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Reconciling the Different Apparent Decay Pathways for Iron(III) Tetraphenylporphyrin Chloride: Evidence for Excited State Branching

Ryan M. Lamb¹, Laura E. Smith², Adi Natan³, John H. Burke², Roberto Alonso-Mori⁴, Leland B. Gee⁴, Patrick L. Kramer⁴, Taylor P. McClain⁵, Ryan D. Ribson⁴, Sanghoon Song⁴, Tim B. van Driel⁴, James E. Penner-Hahn^{1,5*}, Josh Vura-Weis^{2*}, Roseanne J. Sension^{1,6*}

¹ *Department of Chemistry, University of Michigan, 930 N University Avenue, Ann Arbor, Michigan 48109, USA*

² *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

³ *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*

⁴ *Linac Coherent Light Source, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA*

⁵ *Department of Biophysics, University of Michigan, 930 N University Avenue, Ann Arbor, Michigan 48109, USA*

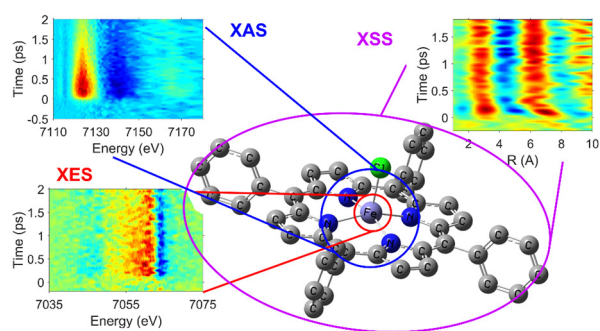
⁶ *Department of Physics, University of Michigan, 450 Church Street, Ann Arbor, Michigan 48109, USA*

Corresponding author email: rsension@umich.edu, vuraweis@illinois.edu, jeph@umich.edu

ABSTRACT

Detailed understanding of the photophysical properties of metalloporphyrins is key to rationally exploiting them in a variety of applications ranging from photocatalysis to opto-magnetics. Previous studies of the ferric-tetraphenylporphyrin chloride have provided contradictory descriptions of the excited state evolution. Optical transient-absorption suggested initial formation of a $\pi\pi^*$ excited state, followed by ligand-to-metal charge-transfer (LMCT) from the porphyrin ring and then decay on the ~ 2 ps time scale to a metal-centered excited state that had a lifetime of ~ 15 ps. In contrast, femtosecond extreme ultraviolet transient-absorption at the Fe $M_{2,3}$ -edge, while agreeing on the initial formation of an LMCT state, found evidence that this decayed in ~ 2 ps to the ground state. We have used K-edge transient X-ray absorption and X-ray emission, together with time-resolved X-ray solution scattering to explore this system. Based on these data, we propose a new model, consistent with both the earlier and the current data, in which photoexcited FeTPPCL evolves through three different states on the LMCT manifold, with the ~ 2 ps decay now seen to involve a branching between return to the ground state ($\sim 70\%$) and formation of a long-lived LMCT state ($\sim 30\%$).

For TOC Graphic Only



INTRODUCTION

Metalloporphyrins are widely used as catalysts and chromophores, in both synthetic and biological contexts, due to their photochemical and electronic properties.¹ Photoexcited metalloporphyrins have the ability to oxidize hydrocarbons,^{2,3} and have been shown to undergo large structural changes following excitation.⁴ Iron porphyrins, which can access a variety of oxidation and spin states, have found particular utility in catalysis, spintronics, opto-electronic thin films, and opto-magnetics.⁵⁻⁸ The effective use of Fe porphyrins in these roles relies on a comprehensive understanding of their electronic dynamics. This study focuses on the photodynamics of a simple, model porphyrin, 5,10,15,20-tetraphenylporphyrin iron(III) chloride (FeTPPCl) (Figure 1).

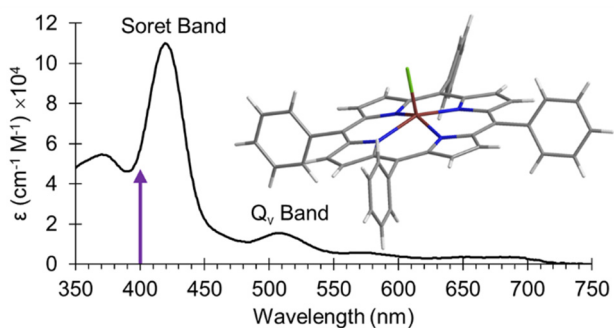


Figure 1 UV-visible absorption spectrum for FeTPPCl (5,10,15,20-tetraphenylporphyrin iron(III) chloride, shown in inset) in toluene. The purple arrow indicates the excitation wavelength.

The photodynamics of FeTPPCl and similar porphyrins have been studied extensively using a variety of methods.⁹⁻¹⁴ Excitation in the Soret band (~400 nm) promotes an electron from porphyrin π to π^* , followed by ligand-to-metal charge-transfer (LMCT) from the porphyrin ring to the Fe center.^{12,13} This LMCT state decays in 1-2 ps at room temperature, but the details of this relaxation are unclear. Broadband UV-visible transient absorption (TA) measurements suggested

that the LMCT state decays to a metal-centered excited state that lives for 13 to 18 ps in toluene, dichloromethane, or a mixture of the two solvents at room temperature, based on the observation that there were significant spectral changes in this time range.^{9,10} More recently, femtosecond extreme ultraviolet (fsXUV) spectroscopy at the Fe $M_{2,3}$ -edge ($3p \rightarrow 3d$) of FeTPPCl in a thin film suggested that the long-lived signal was due to slow vibrational cooling of the ground state.¹⁴ This proposal was based, in part, on the fact that the residual $M_{2,3}$ difference signal was too small and of the wrong sign to be consistent with ligand-field multiplet simulations for a metal centered excited state. On the other hand, the UV-visible TA showed isosbestic decay, which is generally inconsistent with a vibrational cooling over tens of ps. In this study we used a combination of ultrafast Fe K-edge X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and X-ray solution scattering to resolve this conundrum. X-ray spectroscopy gives an element-specific view of the excited state. Fe K-edge XAS ($1s$ initial state) probes the *empty* Fe $3d$ orbitals (in the so-called pre-edge region) and the molecular structure in the XANES region, while XES probes *filled* orbitals via fluorescence produced when the $1s$ core hole is filled.¹⁵ Fe $K\beta$ XES, in particular, measures the emission intensity from $3p \rightarrow 1s$ and is sensitive to the spin state of the iron through $3p$ - $3d$ -exchange coupling. X-ray solution scattering probes the structure of the excited state.

As in the parable of the blind men and the elephant,¹⁶ we find that each of the experimental probes that have been applied to the question of FeTPPCl relaxation (both current and prior) provides an incomplete, and potentially misleading, picture; only by combining all of these can we gain a full understanding of the relaxation. The results described below, combined with those reported earlier, suggest that the excited state dynamics of FeTPPCl are characterized by a cascade through LMCT states with branching between ground state recovery and formation of a final

LMCT state on a ca. 1.6 to 2.3 ps time scale followed by ground state recovery from the final LMCT state on a time scale of ca. 13 to 19 ps in solution⁹ and somewhat longer in the thin films¹⁴ or at cryogenic temperatures.¹⁰ There is no evidence for formation of a metal centered excited state in room temperature samples.

METHODS

X-ray Emission Spectroscopy

X-ray emission spectra of FeTPPCl dissolved in toluene (~4 mM) were obtained by scanning from either -1 ps to 2.5 ps or -1 ps to 20 ps using the liquid jet end station at the XCS instrument of the X-ray free electron laser LCLS at SLAC.¹⁷ The sample was pumped through a glass nozzle to achieve a stable 50 μm diameter jet of solution. The sample was recirculated, and a remote-controlled syringe was used to add toluene to the sample vial to counteract solvent evaporation. The X-ray beam and laser beam travel in a nearly collinear geometry ($\sim 1^\circ$ crossing angle) and were overlapped with the sample about 500 μm from the nozzle producing the sample jet. The optical pump pulse was 400 nm, ~ 50 fs FWHM, and the incident X-ray probe pulse (~ 50 fs) was set to 8.07 keV. Emission spectra were measured with a dispersive X-ray spectrometer operating in the von Hamos geometry using Ge(620) analyzer crystals, providing a pixel resolution of ~ 0.11 eV.

