

Benzene

1 Overview and summary of the results

Figure 1 shows a summary diagram of energy levels in the benzene cation. See Fig. 2 for molecular orbitals (they look the same as EOM-IP Dyson orbitals in this case) and Table 1 (**Todo:** Need to add a table with relevant fc-CVS-IP-CCSD/fc-EOM-IP-CCSD energies computed at the two JT minima).

Observations:

Adiabatically, the two JT states are nearly degenerate. The JT distortion does not affect energies of the core orbitals. The core-*pi* transitions computed at the two JT minima are virtually the same (they are split by 0.051 eV).

As shown long time ago (Grant paper), the B_{2g} and B_{3g} minima are connected by a tiny barrier and zero vibrational level is much higher. So Bz^+ can be described as exhibiting free pseudorotation.

The question is how can we see 2 peaks in the XAS spectrum following valence photoionization? I think only assuming that the 2 lowest adiabatic states of the cation are populated, i.e., that we have population in the cone as well. Then XAS probing 2 states will have 2 peaks split by ~ 0.4 eV.

Experimental: Two photons of 267 nm equal 9.29 eV, which is 0.37 eV above the two JT minima. So it seems that we do have enough excess energy to populate two adiabats. Since the ions cannot lose energy, the population should remain there.

Notes for Michael and Marta :

Sonia 2 Marta: please comment here if you have already taken care of some of the points below

- Please check NTOs for XAS, there were mistakes in the earlier versions of the document.
marta: done.
- To compare theory with experiment for the cation, we should compile the spectrum as a combination of XES transitions from the core to the valence hole plus XAS transitions to higher orbitals, which we calculated by EOM-EE from the open-shell reference, so we do not have to deal with the artificial splitting of the core-valence transition. We should prepare this spectrum and give it to Michael so he does not get sidetracked by using wrong data.
marta: done (after XES results **Table 12**, see **Figures 10, 11, 12 and 13**)
- We should generate two spectra: one corresponding to excitation of the lowest JT relaxed structure (B_{2g} or/and B_{3g} minima) and one corresponding to the excitations into the cone. The latter should be computed as transitions into the higher adiabat, i.e., at the B_{3g} minimum into the B_{2g} hole and vice versa. So it will be something very similar to what Marta has calculated previously by mistake. **marta:** see **Table 13**

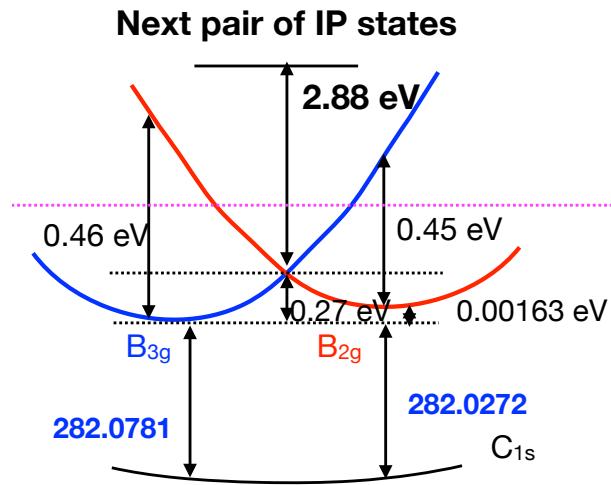


Figure 1: Summary energy diagram of ionized states in benzene computed with fc-CVS-EOM-IP-CCSD/6-311(2+,+)G**(uC). Pink dashed line marks 2-photon excitation (0.37 eV above $^2\text{B}_{2g}/^2\text{B}_{3g}$ minimum.

2 Theoretical Results

2.1 Bz IEs and MOs

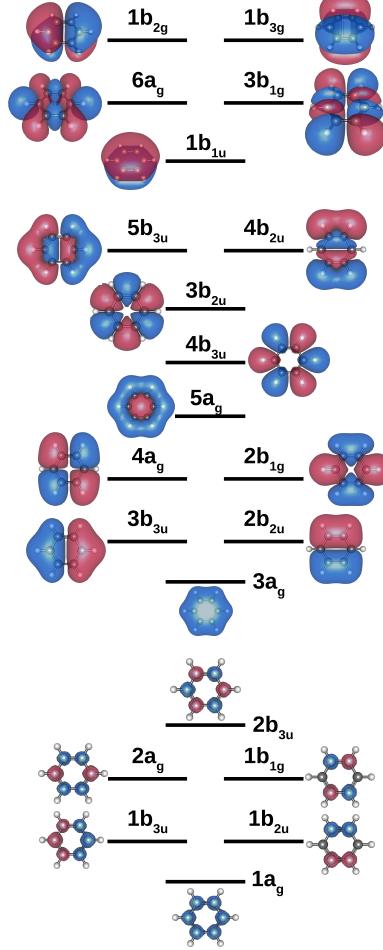


Figure 2: Occupied molecular orbitals diagram for benzene.

