Preliminary calculations on Bz, Cl-Bz, and Br-Bz

1. Relevant structures:

Neutral states: ri-MP2/cc-pVTZ
(For ClBz I happened to use cc-pCTZ by mistake)
Cations: EOM-IP-CCSD/cc-pVTZ

2. Ionized states ordering at the neutral structures: EOM-IP/cc-pVTZ

3. XAS transitions from the neutrals at neutral structures:
CVS-EOM-EE-CCSD with various bases. This is to be compared with "static" spectra.

4. XAS transitions from the cations at the neutral structures: CVS-EOM-EE-CCSD with various bases. These are to be compared with the transient absorption spectra at zero time delay.
Note: I report symmetry of TRANSITIONS, not symmetry of the STATE.

5. Caution: We use largest Abelian subgroup, so to get proper symmetry labels of benzene, these labels should be converted to D6h. It is just a matter of bookkeeping.
Also, I follow Q-Chem's symmetry convention, which is different from Mulliken's.
In C2v, B2 and B1 should be flipped, and I think B2g and B3g in D2h.
6. CORE size in the calculations: I used qchem defaults
Benzene: 6 (6 x 1s(C))
ClBz: 11   6 1s(C) + 1s(Cl) + 2sp of Cl.
BrBz: 15   1s, of C and Br and 2sp of Br and 3sp of Br

Benzene: cc-pVTZ
Lowest ionized states at neutral (D2h) geometry:

State	IE
B2g/B3g	9.3084
B1g	12.1671
Ag	12.1676
B1u	12.6436

Notes:
1. I also found B2g doubly excited states at 9.68 eV.
2. Other states appear above 14 eV

Benzene cation, optimized structures of the JT pair (B2g and B3g)
Lowest state is B3g. It relaxes relative to neutral structure by 0.135 eV. AIE is 9.173
The minimum of the B2g state is 0.0017 eV higher.

REMPI @266 can only get the lowest states

Benzene: 6-311(2+,+)G** at the neutral (D2h) geometry, lowest bright excited states, to see which states are likely produced by excitation of 4.66 eV

Among the low-lying states of Bz, only these two are bright. They are way above one-photon energy. But it is well known that some dark states in benzene are vibronically allowed. So who knows what is produced in these experiments. We can compute the the spectra wrt to the lowest state of Bz for starters.

State	Eex	fl
2B2u	7.0417	0.179571
2B3u	7.1518	0.179579

CI-Benzene:

Lowest ionized states at neutral (C2V) geometry:

State	IE
B2	9.1238
A2	9.6485
B1	11.4031
B2	11.9658
A1	12.6630
B1	12.7148

Notes: Other states above 13.6 eV.
The lowest state (vertically) is B2, but A2 is close.
A2 is dipole forbidden, but in the
REMPI ionization, it is be perfectly allowed.

REMPI:
2 photons at 266 nm=9.322 eV

Optimized B2 state (planar):
Relaxation energy relative to the neutral structure is 0.156 eV, so AIE is: 8.968 eV
Optimized A2 state (planar):
Adiabatically, this state is 0.528 eV above B2 minimum
AEI: 9.4957 eV (also higher than vertical IE for B2)

Vertical state ordering at opt A2 geometry:
B2 state is 0.087 eV BELOW A2 state. No evidence for conical intersections (unless we invoke non-planar geometries).
266 nm is enough to produce B2 state, but 0.327 eV less than needed for A2 vertically.
Adiabatically almost enough. EOM-IP usually overestimates IEs.
We need to refine our ionization energy calculation, may be get (T) from Thomas.

Cl-Bz: Excited states at equilibrium geometry

In experiment, REMPI is used to prepare the cations, with hv=266 nm=4.66 eV. Thus, the nature of the cationic state depends on the excited states of the system.

State	Eex, eV	f_l
2A1	6.314	0.775
3A1	7.206	0.766
1A2	6.764	
2A2	6.969	
1B1	5.079	0.001
2B1	7.097	0.472
1B2	6.311	0.006
2B2	6.842	0.0002

Notes:
Among the lowest bright states:
A1 can yield -> A1, B1, B2 cations
B1 can yield -> B1, A1, A2 cations
B2 can yield -> B2, A2, A1 cations

I think B2 cation should be dominant, because among lowest states A1 are the brightest, and the lowest B1 is not that bright. But we cannot rule out A2.

BrBz calculation, ionized states

State	IE
1B2	9.0175
1A2	9.6335
1B1	10.6611
2B2	11.3632
2A1	12.3185
2B1	12.6139

Next state: at 14 eV

Optimized B2 state (planar):
Relaxation energy relative to the neutral structure is -0.1351 eV, so AIE is: 8.8824 eV
Optimized A2 state (planar):
Adiabatically, this state is 0.597 e above B2 minimum
AEI: 9.4795 eV (~0.4 eV ABOVE vertical B2 IE)
Vertical state order at A2 geometry: B2 state is 0.1799 eV BELOW A2.

