	B_{3g}	9.21589	

Table 4: 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_{2u}/B_{3u}	287.80	0.04405	(B)
	B_{2u}/B_{3u}	288.79	0.00355	(C)
	B_{2u}/B_{3u}	288.83	0.01005	(C)
	B_{1u}	288.91	0.00543	(C)
	B_{2u}/B_{3u}	289.35	0.00324	
	B_{2u}/B_{3u}	289.40	0.00246	
	B_{2u}/B_{3u}	289.46	0.00027	
	B_{1u}	289.66	0.00270	
	B_{2u}/B_{3u}	289.75	0.02059	(D)
	B_{2u}/B_{3u}	290.12	0.00120	
	B_{2u}/B_{3u}	290.14	0.00037	
	B_{2u}/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		

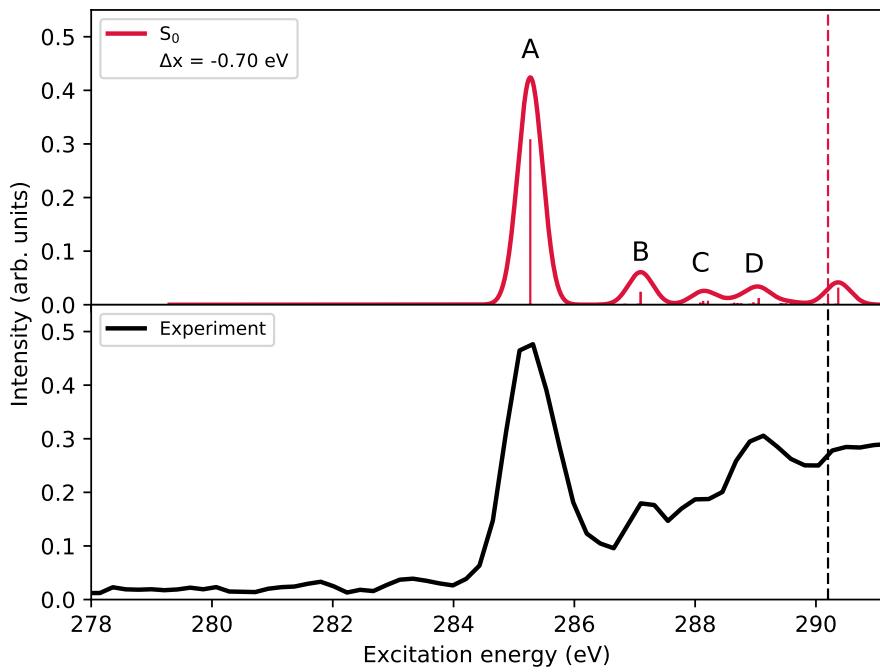


Figure 2: Bz. fc-CVS-EOM-CCSD/6-311(2+,+) G^{**} (uncontracted on C) K-edge X-ray absorption spectra obtained by convolution of the spectral data in Table 4 with a Gaussian function (FWHM = 0.8 eV). Dashed vertical lines correspond to the IEs. The energy shifts required to align the NEXAFS profiles with 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 5: Bz. fc-CVS-EOM-CCSD/6-311(2+,+) G^{**} (uncontracted on C) NTOs of the relevant core excited states. NTO isosurface is 0.005.

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

Table 6: Bz. fc-CVS-EOM-CCSD/6-311(2+,+) G^{**} (uncontracted on C) NTOs of the relevant core excited states.

Excitation	Hole	σ_K^2	Particle
$(C_1) B_{2u}$		0.32	
		0.24	
$(C_1) B_{3u}$		0.33	
		0.23	
$(C_2) B_{2u}$		0.38	
		0.35	
$(C_2) B_{3u}$		0.38	
		0.35	
$(C_3) B_{1u}$		0.38	

Table 7: Bz. fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states.

Excitation	Hole	σ_K^2	Particle
(D) B_{2u}		0.46	
		0.19	
(D) B_{3u}		0.46	
		0.19	

