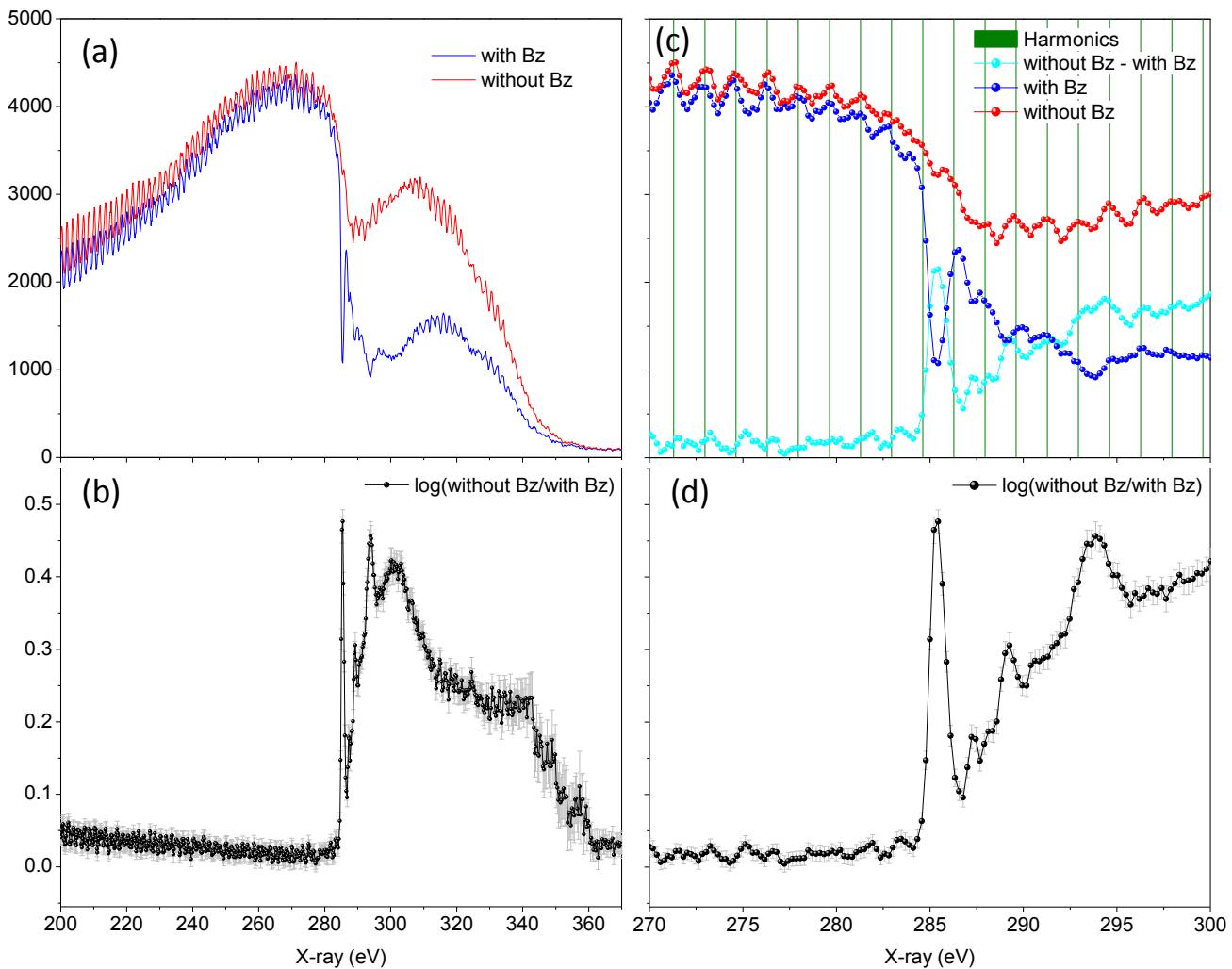


1. Bz static spectrum



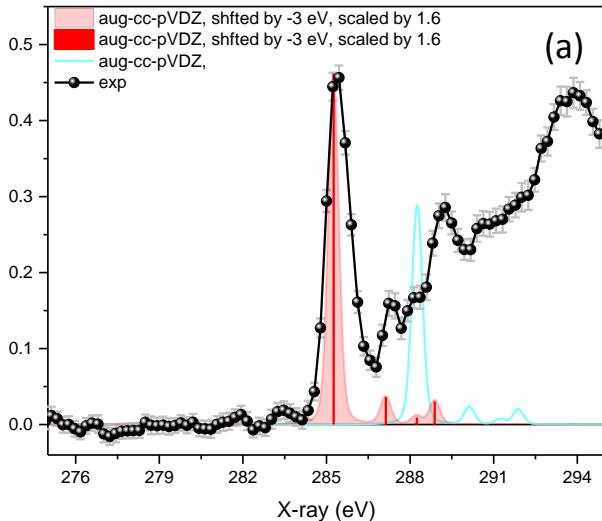
Static x-ray absorption spectra is obtained by measuring the x-rays transmitted photons with and without the sample gas, $A = \log(I_{\text{without gas}} / I_{\text{with gas}})$.

