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Table-Top X-ray Spectroscopy of Benzene Radical Cation

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ABSTRACT

Ultrafast table-top x-ray spectroscopy at the carbon K-edge is used to measure the x-ray spectral features of benzene radical cations (Bz^+). The ground state of the cation is prepared selectively by two-photon ionization of benzene neutral, and the x-ray spectra are probed at early times after the ionization by transient absorption using x-rays produced by high harmonic generation. Bz^+ is well known to undergo Jahn-Teller distortion, leading to a lower symmetry and splitting of the π orbitals. Comparison of the x-ray absorption spectra of the neutral and the cation reveals a splitting of the two degenerate π^* orbitals as well as an appearance of a new peak due to excitation to the partially occupied π -subshell. The π^* orbital splitting of the cation, elucidated on the basis of high-level calculations in a companion theoretical paper [Vidal et al, submitted to J. Phys. Chem. Lett.; ChemRxiv link: doi XXXXX], is discovered to be due to both the symmetry distortion and even more dominant spin coupling of the unpaired electron in the partially vacant π orbital (from ionization) with the unpaired electrons resulting from the transition from the $1s_C$ core orbital to the fully vacant π^* orbitals.

INTRODUCTION

The recent development of tabletop high-harmonic generation (HHG) sources reaching up to 300 eV photon energies in the x-ray^{1,2,3,4,5,6,7,8,9,10} gives rise to a powerful pump-probe technique that combines near-infrared (NIR) or ultraviolet (UV) excitation and soft x-ray spectroscopic probing in the carbon K-edge region. Promotion of an electron from the carbon K-edge 1s orbitals to vacant or partially vacant valence orbitals following NIR/UV excitation or ionization provides the opportunity to follow ultrafast electronic structural changes via the x-ray spectroscopic regime.^{11,12,13}

X-ray spectroscopy is very sensitive to changes in molecular structure and orbital occupancy, giving accurate new information about energetics and dynamics of transient species. Taking advantage of the typical wide spectral range of the HHG flux, light-initiated chemical reactions in the lowest electronic states of isolated CF_4^+ and SF_6^+ molecules were studied in the carbon K-edge and sulfur L-edge regions, respectively. The reaction paths were characterized and the effect of symmetry breaking was observed through the splitting of absorption bands and Rydberg-valence mixing induced by the geometry changes.¹⁴ In parallel, the pericyclic minimum that leads to the ultrafast ring-opened product or the ground state reformation of 1,3-cyclohexadiene was characterized.¹⁵ Dynamics of ring opening in furfural following 267 nm excitation was also observed,¹⁶ as well as intersystem crossing in acetylacetone¹⁷ and additional studies in the carbon K-edge region.^{18,19} Even at higher energies (O K-edge), ultrafast dissociation of water cation²⁰ and formation of the OH radical have been probed.²¹ X-ray spectroscopy can be also applied to probe excited states of cations, which are difficult to observe with UV or visible spectroscopy. This advantage is exploited in the present investigation to probe the electronic structure of the ground-state benzene cation, its unoccupied orbitals and the partially vacant π orbitals, which are known to be affected by Jahn-Teller (JT) distortion.^{22,23,24} The ground electronic state of benzene, \tilde{X}^2E_{1g} , has two $\pi(e_{1g})$ degenerate highest occupied molecular orbitals (HOMO) and two $\pi^*(e_{2u})$ degenerate lowest unoccupied molecular orbitals (LUMO). Removing an electron from one of the degenerate π orbitals leads to electronic states of the cation: $\text{Bz}^+(\text{B}_{2g})$ and $\text{Bz}^+(\text{B}_{3g})$. The geometric relaxation of the cation splits the electronic degeneracy between the orbitals (and the states) and results in two nearly degenerate minima (compressed and elongated structures) connected via a small barrier, well below the zero-point energy.²² From ro-vibrational

spectroscopy and previous calculations it is known that the energetic difference between the two JT structures is very small, approximately 0.0016 eV,^{25,26} much smaller than the spectral broadening due to the short lifetime of the core level (~ 0.1 eV) as well as the experimental resolution (~ 0.3 eV) in the laboratory table-top setup. Therefore, dynamically Bz⁺ behaves as one scrambled structure,²⁵ which can be represented by just one electronic state, while the effect of the two JT structures will be mentioned later.

