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Photoinduced Heterocyclic Ring Opening of Furfural: Distinct Open-Chain Product Identification by Ultrafast X-ray Transient Absorption Spectroscopy

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ABSTRACT: The ultraviolet-induced photochemistry of five-membered heterocyclic rings often involves ring opening as a prominent excited-state relaxation pathway. The identification of this particular photoinduced mechanism, however, presents a challenge for many experimental methods. We show that femtosecond X-ray transient absorption spectroscopy at the carbon K-edge (~284 eV) provides core-to-valence spectral fingerprints that enable the unambiguous identification of ring-opened isomers of organic heterocycles. The unique differences in the electronic structure between a carbon atom bonded to the oxygen in the ring versus a carbon atom set free of the oxygen in the ring-opened product are readily apparent in the X-ray spectra. Ultrafast ring opening via C–O bond fission occurs within ~350 fs in 266-nm photoexcited furfural, as evidenced by fingerprint core (carbon 1s) electronic transitions into a nonbonding orbital of the open-chain carbene intermediate at 283.3 eV. The lack of recovery of the 1s\(*\) ground-state depletion in furfural at 286.4 eV indicates that internal conversion to the ground state is a minor channel. These experimental results, augmented by recent advances in the generation of isolated attosecond pulses at the carbon K-edge, will pave the way for probing ring-opened conical intersection dynamics in the future.

INTRODUCTION

Five-membered heterocyclic organic rings such as furan are key building blocks in polymers, molecular optoelectronics, pharmacological agents, atmospheric compounds, and fuels. As such, the energy relaxation pathways available to these cyclic molecules upon electronic excitation are of great interest. Ultraviolet excitation near the absorption maximum populates a 1\(\pi\pi^*\) (\(S_2\)) at the Franck–Condon point (FC) electronically excited state. The ensuing photochemistry is notably mediated by a conical intersection (CI) with a higher-lying \(\pi\sigma^*\) state (labeled \(S_\delta\)) that can lead to a carbon–heteroatom bond fission, i.e. ring opening (\(\delta\)) can occur via promotion of an electron from a \(\pi\)-bonding orbital to a \(\sigma^*\) antibonding orbital (Figure 1b). This pathway involves nonadiabatic passage of the excited molecule via two successive CIs, an initial \(S_\delta(\pi\sigma^*)/S_\gamma(\pi\pi^*)\) CI close to the FC region and a subsequent \(S_\gamma(\pi\pi^*)/S_\delta(\pi\sigma^*)\) CI. An alternative route of nonadiabatic coupling to the ground state involves a particular nuclear distortion known as ring puckering (\(p\)) in \(S_\delta\) where the molecule loses planarity and the H atom in the \(\alpha\)- or \(\delta\)-position with respect to the heteroatom is bent (Figure 1a).

In this case, the excited molecule evolves on a single electronic state surface (\(1\pi\pi^*, S_2\)) that is the initial photoexcited state, before arrival at a direct CI with the ground state.

Furfural (or furan-2-carbaldehyde, Figure 1) is the simplest aldehyde derivative of furan, it is a potential biomass-derived biofuel, and it is used extensively in agrochemical, petroleum, plastics, and pharmaceutical industries. The photodynamics of furfural can be contrasted with its base compound, furan. Time-resolved photoelectron imaging studies of furan, using both 4.7 and 7.8 eV probe pulses, indicated that ring puckering is the predominant pathway. This is inferred from the temporal invariance of the anisotropy parameter at each observed photoelectron kinetic energy, indicating that the electronic character does not change upon excited state relaxation. In contrast, another femtosecond photoelectron imaging study with 800 nm multiphoton ionization as a
probe revealed biexponential decay kinetics of photoexcited furan, attributed to an initial $S_1 \rightarrow S_0$ internal conversion and subsequent decay of vibronic $S_0$ to the formation of $\alpha$- and $\beta$-carbenes, also reported to be formed in furan pyrolysis. A recent time-resolved photoelectron study reports the effect of aldehyde substitution on the photoinduced relaxation dynamics of furan, i.e. parent compounds furfural and $\beta$-furfural, using a high-intensity, two-photon ionization probe. The relaxation dynamics of furfural are found to be slowed down (approximately hundreds of femtoseconds) in comparison to furan (sub-100 fs) and additionally involve a deactivation pathway via an $\pi\pi^*$ state (not the nonbonding orbital of the carbonyl oxygen). In that same work, the CASSCF geometrical structures of the ground-state, ring-puckered ($C_{1p}$), and ring-opened ($C_{1s}$) conical intersections of furfural are shown at the bottom of the figure. (For detailed calculations, see ref 17.)