(a) x-rays transmitted signal without B_z (red line) and with B_z (blue line), each spectra is average of 64 CCD images (1000 laser pulses per image). The presented energetic region is from 200 to 370 eV. The coverage of the x-ray is up to about 340 eV as can be seen from the spectra without B_z (red line).
 (b) Static x-ray absorption spectra of the ground state B_z presented by black line. (c) red and blue circles connected by lines represent same spectra as in fig a but shown in shorter energetic range, 270 – 300 eV. Cyan spectra represent subtraction between “without B_z ” and “with B_z ” signals. The vertical green lines represent the position of the harmonics peaks. (d) Static x-ray absorption spectra of ground state B_z as in fig b, shown in shorter energetic range, 270 – 300 eV.

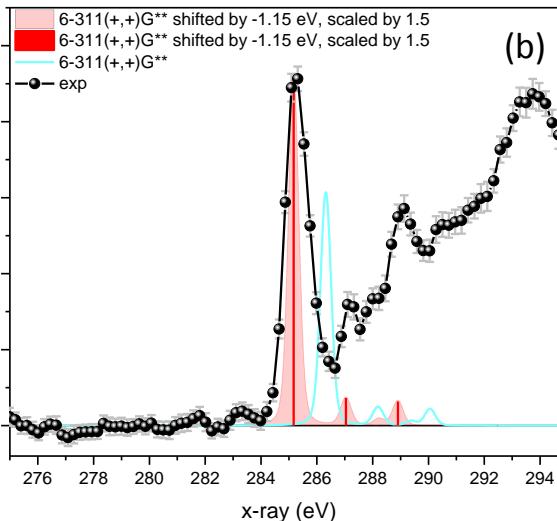
Fig 2

2. Experimental and calculated static spectrum

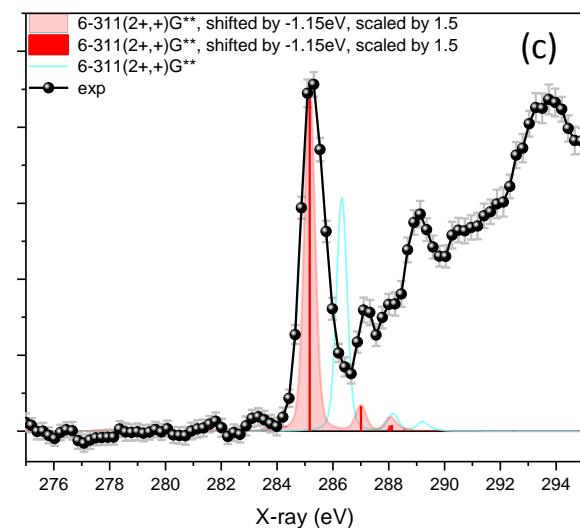
aug-cc-pVDZ



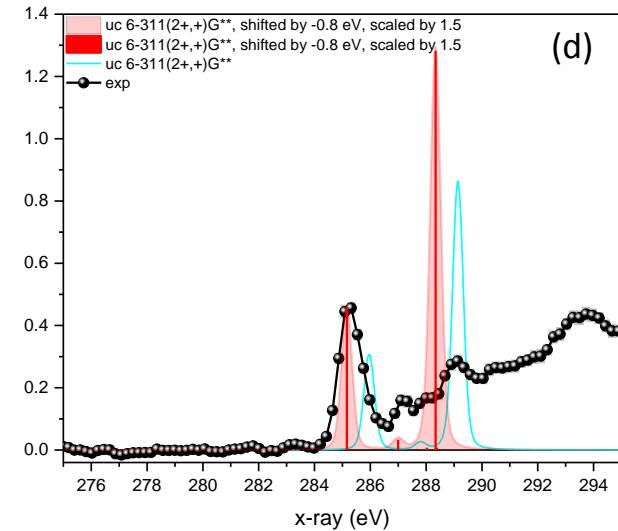
6-311++G**



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

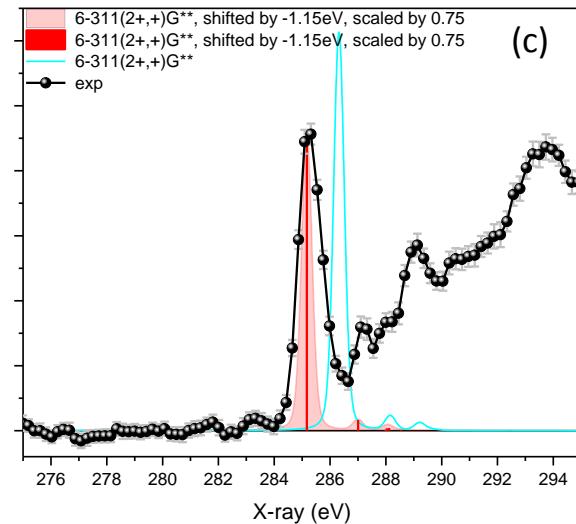