In Bz⁺, the energetic degeneracy of the two $\pi(e_{1g})$ orbitals is lifted due to symmetry lowering, and the same is expected to occur in the virtual orbitals (LUMO); a similar effect was described in core-ionized benzene.^{27,28} In addition, each of the $1s \rightarrow \pi^*$ transitions can be split due to spin coupling in the presence of the partially vacant π orbital, as explained in the companion theoretical paper.²⁹ Analogous splittings were recently reported in N₂⁺,³⁰ as well as at the O K-edge of CO⁺.³¹ In N₂⁺, the features at 402.2 eV and 403.1 eV correspond to the π^* excitation, as assigned through x-ray absorption spectroscopy (XAS) of neutral nitrogen molecules, but with a $3\sigma_g$ spectator hole in the case of the ion, i.e., a $3\sigma_g^{-1} {}^2\Sigma_g \rightarrow 1\sigma_u^{-1} 3\sigma_g^{-1} 1\pi_g {}^2\Pi_u$ transition. There is a splitting of the $1\sigma_u^{-1} 3\sigma_g^{-1} 1\pi_g {}^2\Pi_u$ state, due to two possible spin couplings. Different spin couplings of three unpaired electrons arise from spin adaptation of the wave function and have been discussed in detail.^{32,33}

This paper experimentally investigates the influence of spin-couplings and JT distortion by probing benzene cations by broad x-ray radiation in the carbon K-edge region and comparing to the x-ray spectra of neutral benzene. Specifically, we probe the electronic transitions from the core to the partially vacant π orbital (produced by ionization) as well as to the vacant π^* orbitals of the benzene cations. In addition, we discuss in detail the preparation of the cation by two-photon ionization in the ultraviolet, leading to relatively cold (minimal excitation above room temperature thermal energy) benzene cation on the electronic ground state, probed by x-ray spectroscopy, and examine the relaxation dynamics from the Franck Condon (FC) region of the neutral to the relaxed cation in a time-dependent experiment. The complete analysis of the experimental spectra using high-level ab initio calculations is presented in the companion theoretical paper.²⁹

METHODS

The experimental setup has been described elsewhere.¹⁵ The experiments were carried out with broadband soft x-ray pulses (extending to ~ 360 eV, see Fig. 1(e) and Fig. S1) that probe the

ground state of Bz and Bz⁺ following two-photon ionization with 267 nm light. 90% of the output of a Ti:sapphire laser that delivers 12 mJ pulses at 1 kHz repetition rate, 35 fs pulse duration, with a wavelength centered at 800 nm (Spectra-Physics, Spitfire-ACE-PA) was converted in an optical parametric amplifier into mid infrared 2.5 mJ pulses (1470 nm). Broadband soft x-ray pulses in the carbon K-edge region were produced by high-harmonic generation (HHG) with 1470 nm focused with a 30 cm f.l. lens to a differentially pumped cell with helium atoms at a pressure of ~1300 Torr, to obtain a static spectrum and to probe the neutral benzene molecules, for more details see Fig. S1. The other 10% of the 800 nm beam is used for the generation of the 267 nm ultraviolet pump pulse in nonlinear crystals (25 μJ, 400 cm⁻¹ bandwidth, ~ 90 fs pulse duration). The 267 nm pulses are used to prepare benzene ions by two-photon ionization, and these are probed by the broadband, soft x-ray pulse at the carbon K-edge. The pump and probe beams are focused and overlapped at a ~1° crossing angle into a gas cell that contains benzene at a pressure up to ~25 Torr (backing pressure; the cell has two pinholes for entrance and exit of the laser that allow flow of the gas out). After the cell, the probe pulse is spectrally dispersed by a Hitachi grating (001-0660) onto an x-ray CCD camera (Princeton Instruments, PIXIS:XO 400B), where the entire broadband soft x-ray signal is measured at once as a function of the photon energy.