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.

2.2 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^{**} vertical ionization energy (IE, eV). **SONIA: I am running CC3 as well. Also excitations, not only IE.**

	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	
IE	A_g	290.93		
	B_{1g}	290.93		

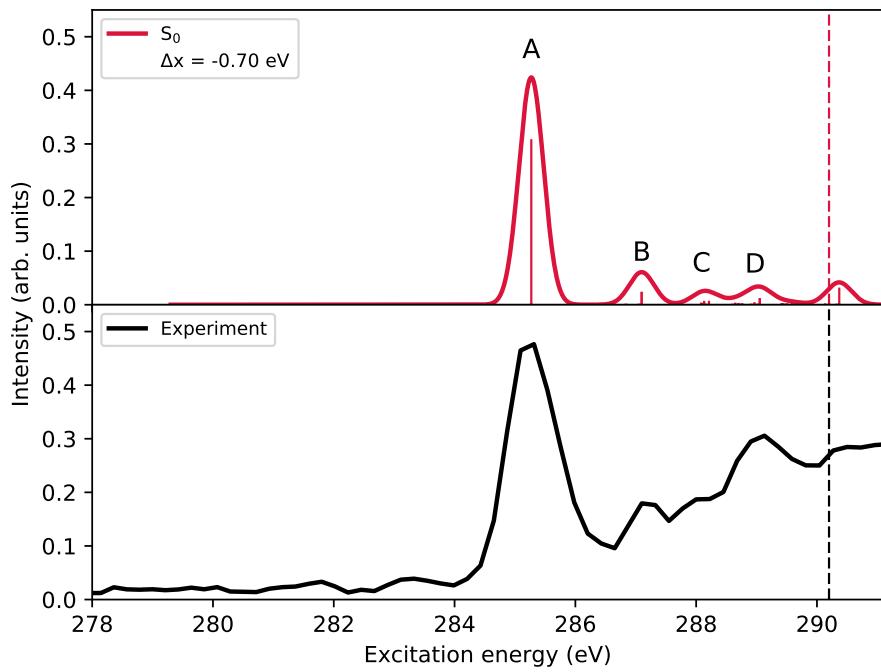


Figure 3: Bz. fc-CVS-EOM-CCSD/6-311(2+,+) G^{**} (uncontracted on C) K-edge X-ray absorption spectra obtained by convolution of the spectral data in Table 4 with a Gaussian function (FWHM = 0.8 eV). Dashed vertical lines correspond to the IEs. The energy shifts required to align the NEXAFS profiles with 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	
		0.35	
(B) B_{2u}		0.50	
		0.20	
(B) B_{3u}		0.50	
		0.20	

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	

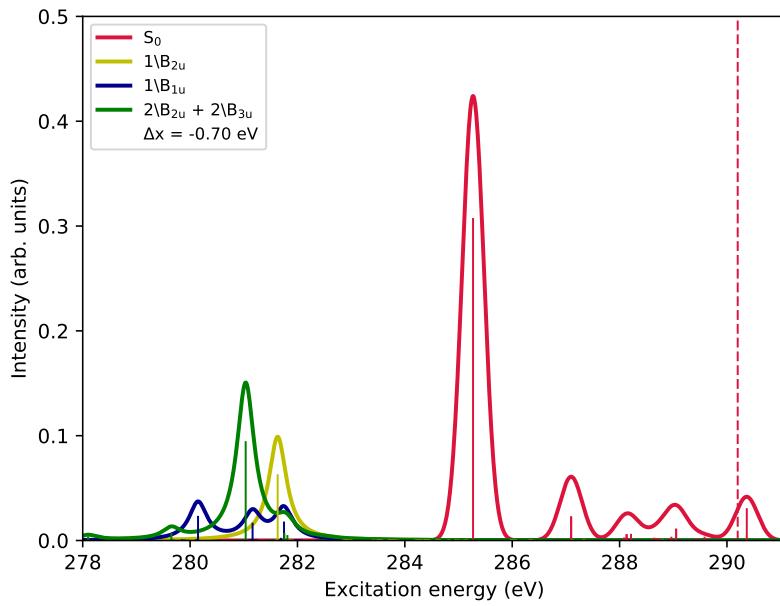


Figure 4: Bz. fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ground and excited-state core absorption spectra at the Franck-Condon geometry optimized at the RI-MP2/cc-pVTZ level of theory. A Gaussian convolution function (FWHM = 0.8 eV) was used.