The energetics is quite similar to ClBz. A2 is probably accessible by REMPI. However, it is above B2 vertically and adiabatically. Hence, here also there is no evidence of populating A2 via conical intersection, unless there is non-planar distortion lowering its energy further.

XAS spectra: Benzene

There are a lot of states, but due to high symmetry many are dark. The only allowed transitions are B1u, B2u, and B3u. However, keep in mind that benzene is known for having vibronically allowed spectral feature, so some of the dark states may appear in the experiment.

Transitions from the neutral, at the neutral geometry, aug-cc-pVDZ

State	Ex	fl
B1u	288.2551	0.2885
B2u/B3u	290.1300	0.0226
B2u/B3u	291.1861	0.0011
B2u/B3u	291.2432	0.0059
B2u/B3u	291.8541	0.0008
B1u	291.8553	0.0191

Note: The wave functions show rather mixed character, so our NTO analysis should be very useful here!

Note: When plotting spectra, lines corresponding to the degenerate pairs of states need to be multiplied by 2

I computed XAS excitation energies for the cation (B3g). As expected some new states appear at lower energies that correspond to the excitation to the B3g valence hole.
The new transitions are of B1u symmetry, they appear at: 283.50 and 284.15 eV (the state symmetry is then B1uxB3g=B2u). Other states look similar to those of the neutral, but of course there are shifts.

XAS-Benzene, different basis sets

6-311++G**

State	Ex	fl
B1u	286.3205	0.30705
B2u/B3u	288.1937	0.02425
B2u/B3u	289.2671	0.00026
B2u/B3u	289.3795	0.00558
B2u/B3u	289.9721	0.00074
B1u	290.0578	0.02117

6-311(2+,+)G**

State	Ex	fl
B1u	286.3193	0.30670
B2u/B3u	288.1570	0.02205
B2u/B3u	289.1399	0.00191
B2u/B3u	289.1844	0.00492
B2u/B3u	289.7011	0.00162
B1u	289.2675	0.00552

6-311(2+,+)G**, uncontracted core

State	Ex	fl
B1u	285.9702	0.30623
B2u/B3u	287.7975	0.02203
B2u/B3u	288.7853	0.00177
B2u/B3u	288.8306	0.00501
B2u/B3u	289.3468	0.00161
B1u	288.9127	0.00550

Note:
1. Pople versus Dunning: Eex redshifted by about 2 eV (makes sense, Dunning favors GS)
2. 2nd set of diffuse functions: changes less than 1 eV
3. Uncontracted core: about 0.5 lower excitation energies. My recommendation is to stick to UC-6-311(2+,+)G**. We can also check additional effect of using Rydberg functions.

C_6H_6

Need to replot using corrected results for UC-6-311(2+,+)G**

Legend:
- aug-cc-pVDZ
- 6-311++G**
- 6-311(2+,+)G**
- UC-6-311(2+,+)G**

Intensity (arb. units) vs Excitation energy (eV)

These are Bz XAS spectra with different bases. As one can see, adding 2nd set of diffuse functions does not have much effect (so we probably converged wrt to augmentation, but uncontracting core does change the shape considerably

XAS spectra, benzene cation, aug-cc-pVDZ

Transitions from the cation (B2g), at the neutral geometry
B1u transitions

283.5016	284.1445	287.6611	288.6304	289.0246	289.3786
0.0465	0.0343	0.0640	0.03943	0.1204	0.0071

B2u transitions

291.8957	292.2604	293.1772	293.2997	293.7144	293.7685
0.00003	0.0298	0.0043	0.0143	0.000002	0.000008

B3u transitions

291.8709	292.2257	292.7350	293.1457	293.2648	293.2684
0.000013	0.008744	0.002628	0.001421	0.005767	0.022871

Transitions from the cation (B2g), at the relaxed cation geometry
B1u

284.0469	287.5078	288.1290	288.7411	289.7954	290.7327
0.079615	0.022959	0.082071	0.084672	0.073773	0.006076

B2u

292.5242	292.9741	293.3562	293.5423	293.8920	294.0099
0.001864	0.032615	0.000095	0.000074	0.006049	0.001706

B3u

291.6325	292.0075	292.5094	292.8605	292.9517	293.0870
0.000622	0.016607	0.000703	0.005121	0.010316	0.007557

There are more bright transitions and the new transitions (highlighted in blue) involving valence hole are indeed bright. Relaxation makes them brighter!