![A schematic of the ultraviolet-induced photodynamics in furfural (also applicable to furan) shows the diabatic electronic states involved along the (a) ring-puckering and (b) ring-opening coordinates. $S_n^*$ defined at the Franck–Condon (FC) region for excitation of the electronic states concerned; $S_0 (\pi^\pi, \pi^\pi^*$, ground-state), $S_1 (\pi\pi^\ast$, optically dark state, not shown), $S_2 (\pi\pi^\ast$, photoexcited state), $S_3 (\alpha\pi^\ast)$. (It must be noted that the $\pi\pi^\ast$ state lies higher than $S_0$ for furan at the FC-point.) It is effectively $S_1$ for this schematic where the intermediate $\pi\pi^\ast$ and $\pi\alpha$-furans are ignored.) The geometrical structures of the ground-state, ring-puckered ($C_{1p}$), and ring-opened ($C_{1s}$) conical intersections of furfural are shown at the bottom of the figure. (For detailed calculations, see ref 17.)

Figure 1. A schematic of the ultraviolet-induced photodynamics in furfural (also applicable to furan) shows the diabatic electronic states involved along the (a) ring-puckering and (b) ring-opening coordinates. $S_n^*$ defined at the Franck–Condon (FC) region for excitation of the electronic states concerned; $S_0 (\pi^\pi, \pi^\pi^*$, ground-state), $S_1 (\pi\pi^\ast$, optically dark state, not shown), $S_2 (\pi\pi^\ast$, photoexcited state), $S_3 (\alpha\pi^\ast)$. (It must be noted that the $\pi\pi^\ast$ state lies higher than $S_0$ for furan at the FC-point.) It is effectively $S_1$ for this schematic where the intermediate $\pi\pi^\ast$ and $\pi\alpha$-furans are ignored.) The geometrical structures of the ground-state, ring-puckered ($C_{1p}$), and ring-opened ($C_{1s}$) conical intersections of furfural are shown at the bottom of the figure. (For detailed calculations, see ref 17.)

**METHODS**

Femtosecond time-resolved X-ray absorption is performed in a recently upgraded table-top apparatus that produces ultrashort (sub-60 fs), broadband soft X-ray pulses between 150 and 310 eV and covers the carbon K-edge ($\sim$284 eV). These soft X-ray pulses are used to probe the dynamics of photoexcited furfural over several picoseconds after ultraviolet excitation. A tunable optical parametric amplifier (1180–2600 nm; HE-TOPAS, Light Conversion) pumped by an ~90% split-off output of a Ti:sapphire laser (800 nm central wavelength, 12 W at 1 kHz, sub-35 fs pulse duration; Spitfire Ace, Spectra Physics) is used to produce high harmonics at a fundamental driving wavelength of 1320 nm (2.1 W at 1 kHz, sub-60 fs pulse duration). The beam is irised down, focused by a 40 cm lens into a differentially pumped, semi-infinite gas cell containing helium ($\sim$750–850 Torr), and the residual infrared is blocked by a 100-nm thick aluminum filter. A toroidal mirror focuses the high harmonic, soft X-ray pulses into a sample cell (2 mm path length), which contains ~300 μm holes to pass the laser beams and through which the vapors of furfural (Sigma-Aldrich, sample heated at 80 °C) are made to exit. Ultraviolet 266 nm pump pulses, produced by third-harmonic generation, are routed by a variable delay-stage (1 fs precision) and focused into the sample cell with a 40 cm focal length lens (~6 mW, sub-70 fs pulse duration, pump-intensity of ~1.2 × 10^11 W cm^-2 at the pump–probe interaction region). The residual pump is blocked by an ~200-nm thick titanium foil, and the transmitted probe is dispersed by a 1200 lines/mm variable line spaced, concave grating onto a CCD chip (1340 × 400 pixels, 20 × 20 μm pixel size; Princeton Instruments). An in situ pump–probe cross-correlation is obtained by measurement of the ponderomotive shift of the core-excited Rydberg states of Argon, which sets the position for time zero and also the instrument response function (IRF) of the apparatus (90 fs, Figure S1). Further details may be found in the Supporting Information.