RESULTS AND DISCUSSION

We first present an overview of the spectra and then discuss in detail how the spectra of benzene cation are obtained and verified. Fig. 1 shows experimental table-top X-ray absorption spectra ($A = \log(I_{\text{without Bz}}/I_{\text{with Bz}})$) of neutral benzene and the benzene cation (ΔA – differential spectra with ultraviolet pump on versus pump off, with an added back percentage of neutral spectrum, see figure caption for details) in their ground states. The spectrum of neutral benzene (Bz) presented in panel 1(a) is taken with a flow of benzene molecules by referencing the high harmonic x-ray flux with no sample in the cell, as previously described¹⁵; the spectrum matches well with previously reported results,^{34,35,36,37,38,39} and it consists of four main peaks (labeled as A-D) below the 1s_C core level ionization energy (290.37 eV).^{40,41} The first peak at 285.2 eV, labeled as A, is the most intense feature and is known as the transition from the 1s_C orbital to the $\pi^*(e_{2u})$ LUMOs,⁴² as can be seen in the energy diagram in Fig 1(c). Peaks B, C and D are due to

core-to-Rydberg transitions, as also discussed in detail in the companion theoretical paper,²⁹ which corrects a previously debated assignment of peak D as a transition to a higher $\pi^*(b_{1g})$ orbital,^{35,38,39,43} to the new assignment of doubly degenerate transitions to Ry(s) and Ry(p) character.

Special care was taken to obtain an unsaturated absorption spectrum of neutral benzene. The high vapor pressure of benzene (~ 100 torr), large absorption cross section at the carbon K-edge, and the low flux per camera pixel of the x-ray radiation make it easy to reach a saturated regime on strong features, where nearly all photons at a specific x-ray energy are absorbed. When the peak structure is broadened due to the system's spectral resolution, the detection of saturation becomes nontrivial, since the observed peak is an average of the saturated signal and nonsaturated signal (for example, peak A consists of several vibrational states with different strengths)³⁸. This leads to a broader 285.2 eV band on the high-energy side due to the saturated vibrational structure, and to a different ratio between the observed band and the core ionization region at higher energy. In this experiment, to avoid the saturated regime, the pressure is reduced until the ratio between the main peak A and the broad ionization region becomes constant, as shown by blue and light blue spectra in the inset of Fig 1(a), and described in more detail in the SI.