XAS spectra, benzene cation (B2g) at neutral geom, UC-6-311(2+,+)G**

B1u transitions
281.3672	285.0114	285.9038	286.3503	287.5735	288.4256
0.081945	0.022177	0.080891	0.090671	0.087737	0.004312

B2u transitions
290.1088	290.6486	291.0249	291.2252	291.5481	291.7560
0.001759	0.032911	0.0	0.0	0.006848	0.001904

B3u transitions
290.1088	290.6484	291.0247	291.2251	291.5480	291.7558
0.000592	0.016846	0.000757	0.004895	0.012353	0.007661

XAS spectra, benzene cation (B2g) at CAT geom, UC-6-311(2+,+)G**

B1u transitions
281.6745	285.1091	285.7941	286.4650	287.5306	288.5568
0.081844	0.022284	0.086657	0.091358	0.080075	0.007117

B2u transitions
290.1750	290.7148	291.0556	291.2657	291.6098	2 91.7263
0.001784	0.033285	0.000078	0.000072	0.006696	0.001888

B3u transitions
289.2711	289.7189	290.1598	290.5642	290.6910	290.8019
0.000568	0.016609	0.000705	0.004968	0.011031	0.007382

$C_6H_6^+$

Neutral geometry

Cation geometry

Can now add relaxed cat in large basis
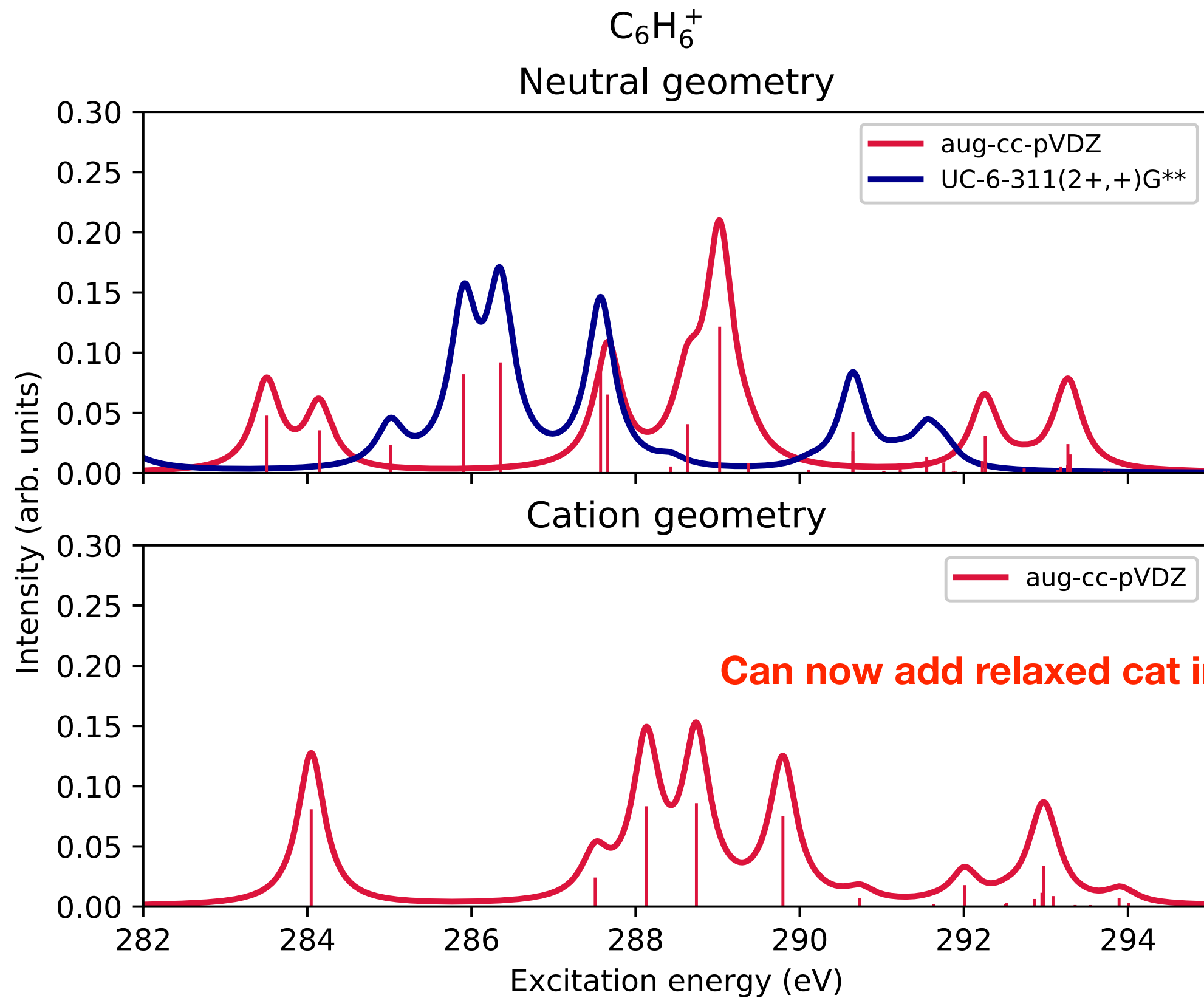
Here again using larger basis changes the shape of the spectrum. Also, we see that structural relaxation (bottom versus top) changes the shape.