The data collected from scanning -1 to 2.5 ps were sorted into 50-fs bins while the data from scanning -1 to 20 ps were sorted into 500-fs bins.¹⁸ A baseline was subtracted from the time-resolved XES spectra and the area was normalized to one. XES difference spectra of FeTPPCl were calculated by subtracting the unpumped signal from the pumped signal at each time, such that $\Delta S(t) = S_{\text{on}}(t) - S_{\text{off}}$. The spectra were smoothed using an 11-point (~ 1.2 eV) sliding average along energy.

X-ray Solution Scattering

X-ray solution scattering (XSS) of FeTPPCl dissolved in toluene was collected simultaneously with the XES using the ePix10k detector.¹⁷ XSS difference spectra were calculated by normalizing each individual pumped x-ray shot by the area under the signal. To compensate for energy and intensity fluctuations in the X-ray beam, each pump-on scattering signal was compared to a pump-off signal that was calculated by averaging shots that had similar time, energy, and intensity to the pump on signal. Specifically, from the 2000 X-ray shots before and after each pump-on shot (4000 shots total), the pump-off shots that had X-ray energies within 5 eV of the pump-on shot, upstream intensities (ipm4) within 6% of the pump-on shot, and scattering intensities within 33% of the pump-on shot were averaged to give the pump-off signal. The averaged pump-off signal was normalized in the same way as the pump-on signal and subtracted from the pump-on signal. The data was sorted into 50 fs bins. The pre-t=0 data was averaged together and subtracted from the dataset.

The scattering data was split into its isotropic and anisotropic components via a Legendre decomposition,^{19,20} and the data was inverted to real space following literature procedures.²¹ The data was smoothed in time by applying a Butterworth low-pass frequency filter (see Figure S5), and the solvent heating signal was then subtracted from the transient data as described in the SI, following methods developed by Kjaer et al.²²

X-ray Absorption Spectroscopy

X-ray absorption spectra of FeTPPCl dissolved in toluene were obtained by scanning from either -1 ps to 2.5 ps or -1 ps to 20 ps using the XCS instrument of the X-ray free electron laser LCLS at SLAC.¹⁷ The sample delivery conditions were identical to the XES conditions since both data were collected during the same beamtime at the same end station. The X-ray beam and laser

beam travel in a nearly collinear geometry ($\sim 1^\circ$ crossing angle) and were overlapped with the sample about 500 μm from the nozzle producing the sample jet. Both the optical and X-ray pulses were linearly polarized. A waveplate in the optical beam was used to rotate the polarization to acquire transient spectra with the polarization of the optical pulse parallel and perpendicular to the polarization of the X-ray pulses. The optical pump pulse was 400 nm, ~ 50 fs FWHM, and the X-ray probe pulse (~ 50 fs) was scanned from 7.089 keV to 7.1855 keV using a Si[111] double crystal monochromator.

The relative timing of the X-ray and optical laser was recorded pulse by pulse and used to sort the XAS spectra into finer time steps. The data collected from scanning -1 to 2.5 ps were sorted into 50-fs bins, while the data from scanning -1 to 20 ps were sorted into 250-fs bins.¹⁸ Iron X-ray fluorescence was collected on an ePix100 detector²³ and used as a measure of X-ray absorption. The fluorescence signal was normalized to the scattering ($1 \text{ \AA}^{-1} < q < 2 \text{ \AA}^{-1}$) from the solvent detected on an ePix10k detector.²³ All X-ray fluorescence was summed for each time bin, then divided by the sum of all solvent scattering for that bin, rather than normalizing every individual scan bin-wise before summing them together. The former results in better signal-to-noise than the latter.

XAS difference spectra of FeTPPCl were calculated by subtracting the unpumped signal from the pumped signal at each time, such that $\Delta S(t) = S_{\text{on}}(t) - S_{\text{off}}$. A baseline (defined by the signal below 7100 eV) was subtracted from the dark XAS spectrum. The spectra were smoothed using a 3-point sliding average along energy. Isotropic (magic angle) difference spectra were calculated as $\Delta S_{\text{iso}} = (\Delta S_{\parallel} + 2\Delta S_{\perp})/3$. Measuring parallel and perpendicular polarizations allows the decomposition of the signal into contributions along the transition dipole initially excited and the sum of the two directions perpendicular to the transition dipole.^{24,25} For FeTPPCl excited into the

Soret band, excitation is into a doubly degenerate state polarized in the plane of the porphyrin ring. Assuming C_{4v} symmetry where $\Delta S_x = \Delta S_y$, the signal can be decomposed into ΔS_{x+y} and ΔS_z using:

$$\Delta S_{x+y} = (4\Delta S_{\parallel} - 2\Delta S_{\perp})/3 \quad (3)$$

$$\Delta S_z = (4\Delta S_{\perp} - 3\Delta S_{\parallel})/3 \quad (4)$$

$$\Delta S_{iso} = \Delta S_{x+y} + \Delta S_z = (\Delta S_{\parallel} + 2\Delta S_{\perp})/3 \quad (5)$$

The data obtained by scanning from -1 to 2.5 ps was measured on two separate days, with slightly different concentrations, and the data obtained by scanning -1 to 20 ps was measured on the same day and under the same conditions as the second early-time data set. Because of the difference in concentration, the overall signal intensity was different between the two early time data sets. To account for this, the first-day 2-ps data were scaled to match the second-day 2-ps data. After scaling the 2-ps data from the first day to match the second day data, the two were averaged together, weighted by the number of scans in each data set. The resulting averaged early time dataset was then combined with the long time data without any further modifications.

Computational Methods

Finite difference method near edge structure (FDMNES; version 2022.06.15) was used to generate theoretical XAS spectra to compare to experimental data.²⁶⁻²⁸

Pre-edge XAS spectra were simulated using ORCA 4.2.1.^{29,30} All time-dependent density functional theory (TD-DFT) calculations for simulating the pre-edge used the B3LYP functional with the ZORA-def2-TZVP basis set. To account for solvent effects, a polarizable continuum model was used, CPCM(Toluene). The output states underwent a Gaussian convolution with a fixed width of 1.6 eV for all Fe pre-edge simulations.

Gaussian 16 (version 16-revC01-avx2)³¹ was used to optimize the molecular geometry of some structures and to calculate vibrational modes. All calculations were carried out using DFT

(B3LYP functional and the 6-311+g(d,p) basis set). A polarizable continuum model (PCM) was used to account for solvent effects.

Representative input files for all three types of calculations are included in supporting information.

EXPERIMENTAL RESULTS

X-ray Emission Spectroscopy

Time-resolved x-ray emission measurements covered the $K\beta_{1,3}$ and valence-to-core (vtc) regions. The ground state spectra for the $K\beta$ and vtc regions are shown in Figure 2. A contour plot of the first 2 ps is shown in Figure 2. Although only the first 2 ps are shown, XES data were measured out to 20 ps (Figure S3). Following photoexcitation, the $K\beta'$ peak (shoulder at ~ 7047 eV) shifts to higher energy while the $K\beta_{1,3}$ peak (intense peak at ~ 7062 eV) shifts to lower energy. The vtc intensity is more than a factor of 200 smaller than the $K\beta$ intensity. The low signal-to-noise prevents extraction of a reliable transient signal in the vtc region.