Ground-state, static X-ray absorption spectra of furfural are measured by referencing 64 high-harmonic transmission spectra (acquiring 1000 laser pulses per spectrum) in the presence (I on) and absence (I off) of the sample to obtain the optical density or absorbance, $A = -\log_{10}(I_{on}/I_{off})$. Time-resolved differential X-ray absorption spectra (or X-ray transient absorption spectra) are obtained by measuring the X-ray absorbance of the sample in the presence ($I_{on}$) and absence ($I_{off}$) of the pump pulse at specified pump–probe time delays while the sample vapors flow continuously. A typical pump–probe measurement averages 24 or 32 spectra (integrating 1000 laser pulses for each “pump-on” and “pump-off” configuration) over 60 pump–probe time delays between ~450 fs and 10 ps, where positive time delays denote the X-ray probe pulse arriving at the interaction region after the ultraviolet pump pulse. The differential absorbance ($\Delta I$) for each time delay is then obtained as $-\log_{10}(I_{on}/I_{off})$ and added back to a scaled ground-state spectrum to derive the X-ray absorption spectrum of the photoexcited molecules alone. The reaction kinetics are calculated by taking single-energy lineouts of the key resonances over the measured time delays and fitting the time traces to
exponential rise or decay functions convolved with a Gaussian instrument response of fixed width (90 fs).

Previously reported electronic structure calculations\(^\text{37}\) are used as a starting point for this work. All geometries are optimized on a complete active space self-consistent field (CASSCF) level of theory with 6-31G\(^*\) as a basis set, except for the equilibrium geometry where coupled cluster CCSD(T) theory is used. Core-excited spectra are computed using the strongly contracted \(n\)-electron valence state perturbation theory (NEVPT2), a specialized version of complete active space perturbation theory (CASPT2) linked to the CASSCF reference states. The basis set employed is the correlation-consistent, core–valence triple-\(\varepsilon\)-\(\zeta\) basis set cc-pCVTZ, which does not describe Rydberg orbitals particularly well, but is accurate for the frontier orbitals of \(\pi/\pi^*\) character. For the sake of comparison, calculations are also carried out using time-dependent density functional theory (TDDFT) with basis sets incorporating diffuse functions. The NEVPT2 energies are found to depend strongly on a balanced description of the electron distribution around all atoms. This necessitated the use of different active spaces for the different molecular geometries. Consequently, all calculations are independently compared to the experimental spectra. At the FC point, an (8,7) active space is chosen, which comprises the whole \(\pi\)-space of furfural. At the conical intersections, the \(\sigma\)-orbitals of the elongated CO-bonds are added, which in the case of \(\text{CIP}\) are delocalized within the \(\pi\)-space, and in the case of \(\text{CIF}\) are essential for the correct description of the electronic states. The spectra are simulated by Gaussian broadening (320 meV) of the NEVPT2 excitation energies and scaling with the transition dipole moments of the respective CASSCF reference states. From comparison of the theoretical spectra with the experimental NEXAFS spectra, the absolute energy shifts needed for the NEVPT2 results were noted to be larger than in the case of valence excitations. At the FC point (shift of \(\sim 6\) eV), it still lies below the shift necessary for TDDFT (\(\sim 10\) eV). We primarily focus on the NEVPT2 results, as TDDFT is not suited to describe the valence-excited states at the conical intersections. Also, the CIs and ring-open structures show many double excitations that are not described within TDDFT.