XAS spectra: Cl-Benzene, aug-ccpVDZ, neutral, default FC

States at neutral geometry (the brightest states highlighted in red):

A1:

205.1586	206.4302	206.6212	207.4412	207.9472	208.1283
0.000022	0.000580	0.003485	0.000012	0.000450	0.000104

A2:

206.4277 207.1324 207.4109 208.0405

B1:

204.8265	206.4810	207.0346	207.5220	207.8338	208.3574
0.007774	0.000924	0.000175	0.000044	0.000002	0.000031

B2:

204.8270	206.4731	206.4866	207.0401	207.8285	208.1494
0.006890	0.000816	0.000982	0.000171	0.000018	0.000010

This is Cl edge

XAS spectra: Cl-Benzene cation, aug-ccpVDZ default FC

Transitions of the cation (B2) at the geometry of the neutral:
A1 transitions
200.6978 204.5583 205.3435 205.8410 207.3388
0.000119 0.000004 0.000033 0.000432 0.000369
B1 transitions

This is Cl edge

204.5908   204.9055 207.6473 207.6511 208.4016
0.001534   0.005202 0.000084 0.000053 0.000141
B2 transitions
200.8126 204.6478 204.8731 205.8307 207.5878
0.000119 0.000747 0.005309 0.000460 0.000063
I highlighted in blue transitions involving valence hole. **They are weak.**

Transitions of the cation (A2) at the geometry of the neutral:
A1 transitions
 204.1840 204.8913 205.3410 205.9861 207.5270
0.0000   0.000001 0.000390 0.000454 0.000100
B1 transitions
200.9934 204.2498 204.4570 205.1903 206.6768
0.000004 0.000702 0.006047 0.000025 0.000047
B2 transitions
200.9936 204.2549 204.4522 205.2030 205.4077
0.000004 0.000528 0.005424 0.000026 0.000473
The transitions to valence hole are even weaker than in B2 cation.
Other transitions seem similar

Transitions of the cation (B2) at the geometry of the B2 cation, aug-cc-pVDZ, default FC

A1 transitions

201.0573	205.3537	205.5958	206.1305	207.2339
0.000160	0.000014	0.000274	0.000445	0.000415

B1 (complex roots, and left ampl. did not converge -- only those conv-d 205.3630 205.6661

205.3629	205.6660	207.8369	207.8369
0.001708	0.006193	-	-

B2

201.1806	205.4188	205.6239	205.6537	207.3968
0.000170	0.000631	0.001662	0.005174	0.000401

This is CI edge

XAS spectra: Cl-Benzene, neutral, 6-311(2+,+)G** basis, default FC

A1

203.1424	204.4984	204.5479	205.2661	205.4015	205.7218
0.000132	0.000494	0.003782	0.000021	0.000017	0.000113

B1

202.7749	204.3575	205.2137	205.3813	205.5588	205.8732
0.008732	0.000797	0.000070	0.000048	0.000080	0.000129

B2

202.7741	204.3508	204.5998	205.4848	205.5520	205.8623
0.007943	0.000695	0.001030	0.0	0.0	0.0

XAS spectra: Cl-Benzene, neutral, 6-311(2+,+)G** basis, uncontracted core on Carbon

A1

203.1359	204.4964	204.5455	205.2657	205.4010	205.7210
0.000134	0.000429	0.003846	0.000021	0.000017	0.000114

B1

202.7680	204.3568	205.2106	205.3808	205.5582	205.8725
0.008720	0.000802	0.000070	0.000048	0.000080	0.000130

B2

202.7672	204.3500	204.5961	205.4842	205.5514	205.8617
0.007938	0.000698	0.001029	0.0	0.0	0.0

This is Cl edge

XAS spectra: Cl-Benzene, neutral, 6-311(2+,+)G** basis, uncontracted core on C and Cl
default FC

A1

202.2238	203.6130	203.6642	204.3730	204.5090	204.8388
0.000156	0.000789	0.003511	0.000022	0.000019	0.000105

B1

201.8370	203.4610	204.3454	204.4955	204.6686	204.9841
0.008674	0.000830	0.000071	0.000050	0.000079	0.000133

B2

201.8370	203.4610	204.3452	204.4954	204.6686	204.9840
0.007884	0.000723	0.001039	0.0	0.0	0.0