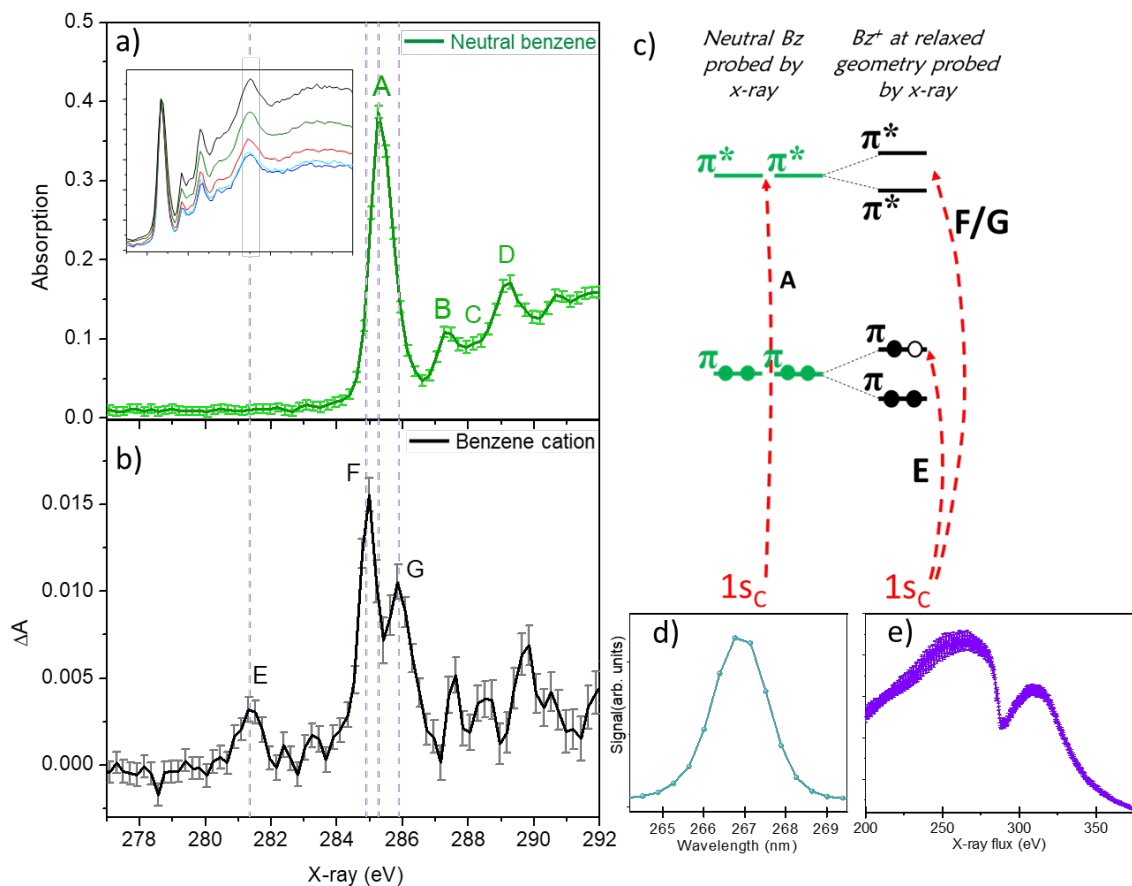


Figure 1. (a) Experimental x-ray absorption spectrum of ground-state neutral Bz presented by the green line with light green error bars corresponding to 95% confidence interval limits, the spectra obtained from $A = \log(I_{\text{without Bz}}/I_{\text{with Bz}})$, where $I_{\text{without Bz}}$ and $I_{\text{with Bz}}$ are the transmitted signal of the broadband x-ray flux without Bz molecules in the interaction region and with Bz molecules, respectively. Each spectrum is an average of 128 CCD images (1000 laser pulses per image). Inset: Raw absorption spectra of neutral benzene (normalized to the highest peak) at different pressures in the interaction region with the x-ray radiation, from highest (black line) to lowest pressure (blue line), respectively. Also 128 CCD images averaged. (b) NEXAFS spectrum of Bz⁺, ΔA , taken at $0\text{-}50 \pm 50$ fs delay, represented by the black line with grey error bars corresponding to 95% confidence interval limits (after adding 2% of the static neutral benzene spectra, see supplemental information (SI) for details). The Bz⁺ absorption spectrum is obtained from $\Delta A = \log(I_{\text{without UV}}/I_{\text{with UV}})$, where $I_{\text{without UV}}$ and $I_{\text{with UV}}$ are the transmitted signal of the x-ray flux without UV and with UV to ionize the molecule by two-photon ionization, respectively. The ionization UV beam is focused with a 45 cm focal length lens. The spectrum is an average of 512 CCD images (1000 laser pulses per image). The wavelength calibrations of the spectra are done with absorption spectra of argon and allyl radical, the calibration procedure is described in more detail in the SI. (c) Molecular orbital diagram illustrating the main transitions responsible for the dominant spectral features in the cation. Peak E corresponds to $1s_{\text{C}} \rightarrow \pi$ transition and peaks F and G to the $1s_{\text{C}} \rightarrow \pi^*$ transitions. (d) The spectral wavelength scan of the UV beam (light blue line). (e) X-ray flux (purple line), see SI for details.

The black line in Fig. 1(b) shows the absorption spectrum of Bz^+ , ΔA , prepared by 267 nm two-photon ionization and probed by the broadband HHG pulse near the carbon K-edge (spectrum of pulse presented in Fig 1(e)) after 0-50 fs time delay. Two-photon 267 nm (the spectral profile presented in Fig 1(d)) excitation is in resonance with the first ionized state in which one electron is removed from a π orbital, creating a hole in the doubly degenerate HOMO. Consequently, the lowest-energy core-level transition in the cation is the $1s_{\text{C}} \rightarrow \pi$, and the assignment of peak E as $1s_{\text{C}} \rightarrow \pi$ is straightforward.