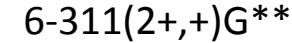
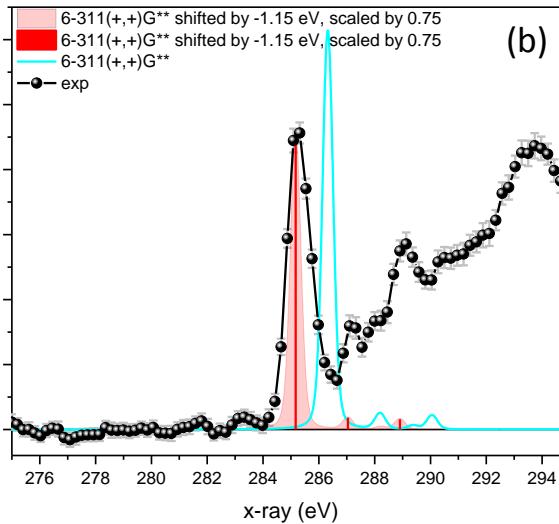
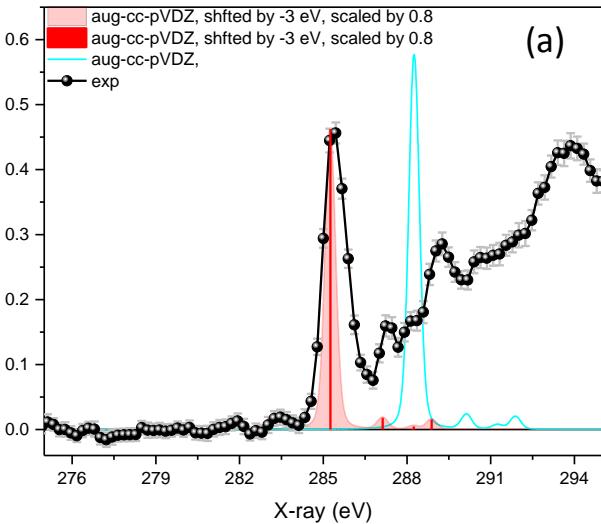
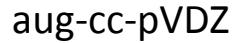


Uc 6-311(2+,+)G**

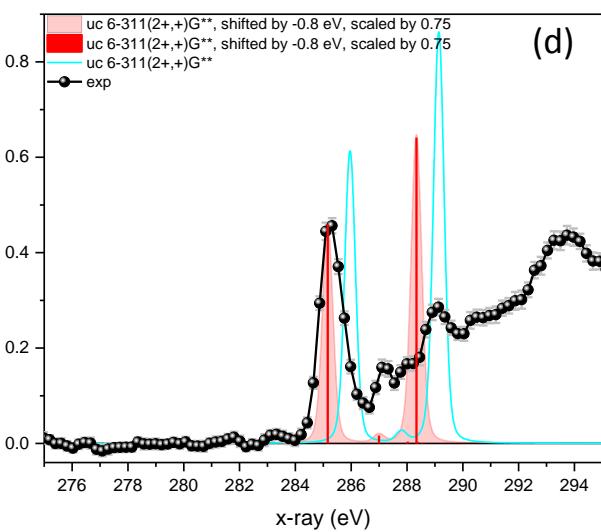


A static x-ray absorption spectra of Bz represented as a black circles connected by black line in panels a, b, c, d. The calculated transitions are shown as a stick spectrum (red sticks). The stick spectrum is uniformly Shifted by different energy for different calculation and scaled (as shown in the panels) to align with the main experimental peak. The solid pink spectrum represents a convolution of the stick spectrum with a Voigt function where the Gaussian broadening profile equivalent to the system resolution of 0.39 eV and the Lorentzian broadening profile is 0.1 eV due to core level life time (Gaussian broadening is obtained from argon spectrum and Lorentzian broadening is taken from ref 1). The cyan spectrum is a convolution of the original calculated stick spectrum with a Voigt function without scaling and shifting.