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 .

	(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

2.3 Bz^+

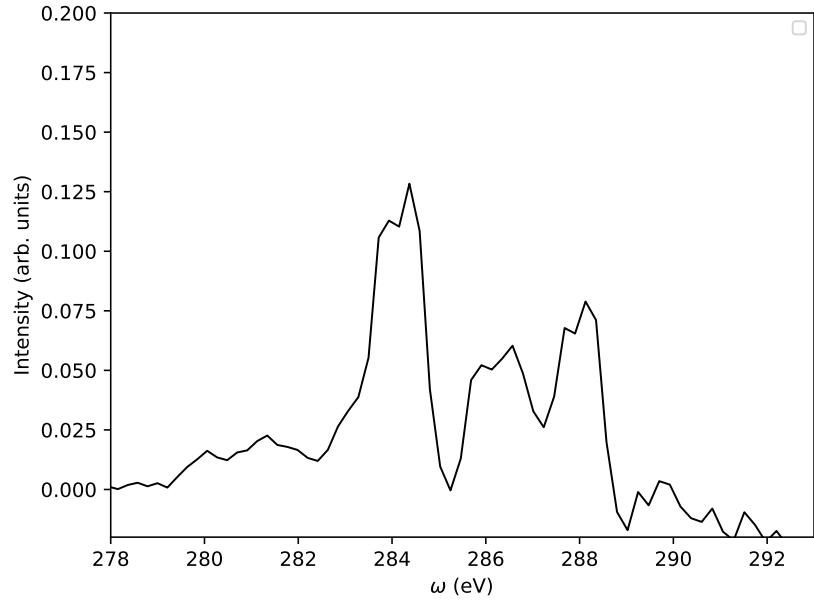


Figure 5: Bz^+ experimental spectrum

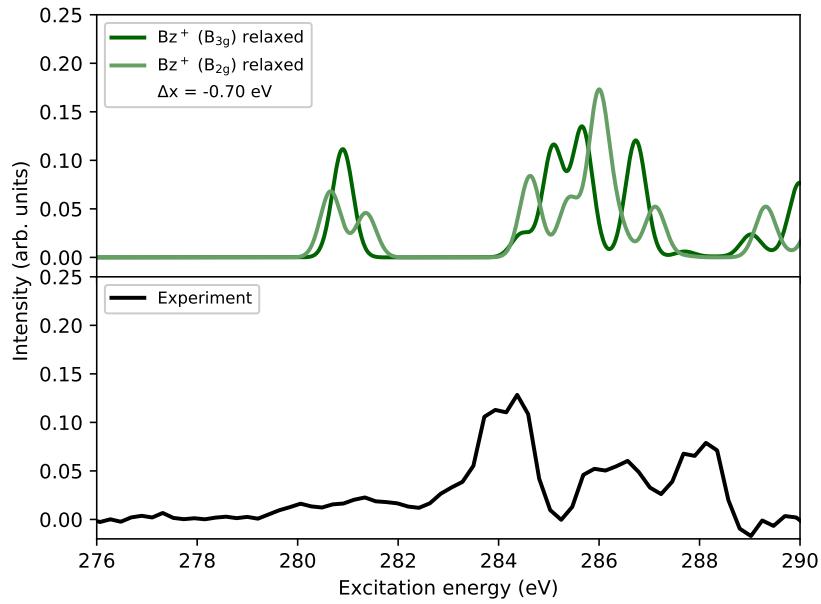


Figure 6: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)-G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