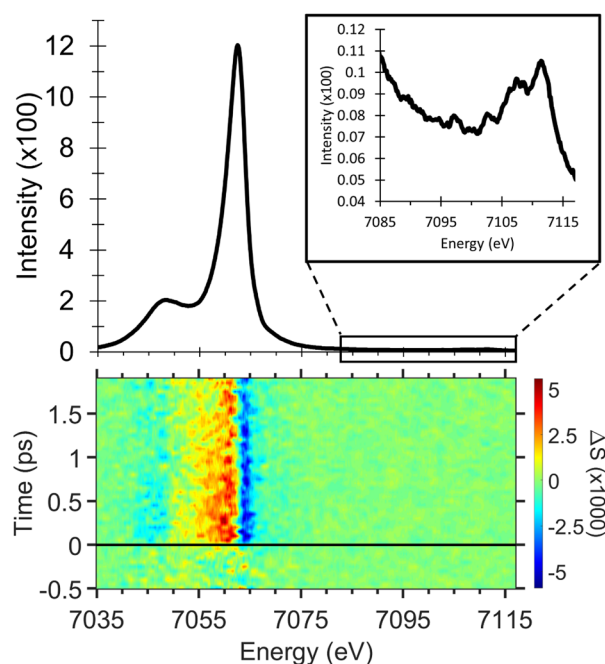


Figure 2. Top: Ground state $K\beta$ mainline and valence-to-core region (inset) for 4

mM FeTPPCl in toluene. Bottom: A contour plot of the first 2 ps of time-resolved XES data shows a blue shift of the $K\beta'$ peak and a red shift of the $K\beta_{1,3}$ peak. See Figure S1 for a different color scheme.

A global analysis procedure, fitting the transient data to a sum of exponential decay components, was performed on the time-resolved XES data spanning the $K\beta'$ and $K\beta_{1,3}$ regions (Figures 3 and S4). A 3-component fit $\mathbf{B} \xrightarrow{k_B} \mathbf{C} \xrightarrow{k_C} \mathbf{D} \xrightarrow{k_D} GS$ was used in order to permit comparison with earlier UV-visible TA.⁹ We begin labels with **B** because a short-lived state **A** ($1/k_A < 100$ fs) is observed in fsXUV and XSS measurements, although not required by the XES measurements. The fit resulted in an instrument response function (IRF) of ~ 130 fs (FWHM) and time constants ($\tau=1/k$) of $\tau_B = 0.5 \pm 0.1$ ps, $\tau_C = 1.6 \pm 0.2$ ps, and $\tau_D = 14 \pm 1$ ps which are in good agreement with previously reported values of $\tau_B = 0.53$ ps, $\tau_C = 1.94$ ps, and $\tau_D = 13.2$ ps obtained from optical measurements.⁹ The evolution associated difference spectra corresponding to 0.5 ps (**B**) and 1.6 ps (**C**) are similar, and thus a 2-component model gives nearly as good a fit. The differences are subtle in the XES measurements, with the most significant impact in the $K\beta'$ region (see Figure S21). The species are distinct in both the XAS and the UV-visible TA measurements, justifying the use of 3 components.

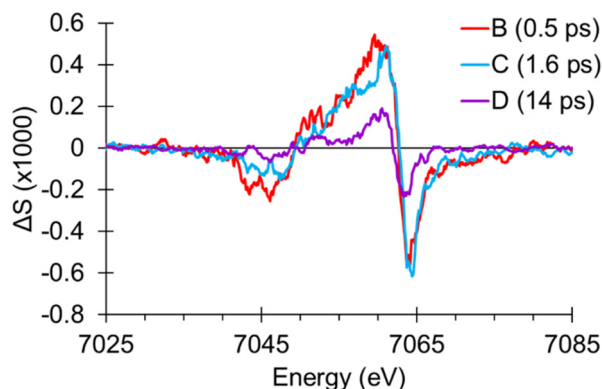


Figure 3. $K\beta$ evolution associated difference spectra of FeTPPCl in toluene after 400 nm excitation.

X-ray Solution Scattering

The inversion of the isotropic time-resolved XSS signal out to 2 ps is shown in Figure 4(a), with slices taken at 50 fs, 100 to 300 fs, and 1 to 1.5 ps shown in Figure 4(b). Initially after excitation, there is a bleaching of distances centered at 1.6 Å, and a simultaneous growth of distances centered at 3.2 Å. After a few hundred femtoseconds, the bleach at 1.6 Å decays and the positive feature shifts to 2.7 Å. Another negative and positive feature pair appears at time zero, with the negative feature initially centered at 5.4 Å, and the positive feature centered at 7.5 Å. The negative and positive feature pair quickly shifts to 4.4 Å for the negative feature and 6.2 Å for the positive feature. There is also a negative feature centered around 9.5 Å, which by 400 fs, shifts to be centered around 7.8 Å. The position of the bleach initially centered around 5.6 Å is plotted as a function of time (Figure 5(a)) and fit to an exponential decay with a time constant of 115 ± 30 fs. The observed shift, which is complete within the first five time points sampled after t_0 , may be instrument-response limited given the 130 fs IRF measured in the transient XES analysis (see below). Nevertheless, the timescale is consistent with the 70 fs component measured in previous Fe $M_{2,3}$ -edge fsXUV experiments that was assigned to relaxation from the initial π - π^* state to an LMCT state.¹⁴ The intensity of the bleach at 1.6 Å was plotted as a function of time (Figure 5(b)), and fit with an exponential decay convoluted the IRF. The time constant of the decay was found to be 400 fs, which is consistent with the first component obtained in the global analysis of the XES. The other features do not decay much after the first 400 fs.

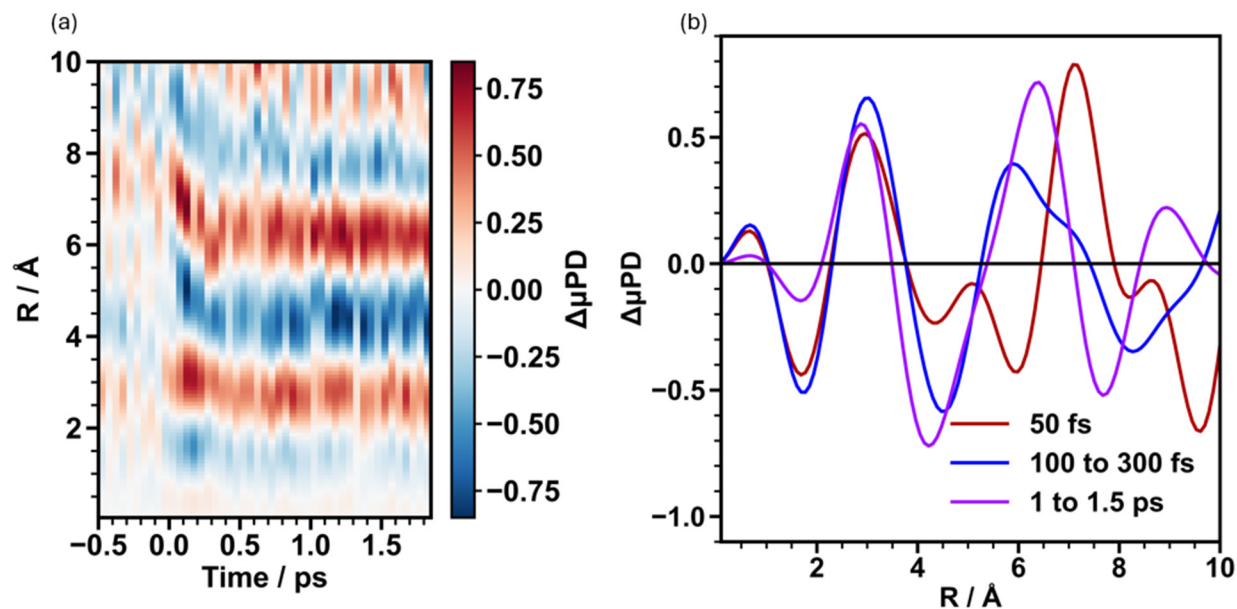


Figure 4. X-ray solution scattering following excitation of FeTPPCl at 400 nm. a) False color image showing the change in the pair distribution function as a function of time; b) Pair distribution functions averaged over three selected time ranges.