Fig 2b 2. Experimental and calculated static spectrum



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



same fig as fig 2, only first calculated transition in all 4 panels multiplied by 2 due to degenerate π^* orbital.

3. Vibrational contribution

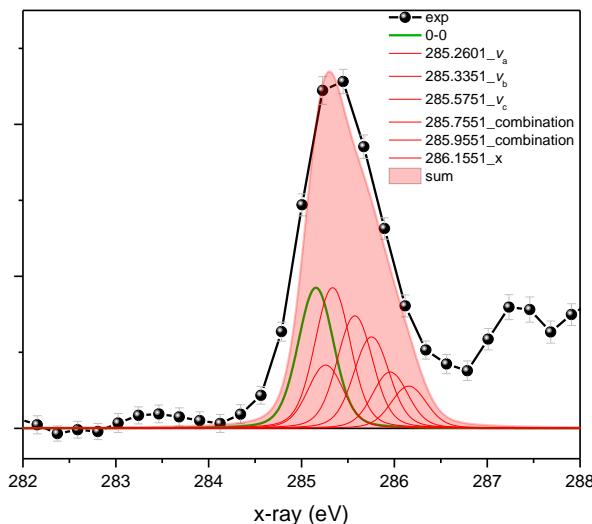
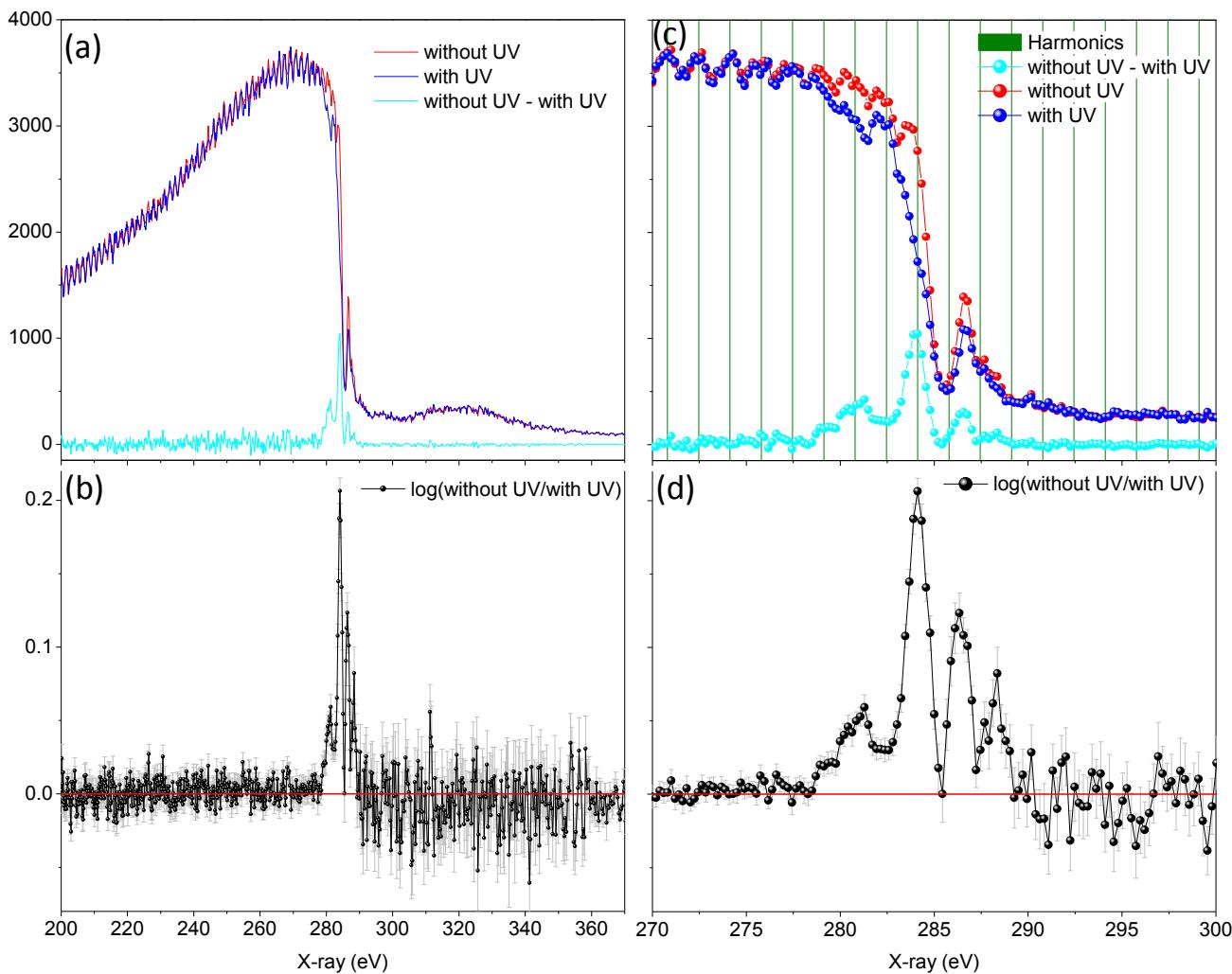