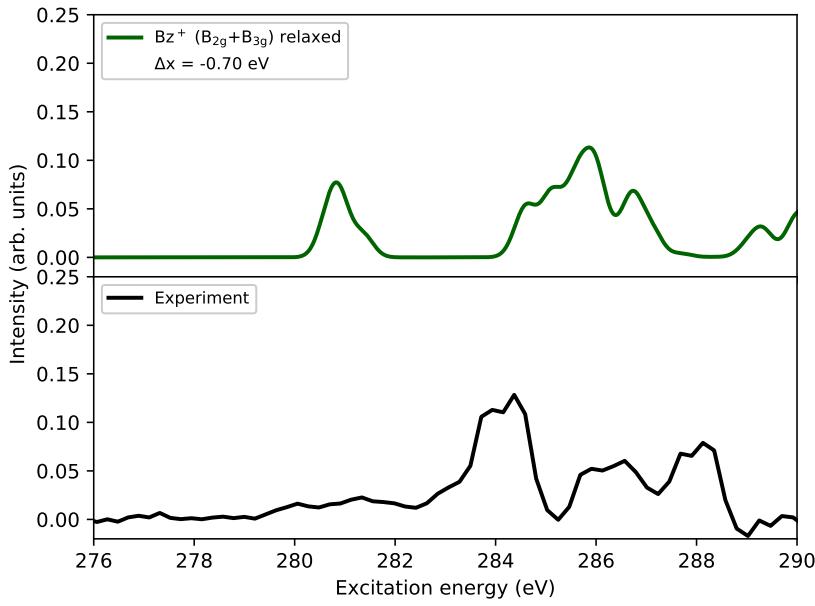


Figure 7: Bz⁺. Sum of the ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry of the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

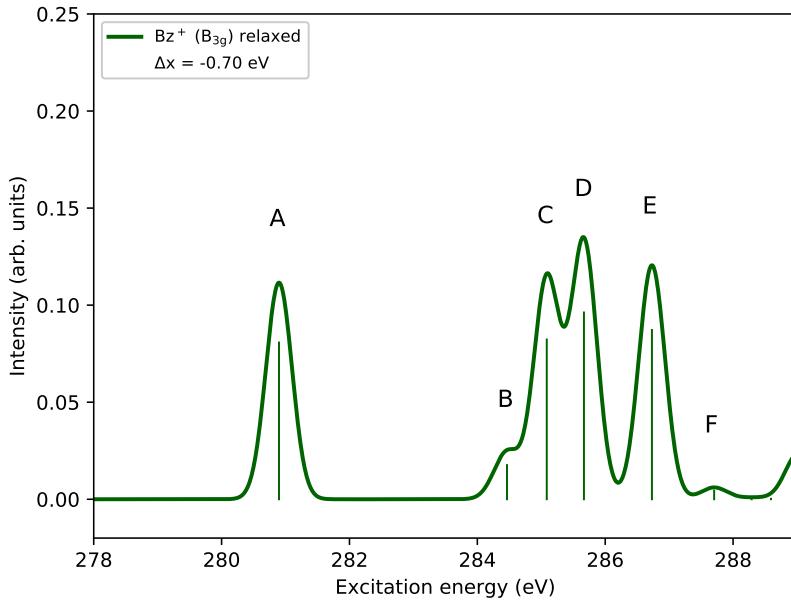


Figure 8: Bz⁺. ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{3g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

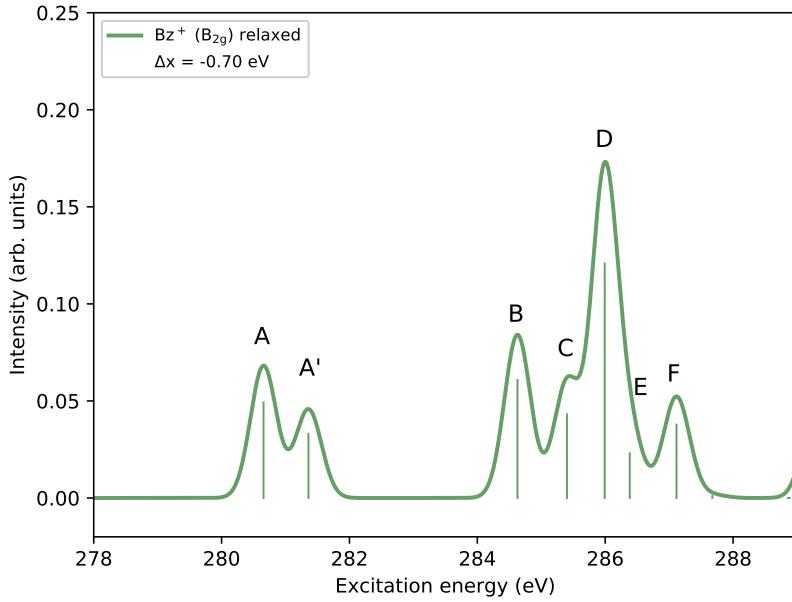


Figure 9: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

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.