The next transition, peak F at 285 eV, is assigned to $1s_{\text{C}} \rightarrow \pi^*$ (LUMO), and it is red-shifted by 0.25 eV relative to peak A of the neutral Bz. Since the two-photon ionization process is performed with 267 nm ($E_{2\text{ph}} = 9.29 \pm 0.04$ eV), benzene cations are prepared in the electronic ground state (ionization energy $\text{IE} = 9.243$ eV)⁴⁴ with an internal energy of approximately 0.05 eV, and there is internal vibrational energy of approximately 0.05 eV in the room temperature benzene neutral (the vibrational population and thermal vibrational energy according to a Boltzmann distribution are shown in the SI). As long as the ionization process is limited to the absorption of two UV photons (discussed below and in the SI), this minimizes the possible contribution of internal vibrational excitation of the ion that could red-shift the observed peak F.

The lowest excited state in neutral benzene corresponds to the $\pi \rightarrow \pi^*$ transition, which is located at 4.72 eV.⁴⁵ This energy differs from the gap between peaks E and F (~ 3.85 eV) observed here for the cation, providing a rough estimate of the energy spacing between the π and π^* orbitals of the ion. The difference can be partly explained by changes in orbital energies (i.e., a decrease of the π^* orbital (0.25 eV) and an increase of the semi-occupied π orbital in the cation, which occur as a result of the symmetry distortion) and partly by exchange interactions arising due to the spin couplings of the unpaired electrons, as discussed further in the companion theoretical paper.²⁹

The preparation of benzene cation in the electronic ground state and the exclusion of possible contributions due to one photon excitation of neutral benzene or three photon or more electronically excited cations are important points for further discussion. It is always a challenging problem to limit an ionization process in an intense field to just two UV photons, nevertheless the two-photon ionization with 267 nm is known to be very effective in benzene.⁴⁶ The first excited state of benzene, $S_0 \rightarrow S_1$, is dipole forbidden and can only be accessed via vibronic coupling.⁴⁷ Thus, because of the low one-photon cross-section ($10^{-20} - 10^{-21}$ cm²/molecule),^{48,49} the probability of populating this state by one photon excitation is low, especially with 267 nm (4.64 ± 0.02 eV),

which is less than the energy of the $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition (4.72 eV).⁴⁵ Therefore one-photon excitation of the neutral is expected to be negligible. Moreover, peak E and the red-shifted peak F are good indications that we observe the ground state of the cation. This pattern would only occur if one electron is removed from the π orbital and the energies of the $1s_C \rightarrow \pi^*$ transition are split due to the structural distortion of the cation and exchange interactions of the three unpaired electrons. High level calculations using equation of motion coupled-cluster theory adapted to core-level states,⁵⁰ reported in the companion paper,²⁹ provide additional support for the assignment of the x-ray absorption spectrum of the ground state of the cation.

Special care was taken to eliminate the possibility of the formation of electronically excited cation states, which may occur due to three-photon excitation with the intense femtosecond UV pulses. Fig. 2 shows the dependence of the x-ray spectra of Bz^+ on UV power. A shorter focal length lens of 20 cm was used to increase the power density over the 45 cm focal length lens used for Fig. 1. Panel (a) shows the x-ray spectrum following 7 $\mu\text{J}/\text{pulse}$ UV pump; only one peak at low x-ray energy is observed and assigned to the $1s \rightarrow \pi$ transition of the cation after two-photon ionization from the π orbital. Absorption of three photons (13.92 eV) leads to resonant ionization from the $\tilde{D}^2 E_{1u}$ state⁵¹ (producing a hole in the σ_{C-H} orbital) and fast relaxation to either the ground cationic state, $\tilde{X}^2 E_{1g}$ with the hole in the π HOMO, or to the $\tilde{B}^2 E_{2g}$ state^{52,53,54} with the hole in σ_{C-H} orbital (HOMO-1). The latter is expected to be observed in the x-ray spectrum at the lowest energy. This behavior is assigned as peaks E^* ($1s_C \rightarrow \sigma_{C-H}$) and E ($1s_C \rightarrow \pi$) in Fig 2(b), in the x-ray absorption spectrum following 30 μJ UV pump energy, and this characteristic is still observed in Fig. 2(c) at 40 μJ UV pump energy. In addition to the appearance of peak E^* , the amplitude ratios of peaks E^* and E compared to F are reduced by almost two times compared to peaks E and F in panel (a). Based on these results, we exclude three-photon ionization when the UV photon density is very low, and this was achieved by working with low UV power or the 45 cm focal length lens for the UV laser beam as presented in Fig 1(b).