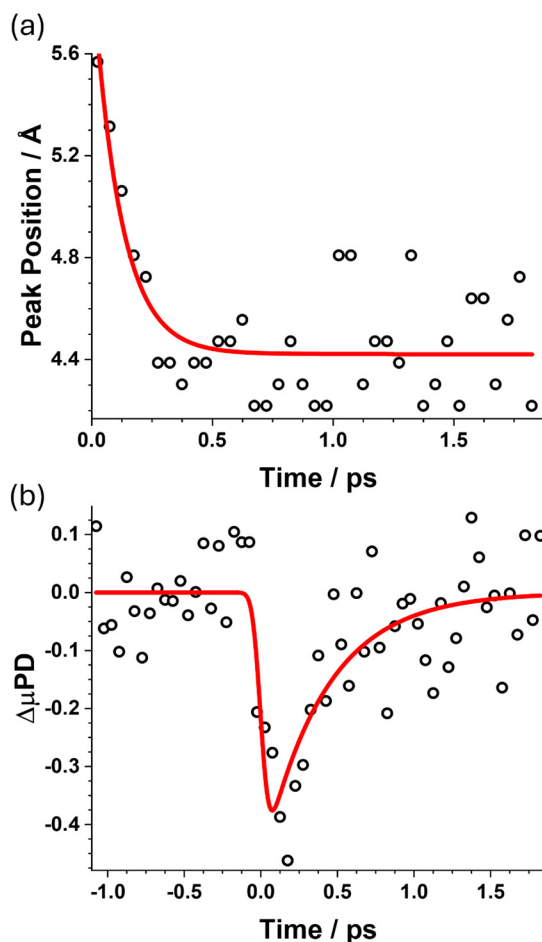


Figure 5. Traces of the position of the bleach initially at 5.6 Å (a) and intensity of the bleach at 1.6 Å (b) with their exponential fits.

X-ray Absorption Spectroscopy

The ground state K-edge XAS spectrum for FeTPPCl and a contour plot of the first 2 ps following photoexcitation are shown in Figure 6. Although only the first 2 ps is shown, XAS data were measured out to 20 ps (see Figure S3). The derivative-type signal (positive at 7125 eV, negative at 7140 eV) seen in the contour plot at early times reflects the fact that photoexcitation of FeTPPCl at 400 nm causes a significant shift of the edge to lower energy.

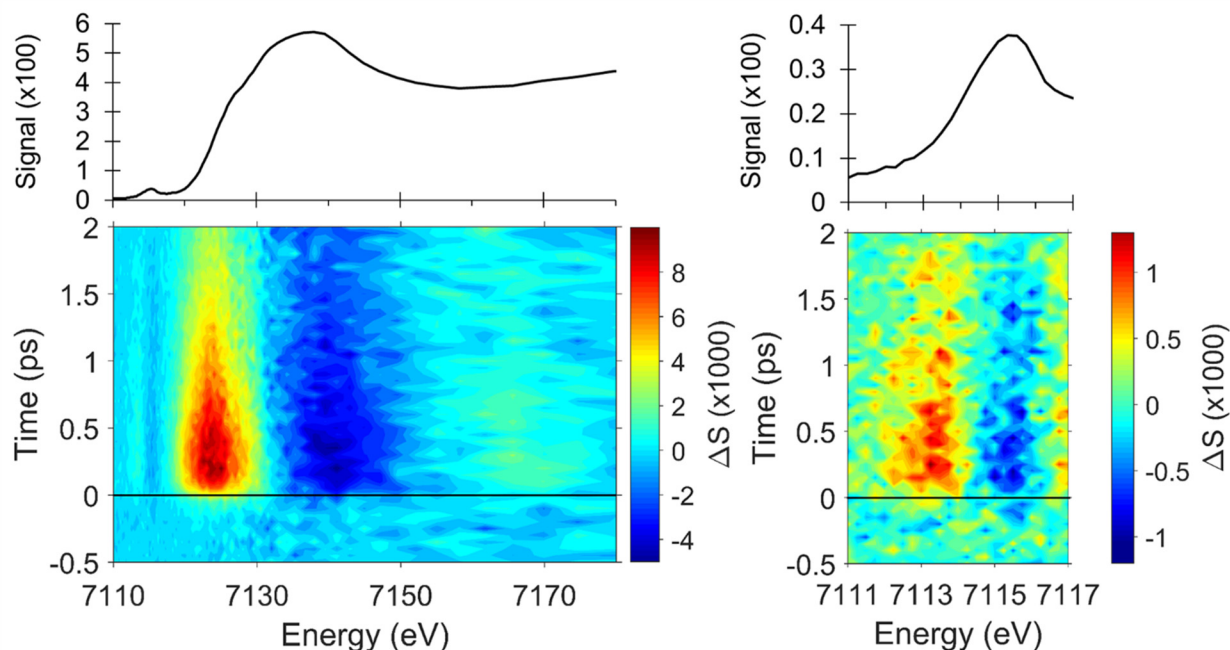


Figure 6. Ground state K-edge XAS spectrum (top) for 4 mM FeTPPCL in toluene.

Contour plots of the first 2 ps of time-resolved XAS data (bottom) show a strong red shift of the edge. The full XAS region is shown in the left panels, and an expansion of the pre-edge region is shown in the right panels. See Figure S7 for a different color scheme.

Structural changes giving rise to spectral evolution in the XANES region may not follow clean exponential kinetics, especially at the earliest times (<500 fs).^{24,32} The time-resolved XAS spectra are constant within the noise from 100 fs to 400 fs (Figure S8). These spectra were averaged to give a difference spectrum for the excited state, **B**, identified in XES and OTA and plotted in Figure 7 along with the z - and $x+y$ -polarized contributions. The initial state is characterized by a large red shift of the edge that has approximately equal contributions from ΔS_x , ΔS_y , and ΔS_z . Above the edge, the equatorial ($x+y$) changes dominate the difference spectrum. There is also a z -polarized bleach of the pre-edge peak at 7115.5 eV and a new peak that grows in at 7113 eV. The signal-to-noise is too poor to determine the polarization of the new peak with certainty.

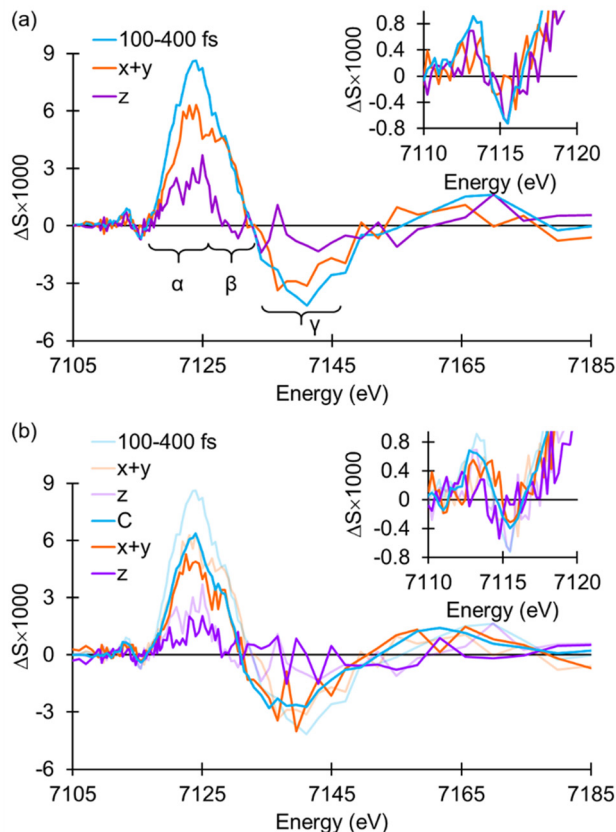


Figure 7. Difference spectra for the excited states **B** as approximated by the average from 100-400 fs and **C** as obtained from the 1.6 ps decay. (a) Difference spectrum characteristic of the excited state **B** with the pre-edge region enlarged in the inset. The isotropic signal is blue, the $x+y$ -polarized contribution is orange, and the z -polarized contribution is purple. The three spectral regions designated α , β , and γ refer to features discussed below. (b) Comparison of the difference spectra for states **B** and **C**. Equivalent spectra for **B** and **C** are shown in the same colors but with different intensities.