Fig 3 represent the main peak of experimental Bz static spectrum by black circles connected by black line (same spectrum as presented in fig 1(b,d)). The pink solid spectrum is a summation of 0-0 transition (green line) and several transitions to different vibrational states (red line) convoluted with Voigt function with 0.39 and 0.1 eV Gaussian and Lorentzian broadening. The intensities are chosen to obtain the best fit to experimental data. The assignments and position of vibrational states relative to 0-0 transition taken from ref 1,2.

2. E. E. Rennie, B. Kempgens, H. M. Köppe, U. Hergenhahn, J. Feldhaus, B. S. Itchkawitz, A. L. D. Kilcoyne, A. Kivimäki, K. Maier, M. N. Piancastelli, M. Polcik, A. Rüdel, and A. M. Bradshaw *J. Chem. Phys.* 113 (2000).

Fig 4

4. Transient absorption spectrum of Bz (Bz^+)

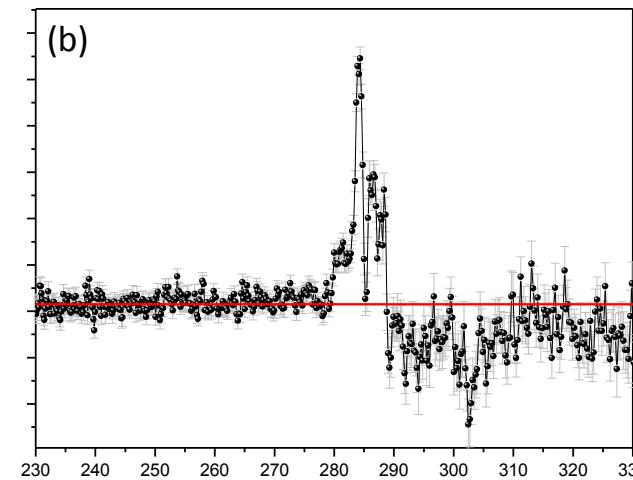
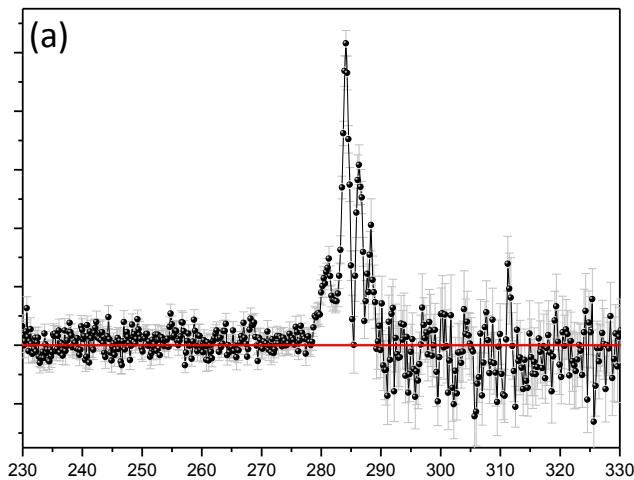
Transient absorption spectra is obtained by measuring the x-rays transmitted photons with and without UV beam (blocked by shutter) with Bz sample gas,

$$A = \log(I_{\text{without UV}}/I_{\text{with UV}}).$$

(a) x-rays transmitted signal without UV (red line) and with UV (blue line), each spectra is average of 32 CCD images (1000 laser pulses per image).

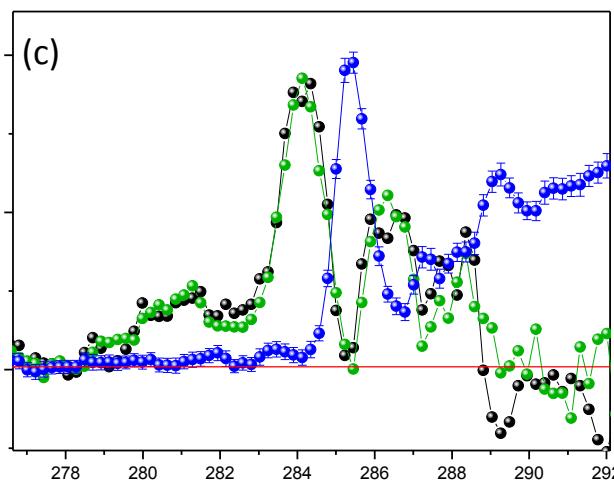
(b) transient absorption spectra of Bz^+ presented by black line. (c) red and blue circles connected by lines represent absorption spectra with and without UV, same spectra as in fig a but presented in shorter energetic range, 270 – 300 eV. Cyan spectra represent subtraction between “without” and “with” UV spectra. The vertical green lines represent the position of the harmonics peaks. (d) transient absorption spectra of Bz^+ as in fig b, presented in shorter energetic range, 270 – 300 eV.