Below 14 eV, the energy from the neutral benzene ground state and other dissociation processes of benzene cation are negligible.⁵⁵ However, by increasing the UV power, the probability of four-photon ionization and consequently the opening of additional dissociation channels becomes greater. The signal at lower energies of the various cation or photofragments is broadened, as observed in the two lower energy peaks in the x-ray spectrum, as can be seen in panel 2(c) achieved by 40 μJ UV pump. Panels (b) and (c) differ from panel (a) in the strongly

increasing peak at 288 eV and the decreasing depletion at 285.2 eV. Further consideration of these intense field effects is beyond the scope of this discussion.

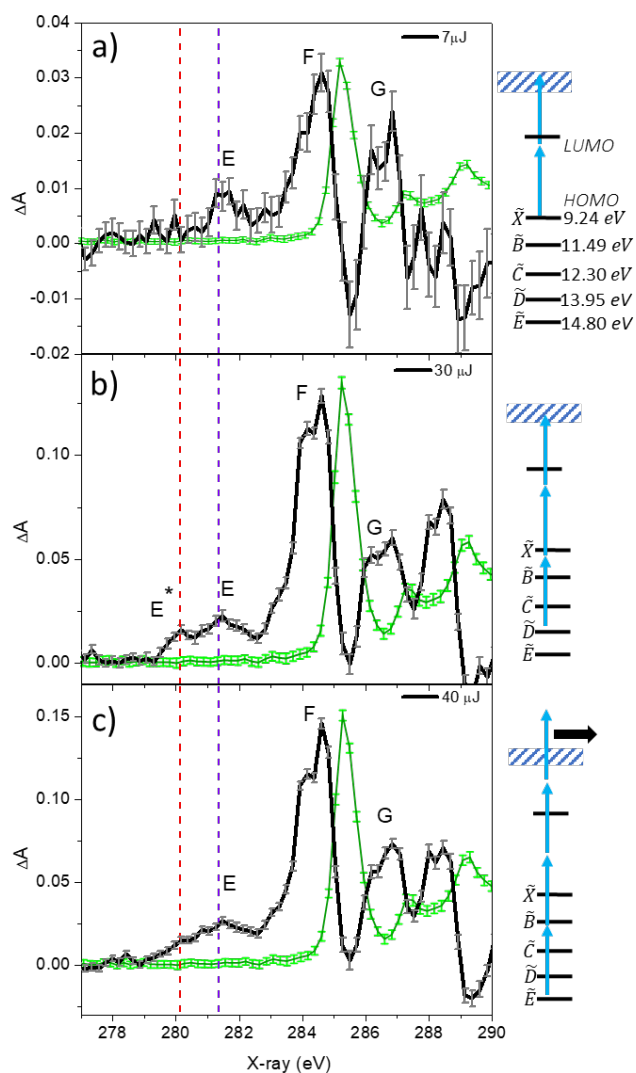


Figure 2. Comparison between x-ray absorption spectra of Bz^+ with different UV powers with a 20 cm f.l. lens to increase the UV power density (a) 7 μJ , (b) 30 μJ , (c) 40 μJ . The spectra are measured at 1 ps time delays between the pump and probe beams. The neutral benzene is presented by green lines and normalized to the main peak of Bz^+ .