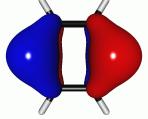
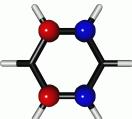
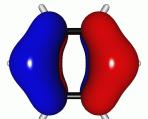
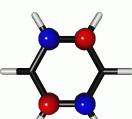
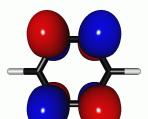
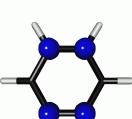
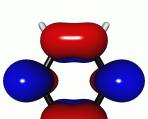
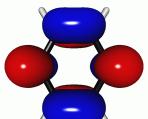
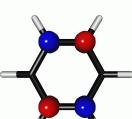
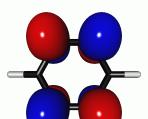
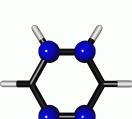
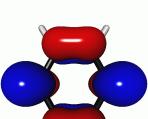
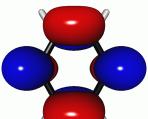
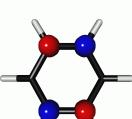
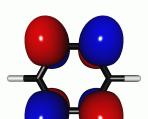
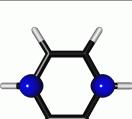
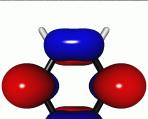
Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.70	
(A') B_{1u}		0.70	
(B) B_{1u}		0.33	
		0.30	
(C) B_{1u}		0.67	
(D) B_{1u}		0.32	
		0.25	
(E) B_{1u}		0.36	
		0.33	
(F) B_{1u}		0.58	