To characterize the subsequent dynamics, the pre-edge data were modeled by constraining the time constants to the values obtained from the XES measurements and the amplitudes were allowed to vary. The resulting pre-edge spectra, shown in Figures 7(b) and 8, make it clear that the

distinction between **B** and **C** is more significant for XAS than for XES. The dominant feature in the pre-edge region appears to involve evolution from a red-shift of a *z*-polarized transition to a red-shift of an *x+y*-polarized transition.

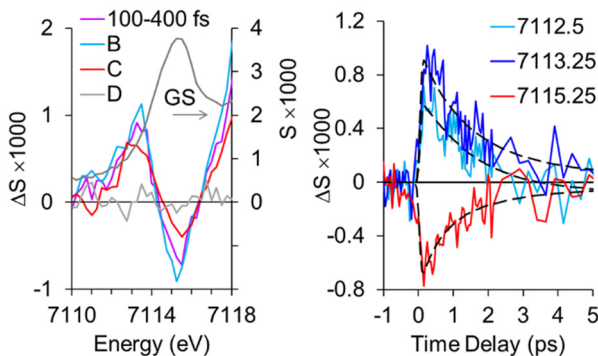


Figure 8. Left: Evolution associated difference spectra in the pre-edge region for states **B**, **C**, and **D** compared with the spectrum averaged from 100 fs to 400 fs.

Right: Time traces with fits at the indicated energies.

ANALYSIS AND DISCUSSION

Global analysis of the Fe K β emission resulted in two fast decay components ($\tau_A = 0.5 \pm 0.1$ ps and $\tau_B = 1.6 \pm 0.2$ ps) in reasonable agreement with prior optical TA measurements.⁹ In the OTA data, an additional fast component <100 fs was also indicated, but analysis was complicated by overlapping coherent signals at early time. Formation of the initial excited state, **A**, is not resolved in the XES and XANES measurements, and is only observed as a delayed rise in the fsXUV measurements.¹⁴ Formation of **A** is observed in the XSS where the initial excitation is accompanied by a loss of carbon-carbon pairs at a distance between 4 to 5 Å, which shift to larger distances (Figure S6). These carbon-carbon pairs are on opposite sides of the porphyrin ring, indicating a ring expansion. The initial positive and negative features quickly shift to shorter distances, suggesting the porphyrin ring contracts to a slightly less expanded state after the initial

excitation. This contraction occurs with a time constant of 80 fs. This initial expansion is consistent with the formation of the $\pi\pi^*$ state, which quickly decays to State **B** measured in the XES and XAS.

Based on the OTA data, it was hypothesized that the < 100 fs component represented internal conversion within the $\pi\pi^*$ manifold, followed by internal conversion to a LMCT πd_π state on a ca. 0.4 to 0.6 ps time scale. However, the current data shows that the difference spectra corresponding to **B** and **C** are similar in XES. Similarly, these components were unresolved in Fe $M_{2,3}$ -edge fsXUV measurements, where a single 1.13 ± 0.04 ps decay was measured.¹⁴ The similarity of **B** and **C** from the X-ray perspectives is not consistent with the transition **B**→**C** involving reduction of the Fe. Rather, the ligand-to-metal charge transfer must occur within 100 fs, consistent with the 80 fs component observed in the XSS and 20 fs rise observed in the fsXUV measurements.¹⁴ The change in shape between **B** and **C** represents relaxation within the LMCT manifold. Using Fe K-edge XAS, XES and XSS, we can better characterize states **B** and **C** and explore the assignment of state **D**.

Estimated Excited State Spectra

Excited state (ES) spectra can be used to compare spectral features of transient species to the spectrum of the ground state species. ES spectra are calculated using the following equation:

$$S_{ES} = (\Delta S + S_{GS} \cdot EF)/EF \quad (6)$$

where ΔS is the difference signal (Laser On – Laser Off), S_{GS} is the Laser Off spectrum, and EF is the excitation fraction. XAS ES spectra can be used to determine the minimum EF because the absorbance signal cannot be negative. For an $EF \leq 0.21$ the pre-edge absorption spectrum at 150 fs would be negative, setting the lower limit (Figure 9). We note that this analysis makes no assumptions about the strength of the excited-state absorption spectrum (for example if the

transition dipole matrix elements are higher or lower in the excited state).

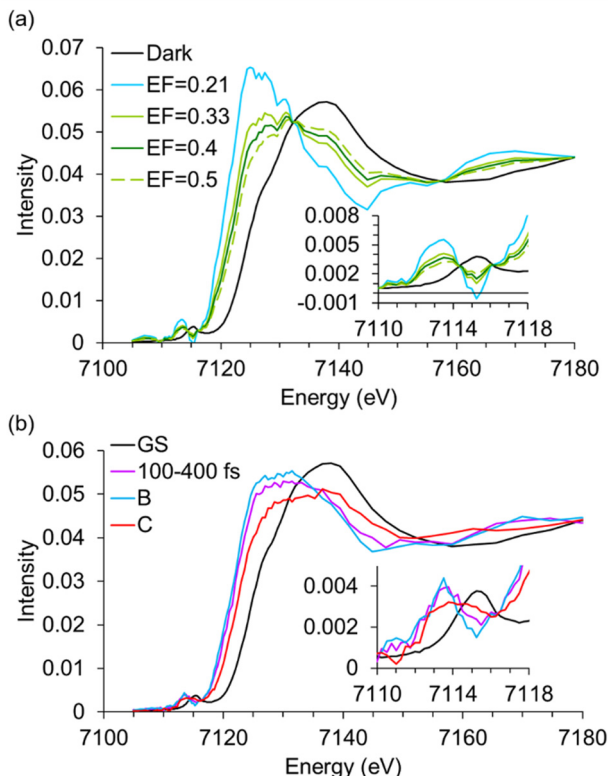


Figure 9. (a) Reconstructed excited state spectrum at a time delay of 150 fs as a function of excitation fraction. The data at 150 fs is used because the pre-edge bleach is a maximum at this time delay. The inset shows an expansion of the pre-edge region. (b) Estimated excited state spectra for states **B** and **C** from global analysis compared with the spectrum using the difference spectra averaged from 100 fs to 400 fs. Calculated using EF=0.4.

The XAS data has reasonable polarization discrimination, as shown for example by the fact that the signal at ~ 7130 eV (region β) is nearly completely $x+y$ polarized (Figures 7 and S9). As the excitation fraction increases, the polarization discrimination will decrease. As a limiting case, when EF=1, all molecules in the probe volume are excited, so there is no selective excitation of those aligned with the pump polarization. Our previous work identified a practical limit of EF=0.5

for observation of polarized spectra within the typical signal-to-noise of an transient X-ray experiment, suggesting that in the present work EF cannot be greater than 0.5 and is likely lower.³³ For $0.21 \leq \text{EF} \leq 0.3$ the edge develops a peak that cannot be modeled by any reasonable molecular structure. With this in mind, the best estimate of the excited state fraction in these measurements is ~ 0.4 ($-0.07, +0.1$), as illustrated in Figure 9(a). Since XAS and XES data were collected in similar conditions, this estimate applies to both datasets.

Fe K β XES Permits Assignment of States **B** and **C** to LMCT states

The XES spectra (Figure 3) demonstrate that the population remains in the excited state manifold for both states **B** and **C**. While there are subtle changes in the difference spectrum, the overall amplitude is unchanged. The change in the K β XES can be used to estimate the spin density at the Fe atom for the excited states.³⁴ In order to estimate the spin state for states **B** and **C**, estimated excited state XES spectra are constructed from the species associated difference spectra (Figure 3) assuming EF = 0.40 (Figure S10). The change in spin, Δ_{spin} , in the excited electronic states is estimated using the linear correlation plot of nominal spin versus the first moment of the Fe K $\beta_{1,3}$ from Lafuerza et al. (Figure S11).³⁴ The first moment (M_1) is defined as

$$M_1 = \frac{\int_{E_1}^{E_2} E \cdot I(E) dE}{\int_{E_1}^{E_2} I(E) dE} = \frac{\sum_j (E_j I_j)}{\sum_j I_j} \quad (7)$$

where E is energy and I is intensity of emission. For this calculation, the limits of integration are set to the energies giving the half-maximum intensity. Prior to calculating M_1 , we aligned our XES data to earlier work (compensating for differences in spectrometer calibration) using the first moment of the entire spectrum. This so-called “center of gravity” has been shown to vary by less than 0.4 eV across various oxidation states, spin states, and chemical environments.³⁴

The change in the first moment relative to the ground state (ΔM_1) is -0.32 eV for **B** and

−0.25 eV for **C**. Using the slope of the correlation in Figure S11, these values predict a reduction of the spin in the excited state, $\Delta spin = spin_{ES} - spin_{GS} = -0.37$ (**B**) and -0.29 (**C**). If Fe^{3+} ($S=5/2$) was fully reduced to high-spin Fe^{2+} ($S=2$), we would expect $\Delta spin = -0.5$. Given the uncertainty in this analysis and the potential complication of covalency diluting the spin on the iron atom,³⁵ the experimental $\Delta spin$ is consistent with the formation of an LMCT state within 100 fs followed by electronic and structural relaxation of this state within the LMCT manifold.