Sudden removal of an electron from a π orbital by ionization changes the bonding pattern, initiating structural changes (JT distortion).⁵⁶ The relaxation time depends on the slope of the potential energy surface (nuclear gradient) and distance between the the initial FC geometry and the relaxed cation geometry. This is discussed in detail in Ref. 56, where the time for structural relaxation was estimated to be on a timescale of 30 fs. Vibrationally excited states formed in the

ionization process may affect the relaxation time, due to different potential energy surfaces for each vibration.^{57,58} As noted above, there is room temperature internal energy in the neutral benzene (estimated average thermal vibrational energy) of about 0.05 eV and 0.05 eV of excess energy available from the two-photon UV excitation, which can prepare the benzene cation with a small amount of vibrational excitation, depending on the FC factors for the two-photon ionization from each neutral vibrational state. The spectrum of a pure vibrationless ground state cation is therefore not expected in the experiment. There can be both vibrational redistribution after excitation, as well as relaxation from the FC region of the neutral to the structurally distorted cation, both of which can lead to significant changes in the x-ray spectra and very early time dependences.^{59,60,61} Importantly, spectral signatures of the spin coupling of the unpaired electrons should be instantly visible upon ionization, as their appearance does not require structural changes and vibrational redistribution. Vibrational excitation alone may produce significant shifts in x-ray spectra, as illustrated in a recent study.^{59,61} In Fig 3, we present a time-dependent study that does show a trend of shifting of peaks E, F, G at different time delays during the period 0 - 150 fs.