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	A	B_{2u}	282.08	0.0674	A

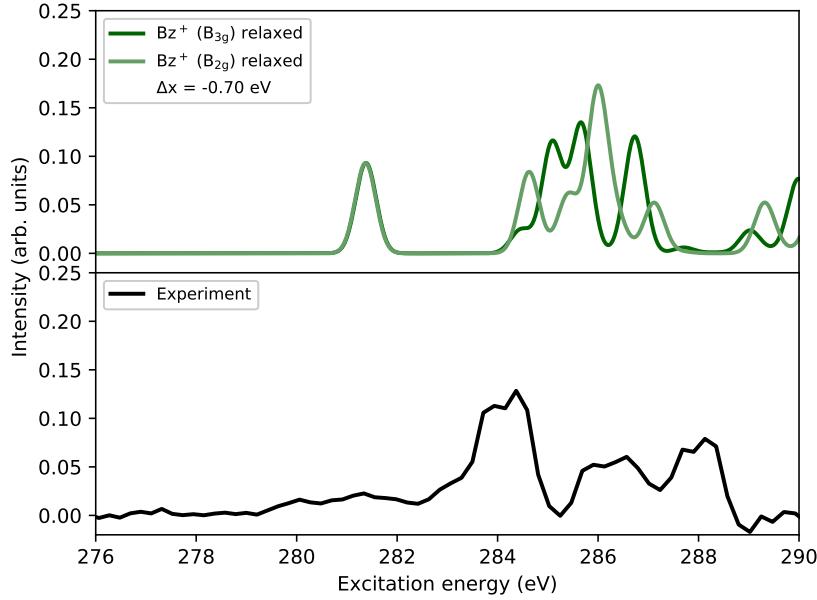


Figure 10: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

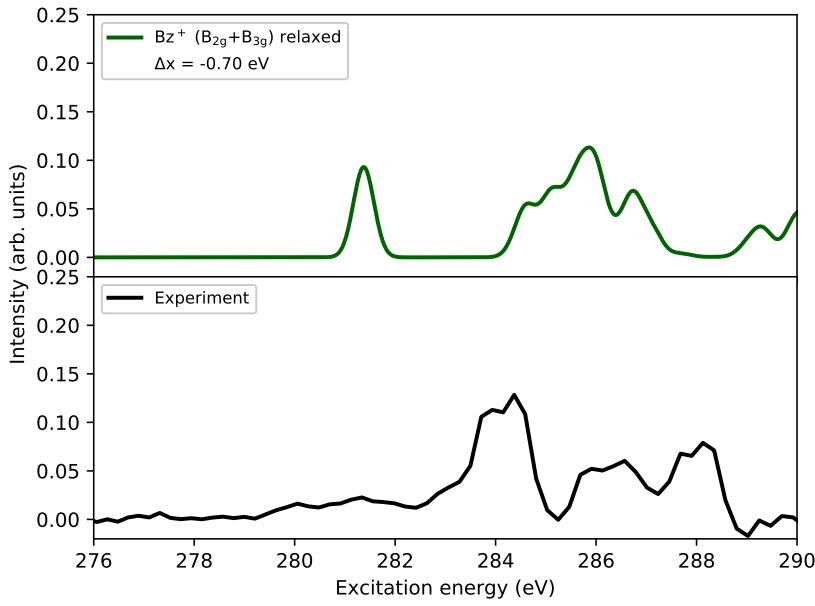


Figure 11: Bz^+ . Sum of the ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry of the B_{2g} and the B_{3g} ionized states. A Gaussian convolution function (FWHM = 0.8 eV) was used.

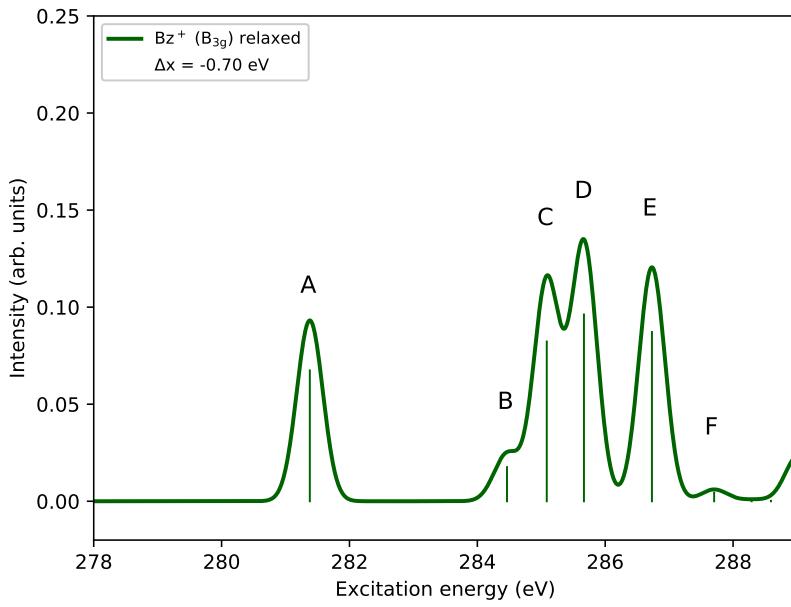


Figure 12: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{3g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

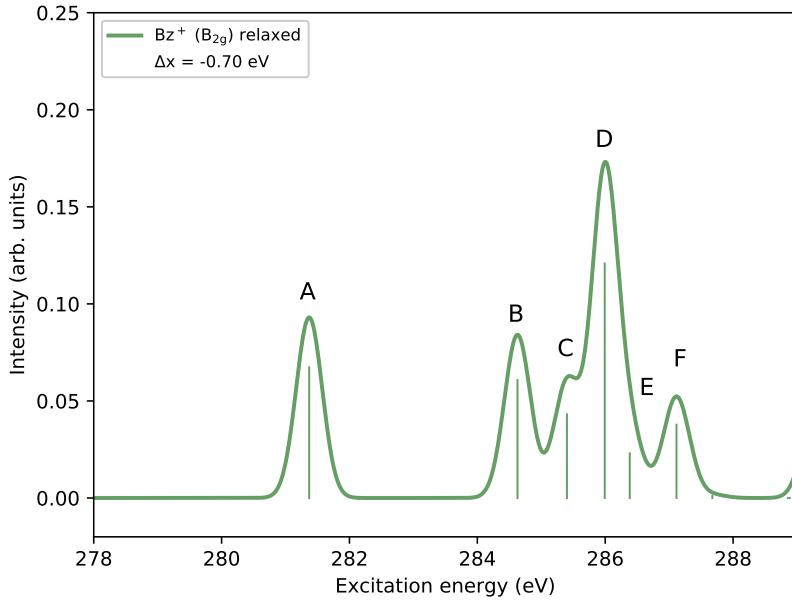


Figure 13: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 13: 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.