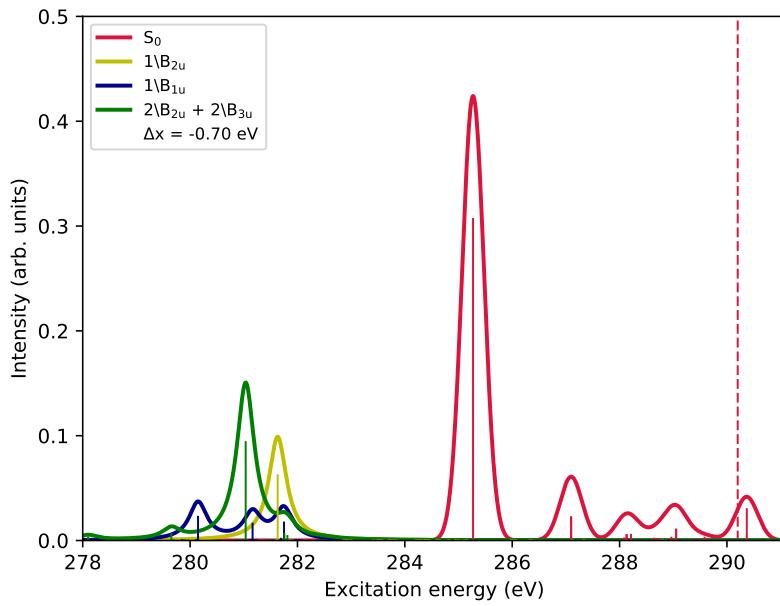


Figure 3: Bz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and excited-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 8: 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).

	(1) B _{2u}			(1) B _{1u}			(2) B _{2u} / (2)B _{3u}		
	Symm.	ω_i	f	Symm.	ω_i	f	Symm.	ω_i	f
EE	B _{3g}	282.3314	0.062241	B _{2g}	278.9926	0.000001	B _{3g}	278.8002	0.001467
	A _g	282.5551	0.000007	B _{3g}	278.9928	0.000001	B _{3g}	280.3508	0.003218
	B _{1g}	282.5551	0.000007	B _{2g}	280.5433	0.000003	A _g	280.6051	0.000001
	A _g	284.1015	0.000001	B _{3g}	280.5434	0.000003	B _{1g}	280.6051	0.000001
	B _{1g}	284.1015	0.000001	A _g	280.8482	0.022587	A _g	280.6556	0.000008
	B _{3g}	284.4005	0.000008	A _g	281.8639	0.016026	A _g	281.6087	0.000003
	A _g	284.5156	0.000001	A _g	282.3945	0.001614	B _{1g}	281.6087	0.000003
	B _{1g}	284.5156	0.000001	A _g	282.4495	0.017111	A _g	281.6502	0.000001
	B _{3g}	285.1504	0.000034				B _{1g}	281.6503	0.000001
	B _{3g}	286.6722	0.000004				B _{3g}	281.7353	0.046915
	B _{3g}	288.0413	0.000113				A _g	282.2019	0.000000
							A _g	282.2510	0.000003
							B _{1g}	282.2511	0.000003
							A _g	282.2569	0.000009