This is Cl edge

C$_6$H$_5$Cl

This is Cl edge

Legend:
- aug-cc-pVDZ
- 6-311(2+,+)G**
- UC (on C) 6-311(2+,+)G**
- UC-6-311(2+,+)G**
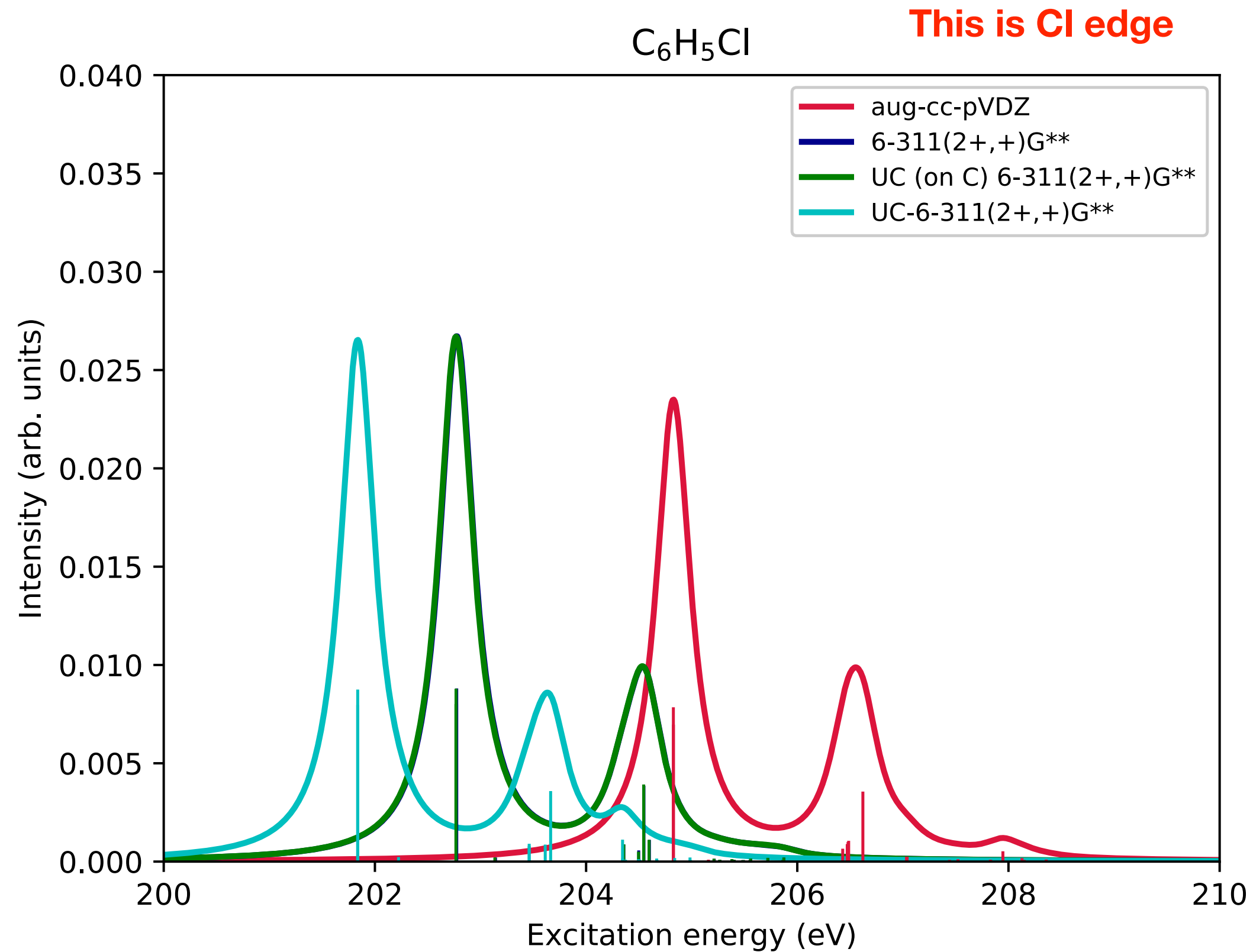
Here change in the shape is less dramatic, but the shift is big. Uncontrating just carbon core does not have much effect, but uncontracting Cl s and p does.