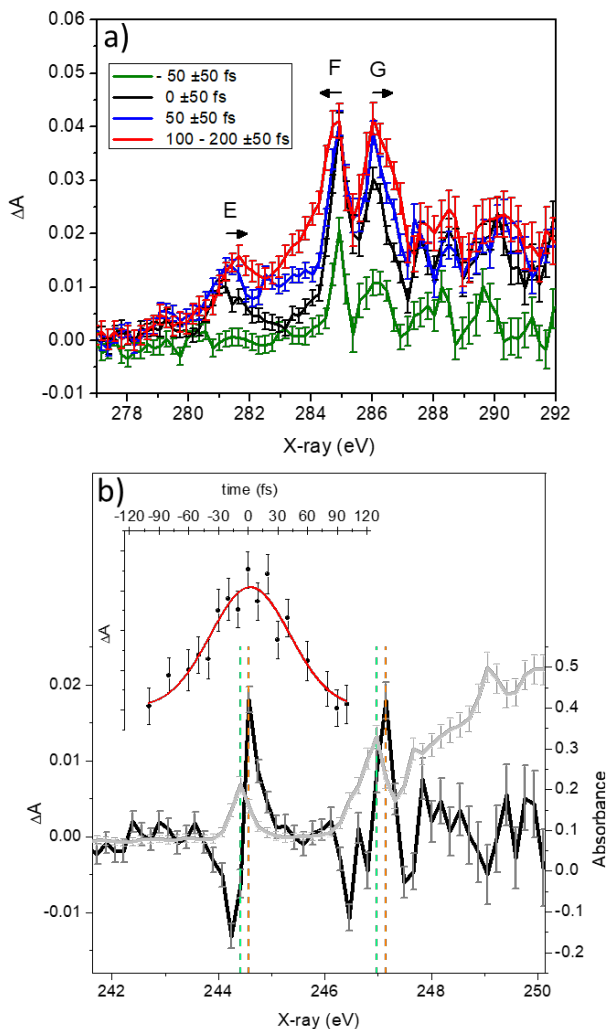


Figure 3. (a). Transient x-ray absorption spectra of ground state benzene cation measured at different time delays between the pump and probe beams. The black line represents 0 ± 50 fs delay where the probe and pump beam fully overlap (similarly to presented data in Fig 1(b)). The blue line represents 50 ± 50 fs and the red line represents $100 - 200 \pm 50$ fs delay. The experiment was performed with low intensity UV beam as can be seen from one open π orbital indicated by only peak E. (b). Temporal resolution of the instrument measured by Stark shifting of XUV transitions of Ar with the UV pulse. In the top panel, the black dots represent the differential absorption (ΔA) spectrum of the argon $2p_{3/2} \rightarrow 4s$ transition measured as a function of the pump (soft x-ray)-probe (267 nm) time delay (each spectrum is the average of 128 CCD images, 1000 laser pulses per image) and the red line is a Gaussian fit with full-width-at-half-maximum (FWHM) of 90 ± 15 fs. The black line represents the differential absorption (ΔA) spectrum with the best temporal overlap (in this work defined as time zero) between 267 nm and x-ray radiation. The gray line represents the absorbance spectrum of argon without 267 nm laser to show the Stark shift of the Rydberg states (green and red dashed lines).

At longer time-delays, peaks E and G move to higher energy (~ 0.2 eV) and peak F moves to lower energy (~ 0.3 eV), as indicated by the black arrows. The direction of the shifts follows

what is expected from the JT displaced structure of the cation: the half-occupied π orbital moves to higher energy and the two π^* orbitals split to lower and higher energies relative to their position in the FC region. In addition to the observed peak shifts, the widths of the peaks change as well. In principle, the observed temporal dynamics should be related mostly to the JT displaced structure and vibrational redistribution, while spin-coupling should be relatively insensitive to time delay an occur immediately. However, with the rather slow experimental temporal resolution of 90 ± 15 fs, it is impossible to distinguish between the exact contributions from the structural and vibrational relaxation, versus exchange interactions due to spin splitting, or to define a precise timescale for the x-ray spectral changes. This task would be further complicated if the spin coupling is also affected by nuclear motion, which could lead to a time-dependent behavior of the splitting energy due to the coupling of the three unpaired electrons.

Because the coupling of the three unpaired electrons is dominated by the valence exchange integral involving π and π^* orbitals, it may be sensitive to the exact shapes of the singly occupied valence orbitals. Therefore, the $1s_C \rightarrow \pi^*$ transition may, in principle, report on changes in electron distribution along pseudo-rotation motion connecting two different JT electronic states of the cation differing by their singly occupied π orbital. This might be an additional reason for observed trends in the peak widths.

It is also valuable to consider whether excitation to the high Rydberg states of neutral benzene by two-photon excitation near the ionization limit could lead to ultrafast relaxation to different electronic states of neutral benzene;⁶² this could be another reason for the broadening of the peaks. However, since the energy of the two-photon excitation is only slightly above the ionization limit, we consider this process as unlikely. Moreover, similar widths of the peaks are obtained even after tuning the UV wavelength by rotating the crystal that generates the third harmonic (264 - 267 nm).

CONCLUSION

To conclude, this work investigates the carbon K-edge spectrum of the benzene radical cation following ionization with two UV photons. While many efforts have been directed to spectroscopic and theoretical investigations of the ground-state benzene radical cation and its JT

distortion, the x-ray spectroscopic regime remained largely unexplored. The differences in the x-ray spectra of the radical cation and the neutral benzene are directly compared in this contribution. In particular, the low-energy transition to the partially vacant π orbital and the prominent splitting of the $1s_C \rightarrow \pi^*$ transition serve as clear fingerprints of the cation. The nature of this splitting is assigned to both the spin couplings of the three unpaired electrons (in the partially vacant $1s$ core, the partially open π orbital and the partly occupied π^* orbital) and reduced symmetry of the cation following the JT distortion.^{38,39} To further deepen the understanding of the structural relaxation and the influence of spin coupling on the x-ray spectrum, the spectral changes in the first 100 fs do show clear shifts and broadenings in energy of the transitions involving π and π^* orbitals. More detailed analysis of the underlying electronic structure is discussed in the parallel theoretical paper.²⁹ For a better understanding of the interplay between these two effects from an experimental perspective, measurements with attosecond or few-femtosecond time resolution are needed to distinguish the fast relaxation to the distorted cation symmetry from the instantaneous splitting due to spin coupling.

Supporting Information

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