\section*{RESULTS}

The ground-state, near-edge X-ray absorption fine structure (NEXAFS) spectrum of furfural (solid black line with shaded-gray error bar, Figure 2) shows a strong peak at 286.4 eV and a low-energy shoulder at 285.1 eV. A NEXAFS calculation at the NEVPT2(8,7) level of theory indicates that the observed peaks correspond predominantly to \(1s \rightarrow \pi^*(\text{LUMO})\) resonances from several atoms. The unique chemical shifts of the inequivalent carbon atoms lend it a double-peak structure, as is also reported for furan.\(^\text{37}\) Specifically, the peak at 286.4 eV corresponds to the core(\(1s\)) \(\rightarrow\) LUMO(\(\pi^*\)) transitions centered on the \(\text{C}_1\) (yellow), \(\text{C}_4\) (brown), and \(\text{C}_5\) (red) atoms (see underlying colored-stick spectrum) whereas the shoulder mainly consists of a 1s(\(\text{C}_3\) green) \(\rightarrow\) \(\pi^*\) transition and a 1s(\(\text{C}_3\), blue) \(\rightarrow\) \(\pi^*\) transition. These individual frequencies are presently not resolvable in the experiment, and only a convolution of the computed stick spectrum with a Gaussian broadening equivalent to the spectrometer resolution (\(\sim 320\) meV, filled orange curve) can be directly compared with the experiment. The chemical shift of the carbon atoms \(\text{C}_1\), \(\text{C}_4\), and \(\text{C}_5\) to higher energies in comparison to \(\text{C}_2\) and \(\text{C}_3\) is expected due to the proximity of the more electronegative oxygen heteroatom. The assignment is also consistent with the reported NEXAFS spectrum of furan, which contains two sets of inequivalent, chemically shifted carbon atoms.\(^\text{37,38}\)

Figures S2–S3 show results obtained at other levels of theory (TDDFT) and for structural isolomers of furfural. As NEXAFS spectra are mainly sensitive to the electronic structure, the contributions of nuclear structural isomers (cis/trans) to the measured spectra cannot be quantified.

In the NEXAFS spectrum of furfural shown in Figure 2, the broad absorption peaks at 288.2, 289.6, and 291.6 eV, barely discernible over the rising edge that results from core-1s ionization, are mainly due to 1s\(\pi^*(\text{LUMO}+1)\) and 1s\(\pi^*(\text{C}–\text{O})\) resonances.\(^\text{37}\) Core-valence and core-Rydberg resonances that dominate this region of the spectrum are particularly difficult to reveal for two reasons: (i) coupling with the ionization continuum broadens these peaks due to a shape resonance, and (ii) the 1s-core ionization significantly depletes the X-ray photon flux at these probe energies, which is evident through the larger error bars (shaded gray curve represents a 95\% confidence interval) that accompany the data points measured over the carbon K-edge in comparison to the near-edge. These broad, high-energy peaks at the carbon K-edge are also reported in the NEXAFS spectrum of furan and share the same assignment.\(^\text{37}\)

Figure 3a shows the measured evolution in the NEXAFS spectrum of furfural at representative time delays following 266 nm photoexcitation. This includes time delays immediately following photoexcitation (\(\sim 80\) to 20 fs, solid blue), intermediate (1.2 to 2 ps, solid green), and long time delays (7 to 10 ps), whereupon no further changes are detected in the transient absorption spectra. These pure "pump-on" NEXAFS spectra are derived by adding the measured differential X-ray transient absorption spectra ("pump-on" minus "pump-off" X-ray absorption signals) for each of the time windows to a suitably scaled, experimental ground-state NEXAFS spectrum. The scaling factor is obtained by an estimation of the percentage of the ground-state molecules that are excited in the pump focal volume. This is found to be approximately 23\%, based on the 266 nm absorption cross section of furfural and the pump fluence (see Figure S4, which is linear over the range of pump fluence between 8 and 20 mJ/cm\(^2\)). Figure S5
shows the complete evolution of the transient absorption data over all time scales up to 10 ps, and the corresponding, derived, pure "pump-on" spectra are shown in Figure S6.