XAS spectra: Cl-Benzene, Cat(B2) @ neu geom, 6-311(2+,+)G** basis, uncontracted core on C and Cl, default FC

This is Cl edge

A1

197.7863	201.5436	202.4320	203.0092	204.5999
0.000125	0.000009	0.000182	0.000516	0.000399

B1

201.5871	201.9247	204.9743	205.0047	205.4767
0.001448	0.006102	0.000028	0.000024	0.000032

B2

197.9335	201.6512	201.8985	203.0155	204.9304
0.000140	0.000585	0.006414	0.000479	0.000021

XAS spectra: Cl-Benzene, Cat(B2) @ cat (B2) geom, 6-311(2+,+)G** basis, uncontracted core on C and Cl

A1

198.1526	202.3395	202.7493	203.2196	204.4917
0.000171	0.000023	0.000208	0.000942	0.000466

B1

202.3588	202.6833	205.2097	205.5572
0.001575	0.007114	0.000029	0.0

B2

198.3061	202.4225	202.6604	202.8136	204.6803
0.000202	0.000498	0.007053	0.001067	0.000434

BrBz, neutral geom, 6-311(2+,+)G**, XAS of the neutral, default FC=15

This is Br edge

A1

187.8984	189.8021	189.8840	190.5207	190.6628	191.0452
0.001694	0.0	0.003493	0.0	0.0	0.0

B1

187.5996	189.6056	190.7556	190.7907	191.0887	191.2645
0.005918	0.002651	0.000013	0.000019	0.000453	0.000121

B2

187.5977	189.5981	189.9958	190.7831	190.8866	191.0742
0.005694	0.002522	0.000176	0.0	0.0	0.000219

BrBz, neutral geom, UC-6-311(2+,+)G**, XAS of the neutral, default FC=15

A1

187.8832	189.7909	189.8747	190.5123	190.6542	191.0365
0.001690	0.000003	0.003488	0.000007	0.000002	0.000007

B1

187.5842	189.5966	190.4570	190.7470	190.7820	191.0803
0.005909	0.002648	0.000016	0.000013	0.000019	0.000450

B2

187.5823	189.5892	189.9842	190.7744	190.8777	191.0658
0.005684	0.002520	0.000175	0.000002	0.000002	0.000217

BrBz, neutral geom, UC-6-311(2+,+)G*, XAS of the neutral, FC=11

CONVERGENCE problems in all irreps, probably because I used wrong eom_shift. Need to rerun!

A1
DNC
B1
288.0059∗   288.1005∗   288.9800∗   288.9824∗   289.0730∗
B2
288.0059∗   288.1006∗   289.5786   288.9798∗   288.9825∗   289.0730∗

BrBz, neutral geom, UC-6-311(2+,+)G**, XAS of the cation (B2)
A1
B1   **Waiting in the queue**
B2

BrBz, cation (B2) geom, UC-6-311(2+,+)G**, XAS of the cation (B2)
A1
B1
B2   **Waiting in the queue**

Thoughts:
Now, when we have large basis set calculations, we need to compare theory vs experiment.
Need to plot theory and experiment on the same plot and get a skype session!

Todo:

1. Should we consider non-planar distortions? I optimized geometries with planar constraint.
2. Plot spectra for comparison with experiment on the same scale.
3. Get NTOs for the important transitions.
4. Finish calculations which are still running…
5. If we are happy with basis and protocol, we can compute more states for each case, if needed.

Anything else?

Core orbitals in ClBz @ neu geom, 6-311(2+,+)G** basis, uncontracted core on C and Cl

Alpha MOs, Restricted
 -- Occupied --
-104.84 -11.31 -11.25 -11.25 -11.25 -11.25 -11.25 -10.57
  1 A1   2 A1   3 A1   1 B1   4 A1   2 B1   5 A1   6 A1
-8.033 -8.031 -8.031 -1.196 -1.124 -1.036 -1.000 -0.850
  7 A1   3 B1   1 B2   8 A1   9 A1   4 B1   10 A1   5 B1
-0.823 -0.715 -0.651 -0.651 -0.607 -0.593 -0.547 -0.520
 11 A1   12 A1   6 B1   13 A1   7 B1   14 A1   2 B2   8 B1
-0.515 -0.471 -0.456 -0.353 -0.338
 15 A1   3 B2   9 B1   1 A2   4 B2
 -- Virtual --
Q-Chem default FC is 7   6 1s(C) + 1s(Cl) ? There are 8 deep orbitals however.
From MO images
1 1sCl
2 C (at Cl)
3 C
4 C
5 C
6 C
7 C
8 Cl (S)
9 Cl (P)
10 Cl (P)
11 Cl (P)
12 VALENCE

Conclusion: Using default FC=11 includes Cl core. So we need tp rerun ClBz calculations with FC=7. No reordering is necessary