1.3 Bz^+

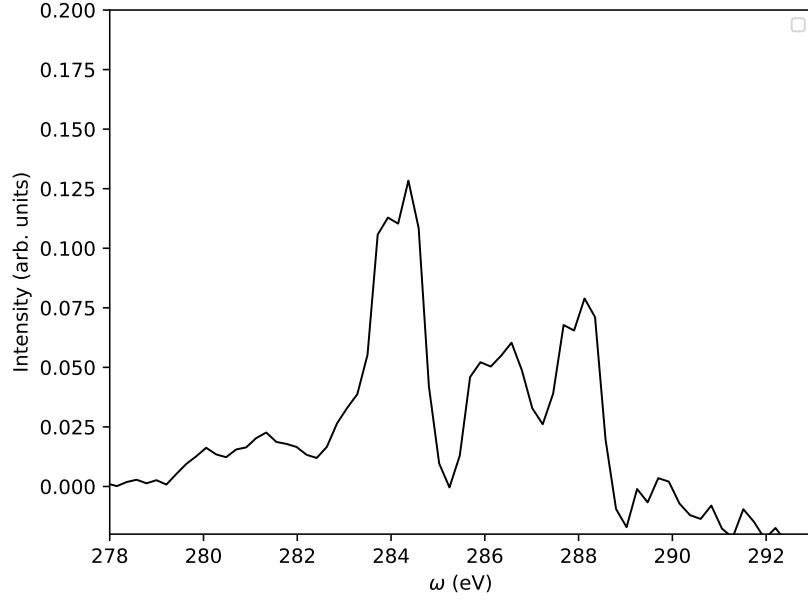


Figure 4: Bz^+ experimental spectrum

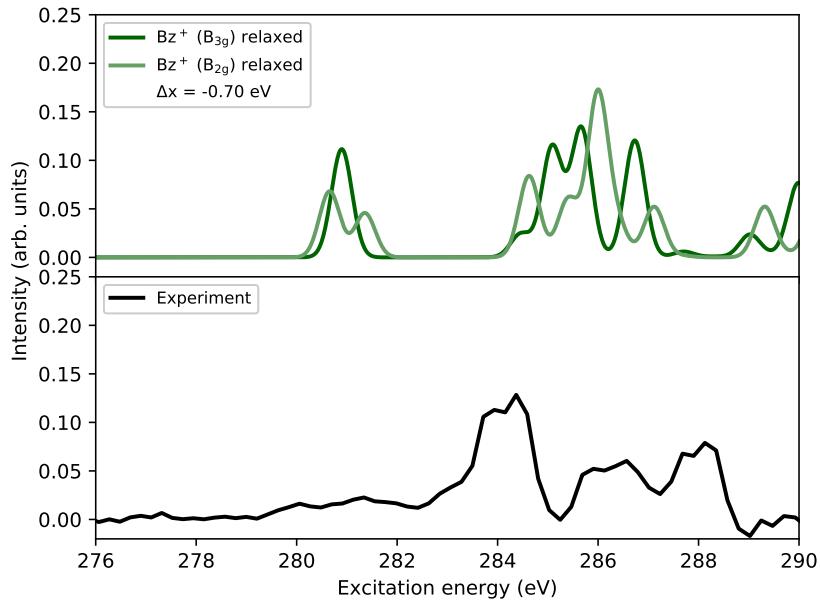


Figure 5: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

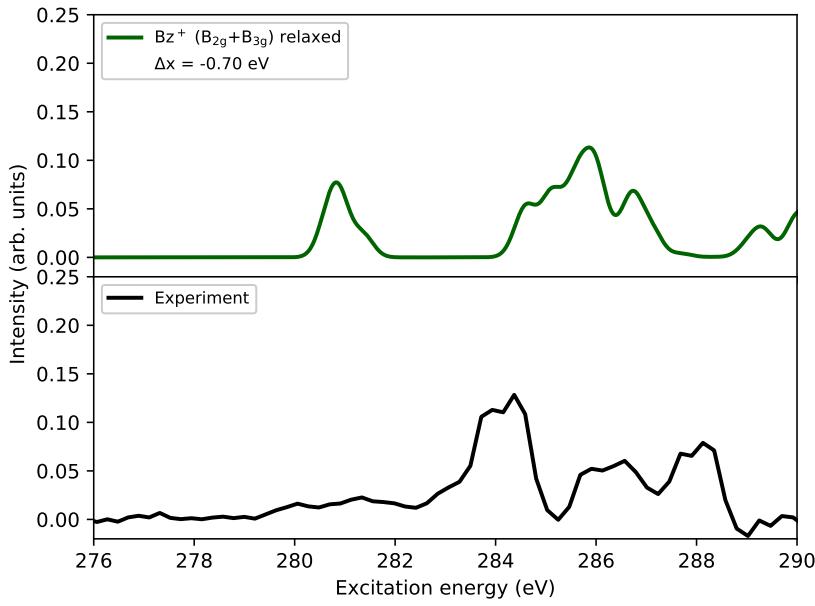


Figure 6: Bz^+ . Sum of the ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry of the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

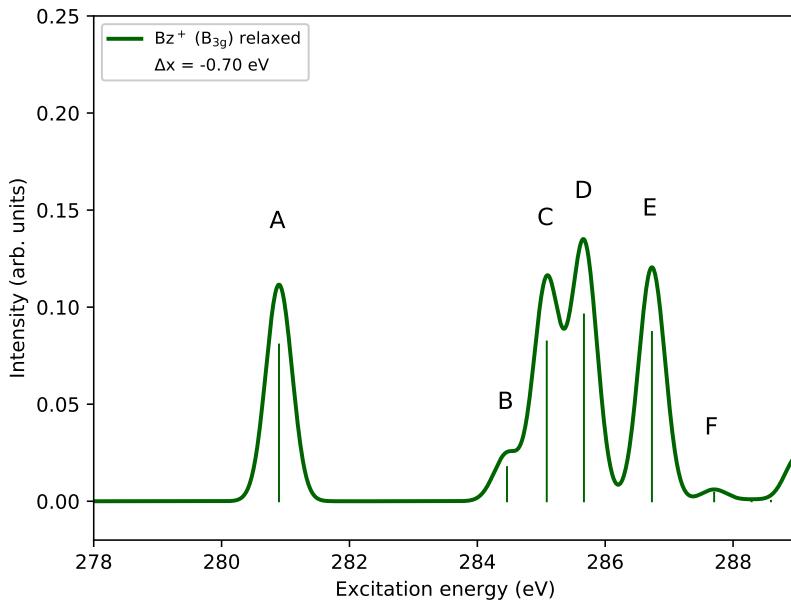


Figure 7: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{3g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