Calculations of the Ground State X-ray Absorption Spectrum

Simulations can be used to help interpret experimental data. We used FDMNES to model the XANES region and TD-DFT calculations in ORCA to model the pre-edge region. As the molecular structure for the ground state we chose a structure based on a room-temperature crystal structure for FeTPPCl.³⁶ The calculated spectra are compared with the ground state XAS spectrum in Figure 10. The calculations agree reasonably well with the experiment. The FDMNES spectrum overestimates the intensity of the low energy shoulder in the edge (7126 eV). However, this appears to be a systematic feature that we found in tests of over 30 different FeTPPCl structures. Fortunately, (see below) this appears to affect the ground and excited states equally, and thus does not interfere with our interpretation of the difference spectra.

FDMNES simulations for molecules are complicated by occasional non-physically large intensities below the edge. This is particularly serious for FeTPPCl, probably because FDMNES does not do a good job of modeling the empty space below the Fe atom. The issue was alleviated using two strategies. These effects depend on the exact energies in the calculation and the peaks generally disappear if the energy grid is shifted by 0.1 eV (far less than the intrinsic width of any real transition). The spurious points can also be suppressed by placing a solvent molecule below the iron atom. In our FDMNES simulations, a single toluene molecule was added to the structure

3.87 Å below the iron with an orientation similar to that found in crystal structures of Iron(III)TPP with benzene or toluene.³⁷ We did not attempt more extensive solvation. Placing a toluene at this distance suppressed most spurious peaks, but did not significantly influence the calculated spectrum (see Figure S14). A toluene molecule with an Fe-C distance < 3 Å does influence the spectrum significantly.

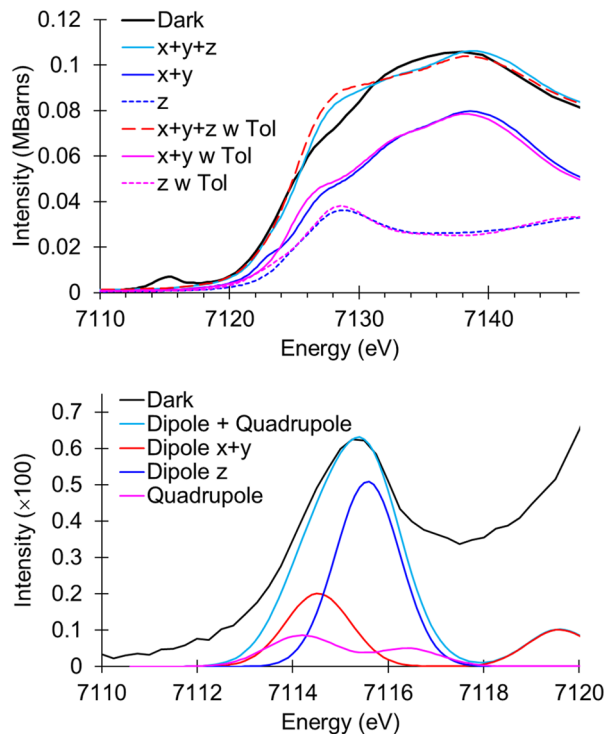


Figure 10. Top: XAS dark spectrum compared to FDMNES simulations using the crystal structure with and without a toluene 3.87 Å below the iron atom. Bottom: a TD-DFT calculation of the pre-edge transitions for the structure without toluene. The dipole allowed contribution is split into $x+y$ - and z -polarized contributions. The quadrupole allowed contribution is also plotted.

The TD-DFT calculations show that the main contributor to the intensity of the pre-edge peak is a z -polarized, $1s \rightarrow \sigma^*(\text{Fe } d_{z^2}/\text{Cl } p_z)$ transition that acquires intensity through Fe p_z/d_{z^2} mixing.

Weaker in-plane polarized dipole-allowed transitions and quadrupole-allowed transitions are also present. Experimentally, we find that 400 nm excitation results in a 2 eV shift of the pre-edge transition to lower energy. The polarization resolved difference spectra in Figure 7 suggest that state **B** is characterized by a red-shift in a *z*-polarized transition while state **C** is characterized by a similar shift in an *x+y*-polarized transition. A shift of the 1s→3d transition to lower energy would be consistent with reduction of the metal from Fe(III) to Fe(II).³⁸

Structural Characterization of State B

In order to characterize the ultrafast structural dynamics of FeTPPCl we need to calculate XANES spectra for both ground and excited states. In the absence of a quantum-chemical prediction for the FeTPPCl excited state structure, we have used the FeTPPCl normal modes as a way to generate chemically plausible structural perturbations. To narrow down the candidates, we turn to resonance Raman spectroscopy and its sensitivity to displacement along normal modes. The resonance Raman spectrum for FeTPPCl in toluene following excitation at 413 nm¹⁰ shows 4 dominant totally symmetric vibrations, ν_8 at 392 cm⁻¹, ν_1 at 1234 cm⁻¹, ν_4 at 1363 cm⁻¹, and ν_2 at 1556 cm⁻¹, (Figures S12 and S13, mode numbering from ref ³⁹). The three high frequency modes involve in-plane C=C stretching of the porphyrin ring with no involvement of out-of-plane Fe-Cl motions: ν_2 is a porphyrin mode with no significant involvement of Fe-N bonds while ν_1 and ν_4 involve Fe-N breathing motions coupled with motion of the porphyrin ring. The lowest frequency mode of this set, ν_8 , involves coupled ring breathing and Fe-Cl stretching motions. Given the strong resonance enhancement of this mode and the observation of the overtone at 778 cm⁻¹, indicating significant displacement upon excitation, this mode makes a good starting point for models of the initial excited state dynamics. When the ground state structure is distorted along this normal mode the FDMNES-predicted XANES reproduces the shift that we see in the early time XAS spectrum