Fig 5

5. Transient absorption spectrum of Bz (Bz^+), comparison of two measurements

(a) Transient absorption spectra measured with about 25 μ J per pump UV pulse and obtained by 32000 pulses with and without pump (b)
 Transient absorption spectra measured with 20 μ J per pump UV pulse, the spectrum is an average over four measurements while each obtained by 32000 pulses with and without pump.

These results taken in similar experimental conditions (20 cm f.l, room temperature), and they are consist in the 270 – 290 eV region. In the higher energetic region the number of measured and averaged spectra became more important factor due to a lower X-ray flux and higher background signal from the ground state Bz.



Transient x-ray absorption spectra (green and black, same as in panel a and b respectively) compared to the scaled static x-ray absorption spectrum of ground-state Bz (blue).

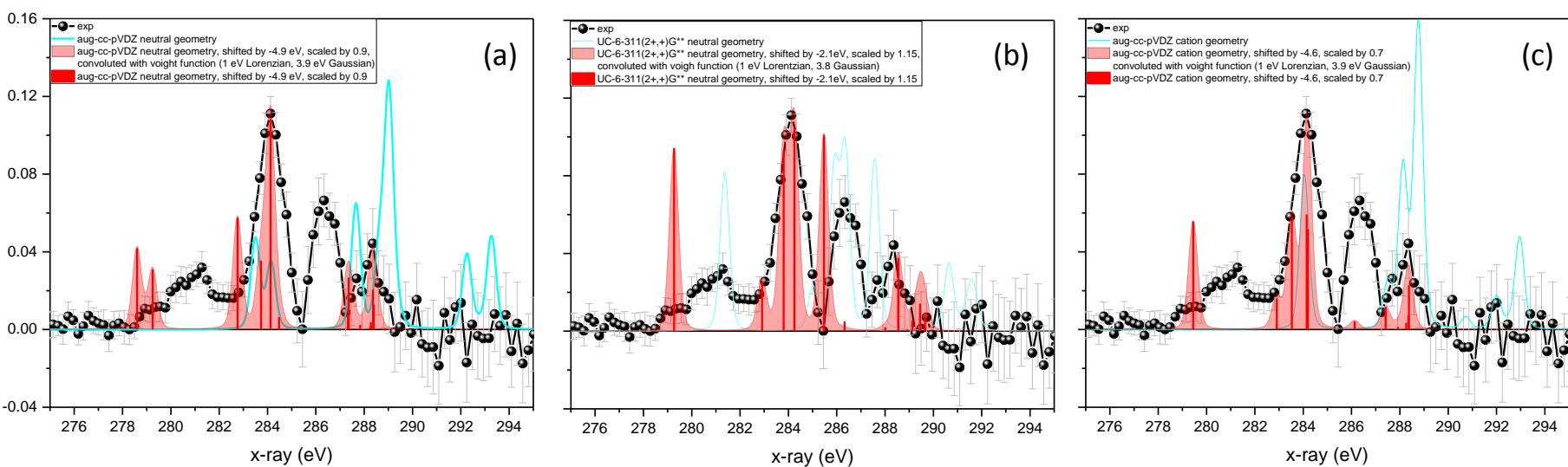
Fig 6

6. Experiment and calculation transient absorption spectra

aug-cc-pVDZ neutral geometry

UC-6-311(2+,+)G** neutral geometry