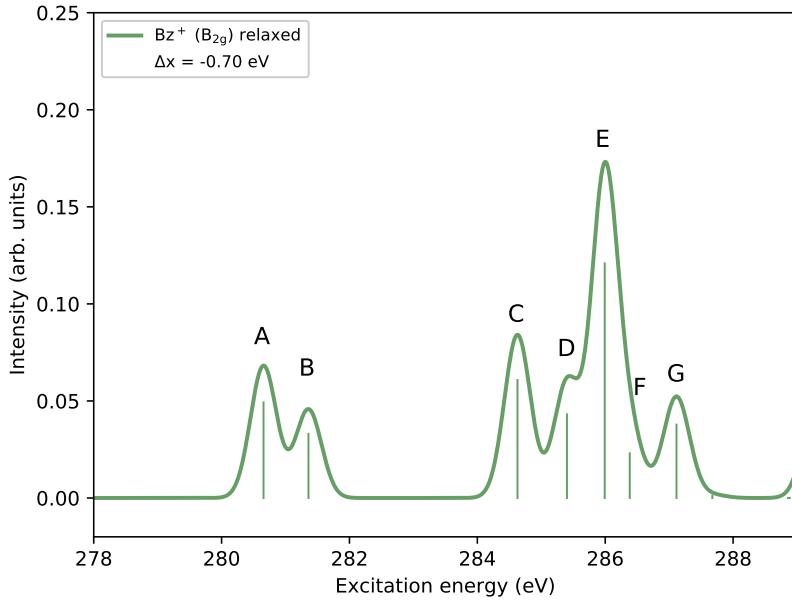


Figure 8: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)-G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 9: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)-G** (uncontracted on C) core excitation energies (EE) ω_i (eV) and oscillator strengths f at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states.

EE	B_{2g}				B_{3g}			
	Symm.	ω_i	f	Assignment	Symm.	ω_i	f	Assignment
B _{1u}	281.36	0.0493	A		281.60	0.0807	A	
	282.06	0.0333	B		285.16	0.0176	B	
	285.34	0.0608	C		285.79	0.0822	C	
	286.10	0.0433	D		286.37	0.0962	D	
	286.69	0.1212	E		287.43	0.0872	E	
	287.08	0.0231	F		288.40	0.0044	F	
	287.81	0.0378	G		288.99	0.0006		
	288.38	0.0012			289.29	0.0002		
	289.99	0.0096			289.72	0.0170		
	290.03	0.0284						

Table 10: Bz^+ (B_3g). fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states.

Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.67	
(B) B_{1u}		0.58	
(C) B_{1u}		0.59	
(D) B_{1u}		0.57	
(E) B_{1u}		0.53	
(F) B_{1u}		0.58	

Table 11: Bz^+ (B_{2g}). fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted on C) NTOs of the relevant core excited states.

Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.70	
(B) B_{1u}		0.70	
(C) B_{1u}		0.33	
		0.30	
(D) B_{1u}		0.67	
(E) B_{1u}		0.32	
		0.25	
(F) B_{1u}		0.36	
		0.33	
(G) B_{1u}		0.58	

Table 12: Bz. XES fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) energies ω_i (eV) and oscillator strengths f at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states.

	B_{2g}				B_{3g}			
	Symm.	ω_i	f	Assignment	Symm.	ω_i	f	Assignment
EE	B_{3u}	282.07	0.0673		B_{2u}	281.62	0.0674	

Table 13: Bz. fc-CVS-EOMIP-CCSD/6-311(2+,+)G** (uncontracted on C) core ionization energies (IE) ω_i (eV) at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states.

	$B_{2g(\min)}$			$B_{3g(\min)}$		
	Symm.	ω_i	Dyson Orbital	Symm.	ω_i	Dyson Orbital
IE	B_{2u} (B_{3u})	290.98		B_{3u}	290.98	
	B_{1g}	290.99		A_g	290.99	
	A_g	291.00		B_{1g}	291.00	
	B_{2u} (B_{3u})	291.03		B_{2u}	291.03	
	B_{3u} (B_{2u})	291.04		B_{3u}	291.04	
	A_g	291.05		A_g	291.05	