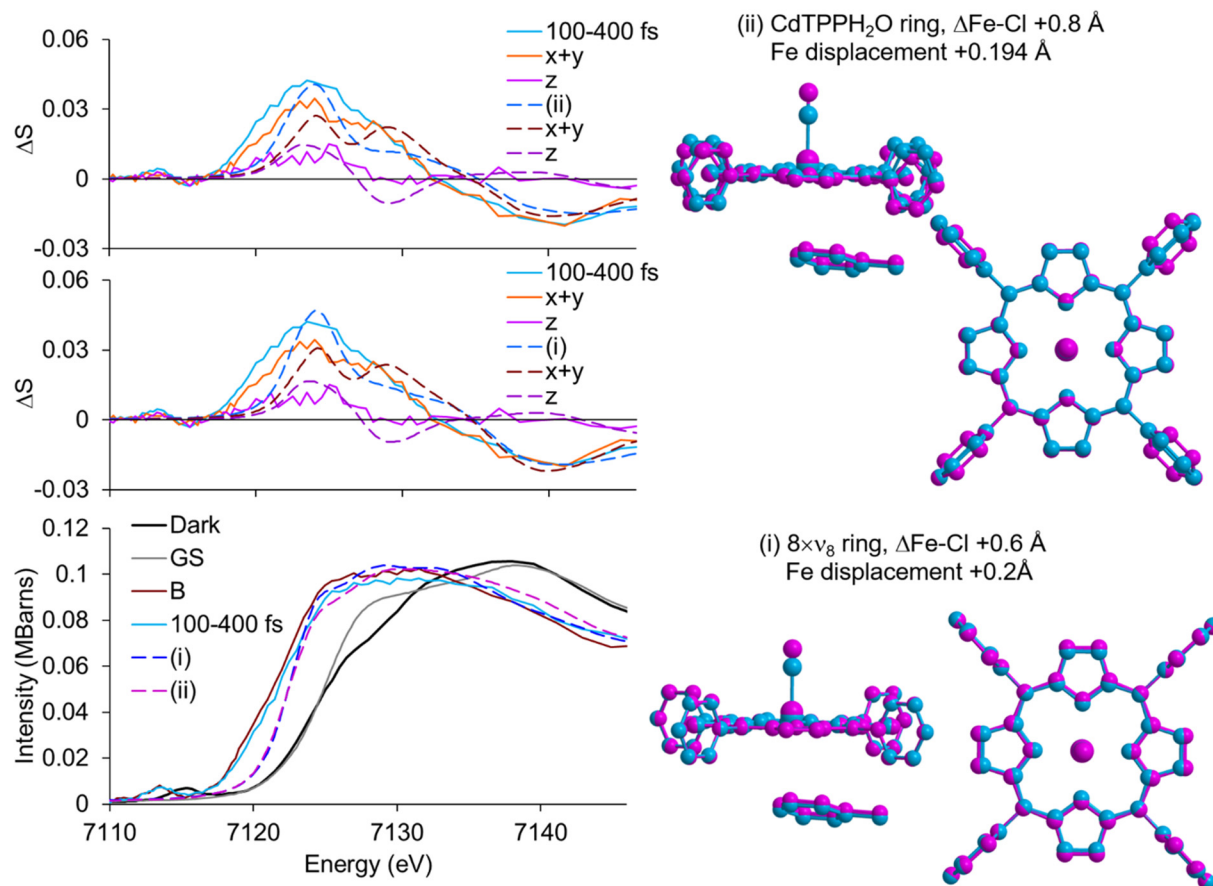
(Figure S14). However, the required amplitude is large (corresponding to a factor of ~ 8 times the Cartesian displacement coordinates). The structural distortion introduced by this mode includes three contributions: (1) expansion of the ring, (2) displacement of the iron into the ring, and (3) expansion of the Fe-Cl bond. It is not obvious that all three of these motions are representative of the actual excited state distortion. This led us to separate the three contributions in simulations and to explore other ways to model the ring expansion.

The red-shift of the $x+y$ contribution to the XANES spectrum, reflected in the region labeled γ in the difference spectrum in Figure 7, is characteristic of a significant ring expansion in the excited state. An expansion along the ring coordinates of v_8 provides one method for producing this expansion. Using the crystal structure for TPP with a larger metal ion provides another method. The crystal structure of a five coordinate Cd(II) bound to tetraphenylporphyrin provides an example of a physically realized ring distortion comparable to that obtained using v_8 as summarized in Table 1.⁴⁰ This structure increases the ring diameter and moves the metal atom significantly further out of the porphyrin plane. XANES spectra and polarization resolved difference spectra were calculated both for the ring distortion resulting from v_8 and for the ring coordinates found in the crystal structure of CdTPPH₂O, while keeping the Fe-Cl distance and Fe displacement at the values found for ground-state FeTPPCl (Figure S15). In the absence of other contributions (i.e., with the Fe-Cl and Fe-displacement held constant), an expansion equivalent to $8 \times v_8$ provides the best agreement with the experimental data.

Table 1. Comparison of structural details for the ground state and expanded structures.

	M Displacement	Fe-Cl Bond	Avg. M-N Bond	Avg. N-N diagonal
GS FeTPPCl	+0.37(2) Å	2.19(0) Å	2.04(9) Å	4.03(0) Å
CdTPPH ₂ O	+0.76(0) Å		2.22(9) Å	4.19(7) Å
8×v ₈	-0.22(6) Å	3.80(1) Å	2.19(6) Å	4.36(8) Å

We next explored the effect of the displacement of the iron relative to the ring, and the expansion of the Fe-Cl bond on the calculated spectrum. XANES spectra and polarization resolved difference spectra were calculated for both the ring distortion resulting from 8×v₈ and the ring coordinates in CdTPPH₂O. The trends as a function of Fe-Cl bond length for a range of displacements are summarized in Figures S16 and S18. The trends as a function of Fe displacement for two Fe-Cl bond lengths are plotted in Figures S17 and S19. From these simulations we conclude that the observed spectra are best modeled with a significant expansion of the porphyrin ring, approximately equivalent to that produced using 8×v₈, and a significant expansion of the Fe-Cl bond, ≥ 0.5 Å. The calculated spectrum is less sensitive to the displacement of the Fe from the plane of the porphyrin ring although the best agreement is found with an increase in the displacement of the Fe from the porphyrin ring. Two calculations exhibiting reasonable agreement with the experimental data for state **B** are plotted in Figure 11.



The structural changes in **B** and the z-polarized pre-edge bleach are consistent with population of an LMCT state with the electron moving from a porphyrin π^* orbital to a σ^* Fe d_{z^2} /Cl p_z orbital (Figure 12). The metal-Cl antibonding character would explain the increase in Fe-Cl distance. This orbital is also anti-bonding with respect to the ring, and this, together with the increase in ionic radius ($\text{Fe}^{2+} > \text{Fe}^{3+}$) would account for the expansion of the ring.

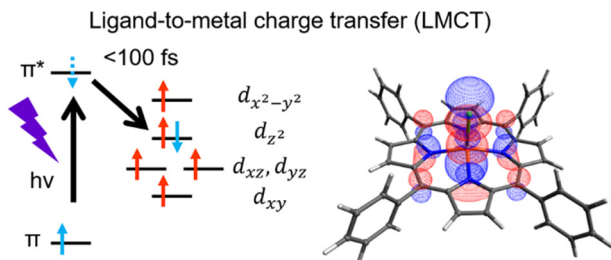


Figure 12. Schematic of the electron configuration for the initial LMCT state with σ^* Fe d_{z^2} /Cl p_z orbital calculated for the ground state structure.

Structural Characterization of Excited State C

The changes in the pre-edge absorption are consistent with electronic relaxation in the LMCT manifold resulting in the reduction in the z-polarized bleaching signal and a red-shift in the x+y-polarized transitions suggesting electronic relaxation within the LMCT manifold of states. As the electron moves from the σ^* (Fe d_{z^2} /Cl p_z) orbital into a π^* (Fe d_{xz} /Cl p_x , Fe d_{yz} /Cl p_y) orbital, the anti-bonding character of the Fe-Cl bond will decrease and the bond length is expected to rebound from the large expansion observed in the **B** state. The **C** state is compared with simulations in Figure 13. The data, especially the z-polarized contribution, is consistent with a Fe-Cl bond length of 2.39 Å, 0.2 Å longer than the ground state, but much shorter than the apparent bond length in the **B** state. The ring distortion is not fully captured by a symmetric expansion along ν_8 , but a more detailed exploration of potential distortions is not warranted at this time and requires a systematic

method to explore the available parameter space.