	B_{2g}				B_{3g}			
	Symm.	ω_i	f	Assignment	Symm.	ω_i	f	Assignment
$\text{B}_{2g}(\text{min})$	B_{1u}	281.36	0.0493	A	B_{1u}	281.26	0.0822	A
	B_{1u}	282.06	0.0333	A'				
$\text{B}_{3g}(\text{min})$	B_{1u}	281.02	0.0472	A	B_{1u}	281.60	0.0807	A
	B_{1u}	281.68	0.0370	A'				

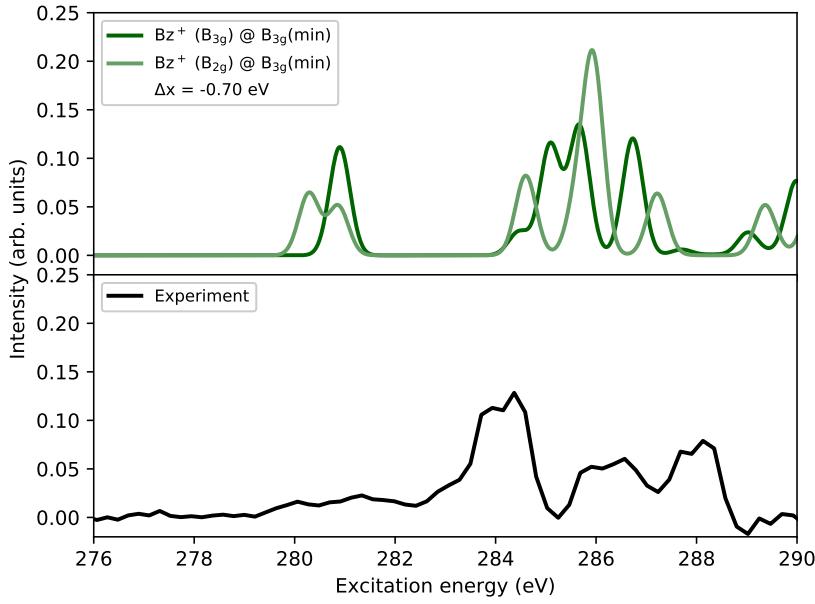


Figure 14: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{3g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

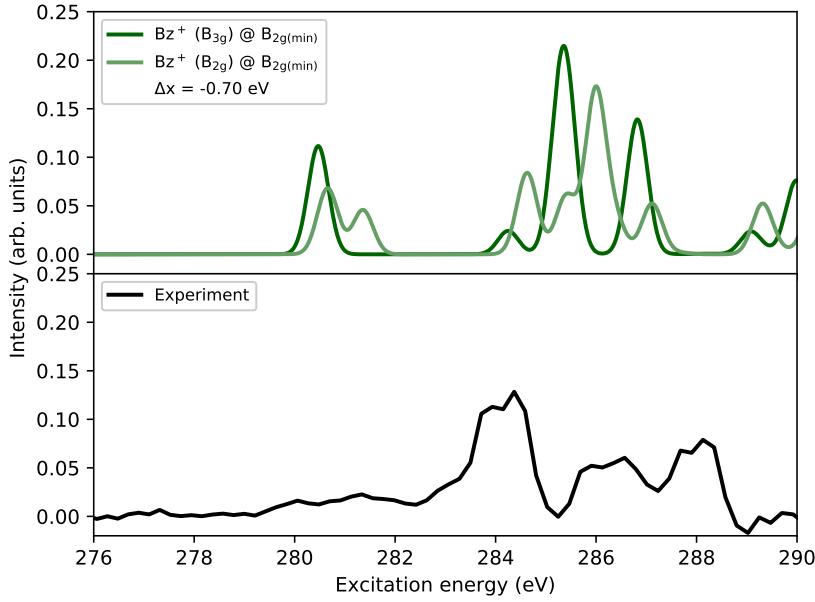


Figure 15: Bz^+ . ROHF fc-CVS-EOMEE-CCSD/6-311(2+,+)G** (uncontracted on C) ionized-state core absorption spectra at the relaxed EOM-CCSD/cc-pVTZ optimized geometry for the B_{2g} ionized state. A Gaussian convolution function (FWHM = 0.8 eV) was used.

Table 14: 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	