Core orbitals in BrBz @ neu geom, 6-311(2+,+)G** basis, uncontracted core on C and Br
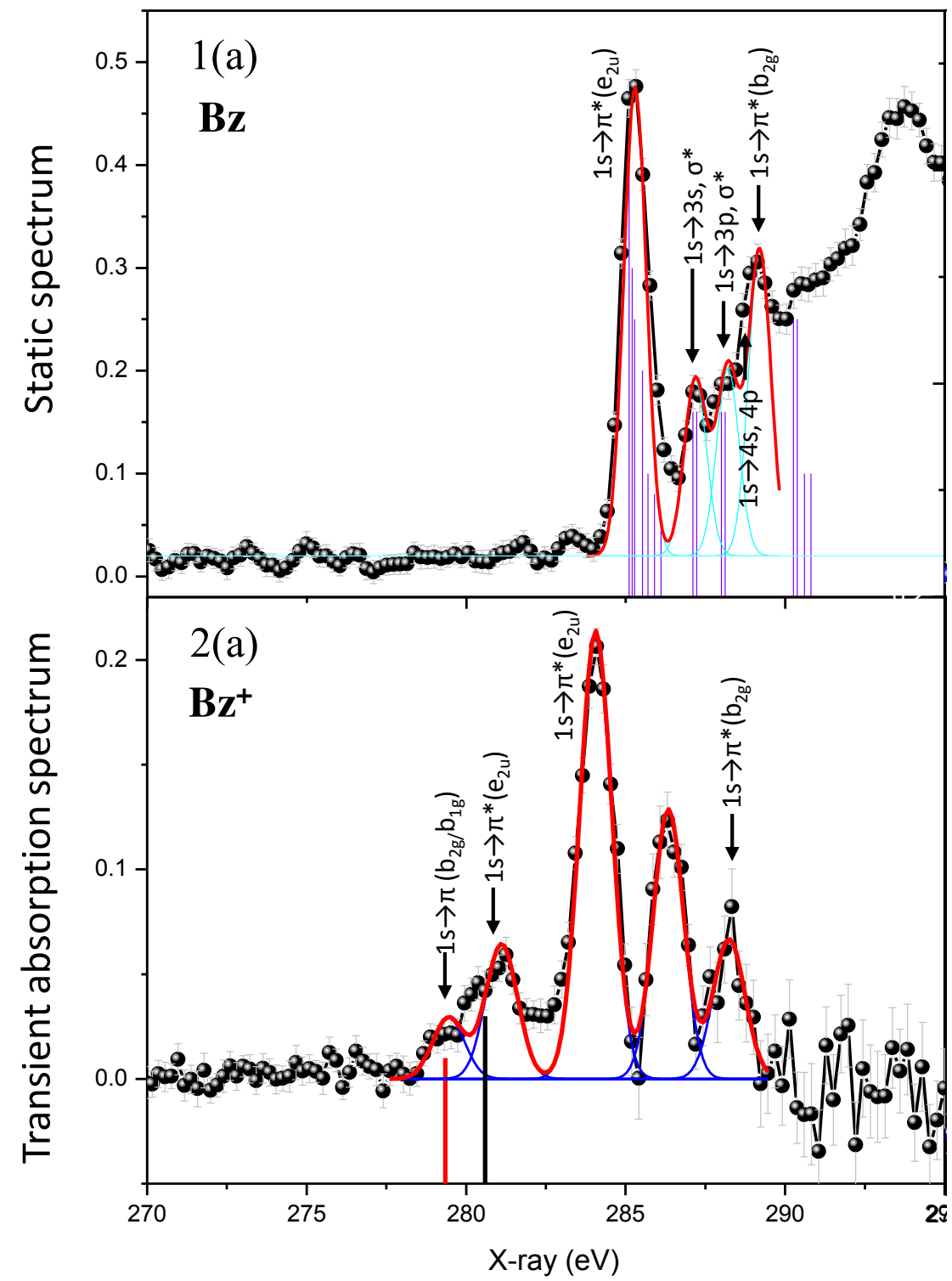
Alpha MOs, Restricted
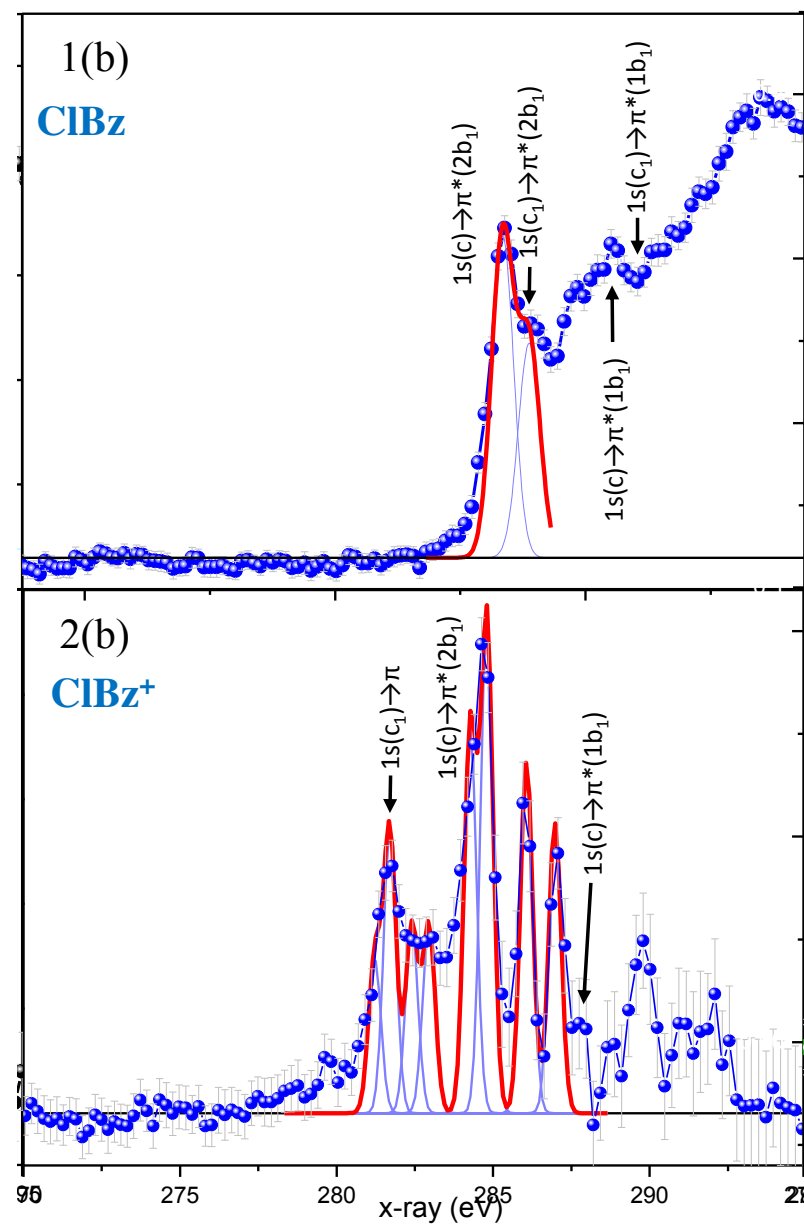-- Occupied --
-490.03 -65.16 -58.52 -58.52 -58.52 -11.30 -11.26 -11.26
  1 A1   2 A1   3 A1   1 B2   1 B1   4 A1   2 B1   5 A1
-11.254 -11.254 -11.251 -9.841 -7.454 -7.445 -7.445 -3.193
  6 A1   3 B1   7 A1   8 A1   9 A1   4 B1   2 B2   10 A1
 -3.189 -3.189 -3.179 -3.179 -1.180 -1.076 -1.036 -0.977
  3 B2   5 B1   11 A1   1 A2   12 A1   13 A1   6 B1   14 A1
 -0.849 -0.820 -0.714 -0.648 -0.647 -0.608 -0.578 -0.535
  7 B1   15 A1   16 A1   8 B1   17 A1   9 B1   18 A1   4 B2
 -0.518 -0.496 -0.440 -0.417 -0.354 -0.335
 10 B1   19 A1   5 B2   11 B1   2 A2   6 B2