At time delays $\leq -100$ fs (solid black line, Figure 3a), the pump pulse arrives after the X-ray probe pulse, and this spectrum is therefore equivalent to the ground-state NEXAFS of furfural (Figure 2). At early times ($-80$ to $20$ fs, blue trace), a depletion of the ground-state 1s$\pi^*$ (LUMO) core-excited resonances is noted at 285.1 eV (P4) and 286.4 eV (P6) due to the $\pi \rightarrow \pi^*$ optical excitation (vertical black dotted lines to guide the eye). These depletions occur immediately after photoexcitation (50 $\pm$ 40 fs, Figure 4), as revealed by a temporal lineout taken at P6 and show a constant amplitude up until the longest measured time delays (10 ps). Three new, weak absorption peaks (vertical blue dashed lines to guide the eye) are also identified in the blue trace, at 281.6 eV (P1), 284.0 eV (P3), and 287.5 eV (P7). P1 and P3, which appear lower in energy than the ground-state NEXAFS peaks of furfural at P4 and P6, must correspond to the transitions of a 1s-core electron into the hole produced in the singly occupied $\pi$-orbital resulting from the valence excitation. Specifically, these represent chemically shifted, core-to-(singly occupied) HOMO transitions in photoexcited furfural. It must be noted that these spectral features that appear as "single" peaks actually contain a number of underlying core-to-valence resonances from inequivalent carbon atoms, which cannot be spectrally resolved (see representative stick spectra, Figure 3b).

Interestingly, a minor, broad depletion is also noted in the region between 291 and 292 eV which represents a decreased absorption of the 1$s\sigma^*$ resonance. As the $\sigma^*$ orbital is not involved in the optical excitation, a depletion in the 1$s\sigma^*$ resonance at early times may possibly arise from nonadiabatic population transfer from the $\pi\pi^*$ to the $\pi\sigma^*$ state, as required in a ring-opening process. However, the low probe-photon counts above the absorption edge, together with the broad
widths of the absorption peaks in this region, render a concrete assignment to ultrafast nonadiabatic dynamics far from unambiguous at this stage.

All three peaks (P1, P3, and P7) are found to grow in amplitude for several hundreds of femtoseconds (Figures S5–S6). As the photochemical reaction proceeds to intermediate time delays (>1 ps, solid green line in Figure 3a), P7 continues to grow whereas the amplitudes of P1 and P3 gradually decrease with the concomitant appearance of two new peaks, P2 (283.3 eV) and P5 (285.8 eV) (red dot-dashed lines). The kinetics of P1 (Figure 4) reveals an exponential decay constant of 330 ± 60 fs which represents the excited-state lifetime. Finally, at the longest measured time delays (7–10 ps, solid red line in Figure 3a), only three new peaks remain at 283.3 eV (P2), 285.8 eV (P5), and 287.5 eV (P7). Of these, the position of P2 is strikingly similar to a core-1s transition into a nonbonding (2p) orbital of a carbon atom, and it has been identified earlier in the soft X-ray absorption spectra of organic radicals.28,32,39 Therefore, it is assigned to a carbon 1s → 2p transition in ring-opened furfural. A 266 nm power-dependence study of the most intense peak (P7, 287.5 eV) shows a linear scaling with a slope of near-unity and is consistent with a one-photon excitation process (Figure S4). This peak rises with a time constant of 340 ± 25 fs, as shown in Figure 4, and its kinetics are similar to that of P2 (350 ± 50 fs, Figure S7). Thus, these peaks are most likely representative of the same final state.