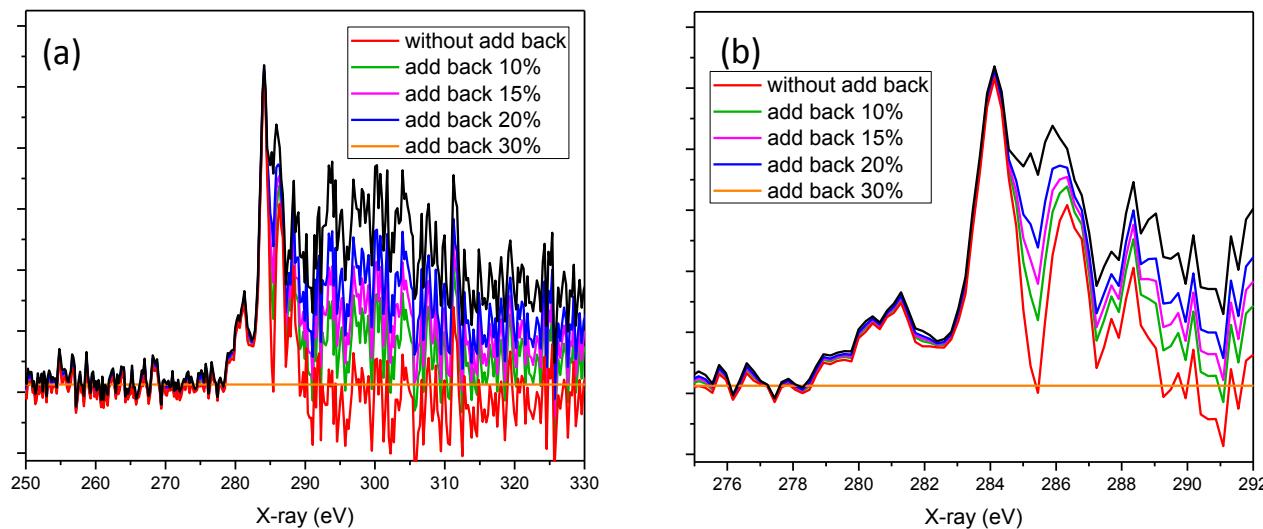
aug-cc-pVDZ cation geometry



A transient absorption spectra of Bz^+ represented as a black circles connected by black line in panels a, b, c (the same from fig 4(b,d)). The calculated transitions are shown as a stick spectrum (red sticks). The stick spectrum is uniformly Shifted by different energy for different calculation (as shown in the panels) to align energetically with the main experimental peak (284 eV). The solid pink spectrum represents a convolution of the stick spectrum with a Voigt function where the Gaussian broadening profile equivalent to the system resolution of 0.39 eV and the Lorentzian broadening profile is 0.1 eV due to core level life time. The intensity scale of the calculated solid pink spectrum is normalized to the main experimental peak. The cyan spectrum is a convolution of the original calculated stick spectrum with a Voigt function without scaling and shifting.

Fig 7

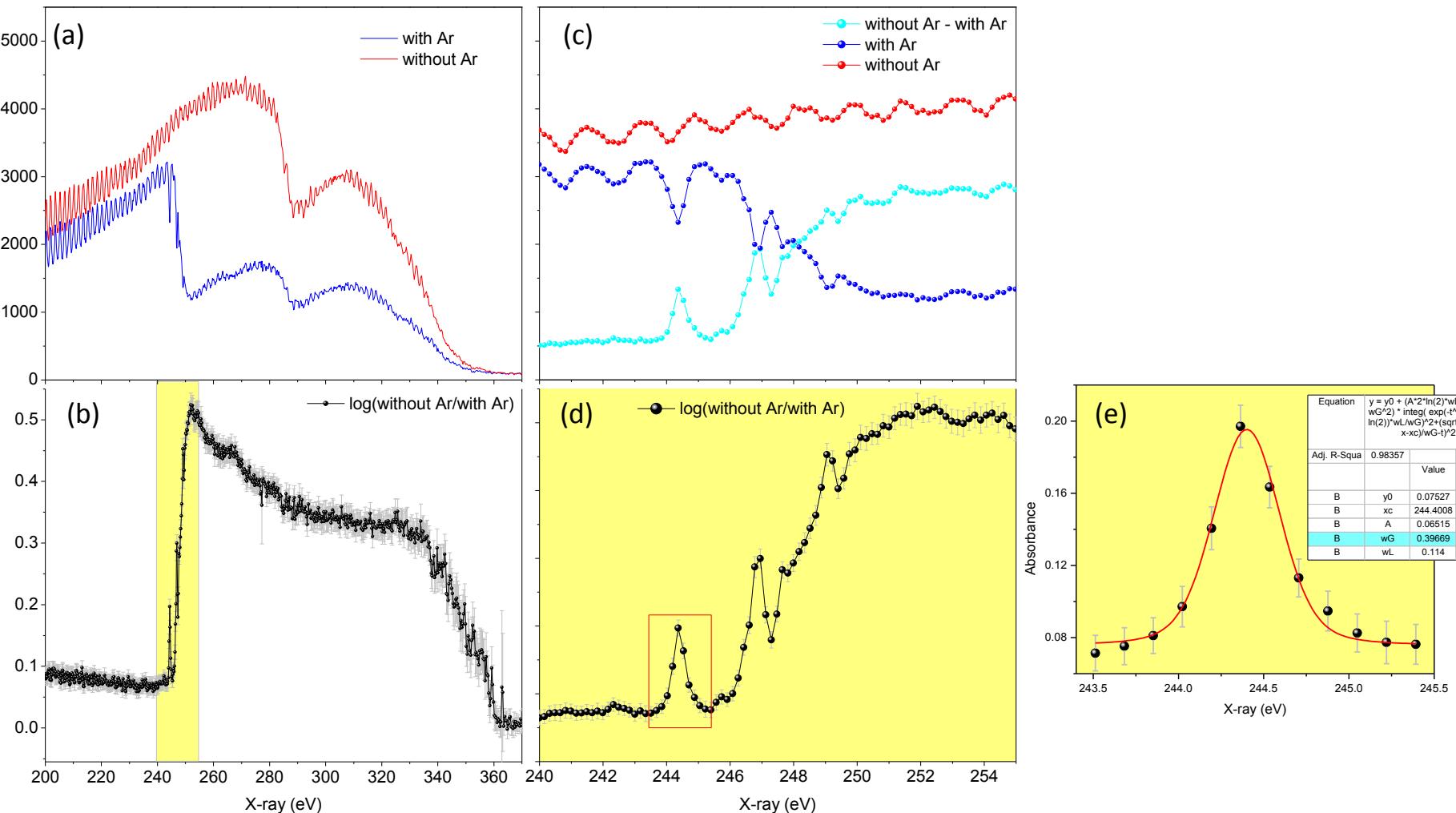
7. Bz transient absorption add back spectrum