Orbitals
1 1(Br)
2 2s (Br)
3 Br?
4 Br
5 Br
6 C (Br)
7-11 C
12-15   Br

So here we want to use FC=11 (the QChem default was 15, which includes Br cores)
Calculations need to be redone, but no reordering of core orbitals are necessary.

Figure showing two panels. Panel 1(a): Static spectrum of Bz. Panel 2(a): Transient absorption spectrum of Bz⁺.

Panel 1(a) labels:
- Bz
- $1s \rightarrow \pi^*(e_{2u})$
- $1s \rightarrow 3s, \sigma^*$
- $1s \rightarrow 3p, \sigma^*$
- $1s \rightarrow \pi^*(b_{2g})$
- $1s \rightarrow 4s, 4p$
- Y-axis: Static spectrum

Panel 2(a) labels:
- Bz⁺
- $1s \rightarrow \pi (b_{2g}/b_{1g})$
- $1s \rightarrow \pi^*(e_{2u})$
- $1s \rightarrow \pi^*(e_{2u})$
- $1s \rightarrow \pi^*(b_{2g})$
- Y-axis: Transient absorption spectrum
- X-axis: X-ray (eV)

1(b)

ClBz

1s(c)→π*(2b₁)

1s(c₁)→π*(2b₁)

1s(c₁)→π*(1b₁)

1s(c)→π*(1b₁)

2(b)

ClBz⁺

1s(c₁)→π

1s(c)→π*(2b₁)

1s(c)→π*(1b₁)

x-ray (eV)

ClBz⁺

<200 fs

100 fs

0-50 fs

Intensity (arb. units)

x-ray (eV)