**DISCUSSION**

The formation of a vibrationally hot furfural molecule from nonreactive internal conversion to the ground state is expected to lead to a broadening of the ground-state NEXAFS peaks and partial or full recovery of the parent depletion at longer time delays, depending on the branching fraction. In the ring-opening reaction of 1,3-cyclohexadiene (CHD), where a significant percentage (∼60%) of the molecules internally convert to the ground state, nonadiabatic molecular dynamics simulations were used to obtain the NEXAFS from the vibrationally hot CHD at the carbon K-edge.24 The simulations predicted a decrease in the oscillator strength with increasing CHD at the carbon K-edge, 300 K. In a NEXAFS study of thymine photochemistry (266 nm) at the oxygen K-edge, a partial or full recovery of the parent depletion at longer time delays are included in Figure 3b for a representation of the overall reaction pathway. The computed NEXAFS spectrum for the FC-region in the optically bright S2 state (where only the electronic structure changes at the frozen ground-state geometry) agrees remarkably well with the observed early time-delay spectrum, in regard to the positions of P1 and P3 (within instrumental resolution). As mentioned earlier, these peaks arise mainly from a core-1s electronic excitation into the hole left in the HOMO of the parent molecule upon ultraviolet excitation. The computed peak at 279.9 eV for the FC-point is not observed as a distinct peak in the experiment but rather as a low energy tail (see comparisons of the differential absorption spectra, Figure S9). The computed spectrum of the ClO region fits the experimental spectrum between 120 and 200 fs (Figure S9) very well, suggesting that a distribution of opened structures likely dominate the early time NEXAFS spectra.

Most importantly, the positions of P2 and P7 observed at the longest time delays are in excellent agreement with the computed NEXAFS of an open-chain carbene intermediate (filled red curve, Figure 3b) which is found to be a minimum energy structure for ring-opened furfural. P2 and P5 mainly represent the chemically shifted, core-to-2p (LUMO) and core-to-π* (LUMO+1) resonances of the ring-open isomer, whereas P7 is predominately core-to-π* (LUMO+1) and core-to-π* (LUMO+2) resonances. The minor discrepancy in the experimental and theoretical positions of P5 could be due to the fact that the computed peak center overlaps with a ground-state depletion (P4), which might shift the observed P5 peak center to slightly higher energies. A previous study on the ultrafast relaxation dynamics of furan tentatively assigned the observed photoelectron bands to the formation of carbenes.15 A ring opened furfural is also implicated in pyrolysis measurements42 and hypothesized to involve a carbene intermediate in the pyrolysis of furan16 and 2-methyl furan.43 Herein, the unique sensitivity of NEXAFS spectroscopy to electronic structure provides direct evidence for photochemical ring opening in furfural via a carbene intermediate, through core electronic transitions into its unoccupied, frontier molecular orbitals. A biradical structure (see Figure S10 and related note) arising from homolytic C–O bond fission could also be computationally identified in a few trajectories in the ring opening of furfural; however, it does not correspond to a minimum energy structure.