The transient absorption spectra is converted to pure photoexcited cation/molecules only, without any contribution from the ground state Bz by adding back a scaled static spectrum based on the percentage of the molecules in the interaction region that are photoexcited. The uncertainty in the estimation of the excitation percentage is quite big, therefore at this stage different percentages are presented.

Fig 8

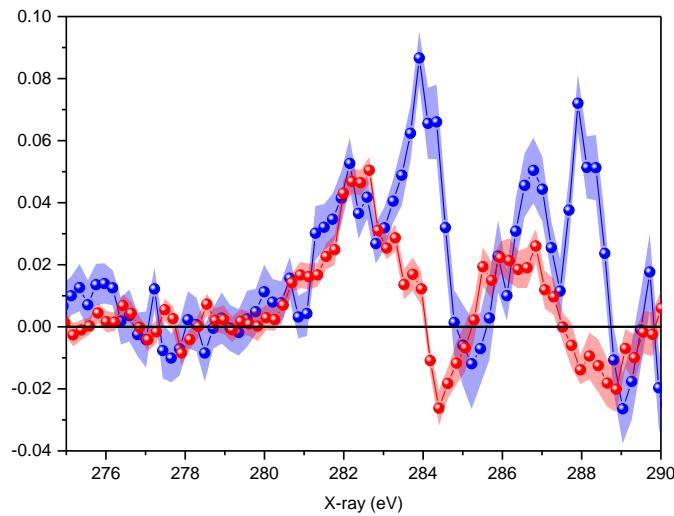
8. Argon calibration and experimental resolution



(a) x-rays transmitted signal without Argon (red line) and with Argon (blue line). (b) static spectrum of argon shows the atomic core-to-Rydberg state resonances that are used to calibrate the spectrometer. (c) red and blue circles connected by lines represent same spectra as in fig a but shown in shorter energetic range, 270 – 300 eV. Cyan spectra represent subtraction between “without Argon” and “with Argon” signals.(d) same spectrum as in panel b presented in shorter energetic range (e)Inset shows the fitting of the first peak to a Voigt lineshape with a fixed Lorentzian width of 114 meV (core-hole lifetime broadening in Aargon) in order to extract the Gaussian width, which provides a spectrometer resolution of 390 ± 50 meV.

Fig 10

10. Focusing condition



Transient absorption spectrum of allyl iodide after UV (266 nm) excitation with 45 (red line) and 20 (blue line) cm f.l.

The peaks at 282.2 and 286 and 287 eV related to one photon excitation observed in both focusing conditions, while the two new peaks at 284.1 and 288.3 eV observed only with 20 cm f.l, these two peaks related to multi photon ionization.

Allyl iodide and benzene cross section for one photon absorption at 266 nm is about 5×10^{-18} and $10^{-20} \text{ cm}^2/\text{molecule}$ respectively. (with similar vapor pressure at room temperature) therefore by focusing with 20 cm f.l we expect to observe signal of Bz only due to multi photon ionization.