The key photochemistry accompanying the photoinduced ring-opening reaction and associated time scales are illustrated in Figure 4. The depletion of the 1sπ* (LUMO) resonance at P6 sets in sharply near time zero with a time constant of ∼50 ± 40 fs, reaches a plateau by 200 fs, and shows no subsequent recovery up to the longest measured time scales (∼10 ps), indicating that nonreactive internal conversion to the ground
state does not occur or is only a minor channel (within one standard error of the fitted P6 amplitude which corresponds to ∼5%). If the return to the ground state leads to vibrationally broadened features (∼200 meV, by analogy to theoretical results reported for CHD), the integrated peak area may be taken into account to estimate the repopulation of S0. This procedure returns a standard error of ∼8% with respect to the mean integrated differential absorbance (between 286 and 287 eV, Figure S11). A conservative upper limit for the return to the ground state is further derived by the effect of the vibrational broadening expected in the hot ground state (∼200 meV) on the measured peak width of P6 in ground state furfural (0.95 eV, Figure S12), which is ∼10% when weighted by the instrumental resolution. The best upper estimate of S0 repopulation is therefore 8% based on the signal-to-noise ratio in the integrated differential absorbance, and is adjusted to 10% due to anticipated vibrational broadening. Previously reported on-the-fly dynamics of furfural averaged over 100 trajectories, initiated in the electronic state nearest to the HOMO–LUMO energy gap (labeled S1 in that paper but S2 according to Figure 1), indicate little ground-state population recovery (<15%) up to 500 fs. Time-resolved infrared measurements of the closely related molecule, 2-furanone, in acetonitrile at 225 nm, also reveal prompt ring opening on a sub-1 ps time scale with less than 10% of the molecules reported to undergo internal conversion to the ground electronic state. With improved flux in table-top soft X-ray setups, independent quantitative estimates of branching fractions in photochemical reactions will be feasible in the near future. The significantly low fraction of return to the ground state and lack of other features over the many picosecond time scales suggest that ring opening is the predominant photodynamical pathway in gaseous furfural at 266 nm and likely involves a carbene intermediate. The ultrafast rise of P2 (350 ± 50 fs) and P7 (340 ± 25 fs) (Figures 4 and S7), characterized by similar time constants, is indicative of these peaks originating from the same ring-opened photoproduct. This sub-400 fs ring opening originates on the barrierless excited state surface, since any ring opening in the ground state is expected to be significantly slower. The products are formed with high internal excitation and may undergo further isomerization (via H atom migration) or even fragmentation, which can be better probed in the future with higher NEXAFS spectral resolution and by sampling longer time delays. P1, characterized by an ultrafast rise (73 ± 20 fs with respect to the onset of ground-state depletion) and decay (330 ± 60 fs), is indicative of an intermediate photoexcited state that rapidly decays into the product. The temporal behavior of P1 in Figure 4 is plotted after subtraction of the contribution from the low-energy wing of P2 in the long-delay limit differential absorption signals in this region (Figure S13). The quoted error bars for the time constants correspond to one standard error from the least-squares fitting routine. Future experiments with even shorter pulses are likely to reveal the dynamics of the intermediate excited states and passage through conical intersections. Complementary experiments at the oxygen K-edge (∼543 eV) can also enable an alternative view of the photochemical reaction pathway via a much simplified 1s-core spectrum of the heteroatom.

CONCLUSION
Femtosecond X-ray transient absorption spectroscopy is a powerful technique to unravel photoinduced isomerization in ring compounds via changes in fingerprint core-to-unoccupied frontier orbital resonances. Carbon K-edge spectroscopy of the 266 nm induced photochemistry of furfural provides direct evidence for an ultrafast ring-opening reaction on an ∼350 fs time scale. Internal conversion to the ground state is ruled out to within 10%, from the negligible recovery of the parent 1sπ* resonance at 286.4 eV and expected vibrational broadening effects. No particular X-ray spectral signatures are obtained to specifically rule out the ring puckering channel; however, the estimates of internal conversion to the ground state indirectly set an upper limit for this pathway. While the NEXAFS spectra are mostly sensitive to electronic structure changes, improvement in high harmonic generation efficiencies and flux above the carbon K-edge will enable tracking changes in the nuclear geometry through the extended X-ray absorption fine structure (EXAFS). These experimental results lay an initial groundwork for the application of core-level spectroscopy to a broad class of ring-opening photochemical reactions in organic heterocycles, such as epoxide ring opening in organic aerosols, radical chain-initiation steps in ring-opening polymerization reactions, etc. An increase in the temporal resolution via pump (266 nm) pulse compression and using isolated attosecond pulses at the carbon K-edge will open exciting new possibilities of probing wavepacket dynamics at conical intersections in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07155.

1 Instrument response; comparisons of experimental NEXAFS spectra with theory; pump-power dependence study; transient absorption data and associated temporal evolution over the full time-window probed (PDF)

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Notes
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