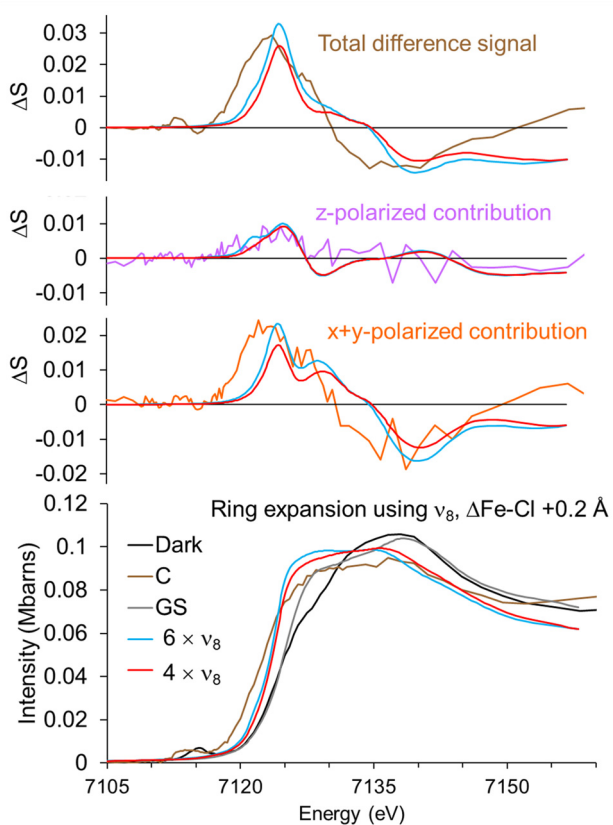


Figure 13. Comparison of calculated spectra to experimental spectra for the ground state and excited state **C** for two different estimated ring expansions. Polarized difference signals are also shown for each simulation.

Structural Information from XSS Complements the XANES

The negative feature of the isotropic XSS data centered around 1.6 Å is near the Fe-Cl (2.2 Å) bond distance in the crystal structure of the ground state. The contributions of each atom pair in the ground state and excited state structures of FeTPPCl are shown in Figure S6. The bleach of this distance, and the growth of slightly larger distance around 3.0 Å is consistent with the stretching of the Fe-Cl bond due to the formation of an LMCT state with the transferred electron in a σ^* Fe d_{z^2} /Cl p_z orbital, as well as the stretching of the Fe-N and N-N distances caused by the

ring expansion. The bleach decays with a time constant of 0.4 ps as the Fe-Cl bond shrinks and the ring contracts, which is consistent with the decay of State **B** found in the XES and XAS analysis. The bleach of distances around 5.4 Å and growth around 7.1 Å is consistent with a rapid, large expansion of the porphyrin ring.

Assignment of State D

It remains to assign the longer-lived state **D**. Based on optical TA measurements this was assigned to a metal centered excited state,^{9,10} while Fe M_{2,3}-edge measurements suggested that **D** is a vibrationally hot ground electronic ground state.¹⁴ State **D** has an excited state optical spectrum that is similar to the GS spectrum but slightly red-shifted. A red-shift would be consistent with a metal centered excited state since this would increase in the energy of the HOMO. Vibrational cooling manifests itself in UV-visible TA as difference signals that become narrower over time as the distribution of thermally populated states decreases. This phenomenon results in zero-crossings in the difference spectrum that shift as a function of time. In contrast, a transition between two species will result in a difference spectrum where the zero-crossing remains constant while the intensity of the difference spectrum decreases. Based on this, **D** is not consistent with a vibrationally hot ground state. At the same time, Fe M_{2,3}-edge measurements on an FeTPPCl thin film showed that the state analogous to **D** had a difference signal that was similar to, but much smaller than, that seen for the LMCT state. Since a metal-centered state would be expected to have a large signal, but with a different phase than the LMCT state, these data rule out a metal-centered state for **D**. Similarly, the current data showing that **D** has a much smaller XES signal than **C** confirms that **D** cannot be a metal centered excited state, since this would show a larger, not smaller XES signal.

A hint of a solution to this apparent contradiction comes from longer-time measurements.

Optical TA on FeTPPCl thin films show two long-lived components (23.2 ps and 27 ns) that appear to follow the decay of State **D** observed in the fsXUV spectra. Similarly, power-dependent resonance Raman measurements at 77K and UV-visible TA measurement at 88K on FeTPPCl in a 1:1 mixture of dichloromethane and toluene both showed evidence for a long-lived excited state.¹⁰ Optical TA indicated a lifetime $\gg 500$ ps and resonance Raman using 413 nm excitation showed formation of a photostationary mixture of ground state FeTPPCl and photoproducts produced by sequential two photon absorption. Based on its power dependence, the sequential two photo absorption required an excited state with a lifetime longer than 1 ns.¹⁰ Although they were interpreted differently, both measurements provided support for the idea that some fraction of photoexcited FeTPPCl forms a long-lived excited state.

A resolution that explains both the earlier data and the present data is to consider branching from state **C** to give *both* an excited electronic state **D** within the LMCT manifold and repopulation of the ground state. Although such a model was not considered in either the optical TA or the XUV studies of FeTPPCl, it was proposed by Consani et al. for the ferric heme in met-myoglobin.⁴¹

Limits on the Quantum Yield for Formation of an Electronic Excited State D

Analysis of the $K\beta_{1,3}$ M_1 values suggests that the quantum yield for formation of **D** (ϕ) between ~ 0.1 and ~ 0.4 could be consistent with formation of MC or LMCT excited states, respectively (Table S1). If $\phi = 0.12$, the apparent Δ_{spin} relative to the GS would be ~ 1.0 , consistent with formation of a quartet MC excited state. The reconstructed excited state $K\beta$ spectra are plotted in Figure S10 as a function of quantum yield. To explore the sensitivity of the XANES to the nature of the excited state, the molecular structure of FeTPPCl was optimized for the lowest sextet and quartet spin states and FDMNES was used to simulate spectra of these structures. The resulting structures, and thus spectra, are very similar to each other and to the observed ground

state (see Figure 14). If **D** was formed with a quantum yield as low as $\phi = 0.12$, the XANES spectrum of this state would shift to much lower energy and would be inconsistent with the expected XANES for a MC state. Thus, the XANES provides additional evidence against a MC state for **D**, in agreement with XUV and XES measurements.

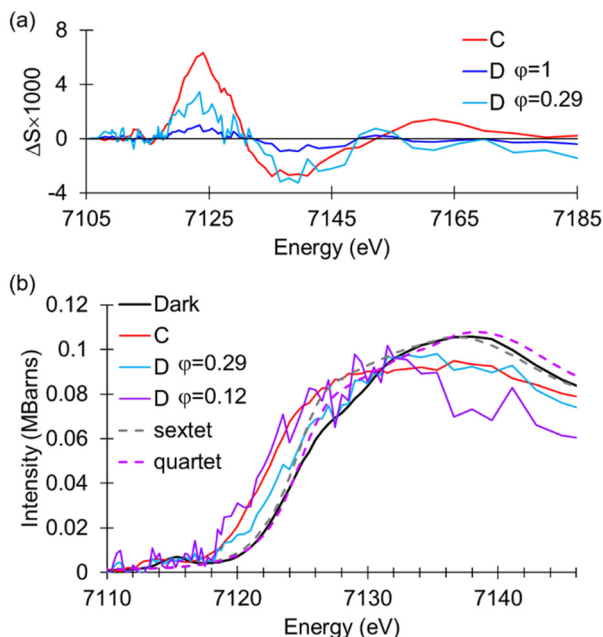


Figure 14. (a) Comparison of the isotropic difference spectra for the **C** and **D** states assuming a quantum yield of 1 for the **C** state and 1 or 0.29 for the **D** state. (b) FDMNES spectra of DFT-optimized FeTPPCl as a sextet ($S=5/2$) and as a quartet ($S=3/2$) compared to GS XAS spectrum and the estimated ES spectra of **D** for the indicated quantum yields. The estimated spectrum for $\phi=1$ would be similar to the ground state and is omitted for clarity (see Figure S20).

In contrast, if **D** is an excited state, but within the LMCT manifold, not the MC manifold, Δ_{spin} should be similar to that seen for **B** and **C**. A quantum yield $\phi = 0.42$ would give the same Δ_{spin} for **D** as was found for **B**. In this scenario, the largest expected Δ_{spin} would be 0.5, assuming no

delocalization of spin onto the porphyrin; this would correspond to $\phi \approx 0.3$. For ϕ_D values in this range, the XANES spectrum for **D** shows evidence for a structural distortion relative to the ground-state, but a distortion that is smaller than that seen in **C** (see Figure 14). It is noteworthy that if $\phi \approx 0.3$, the transient signal corresponding to **D** at the Fe $M_{2,3}$ -edge¹⁴ would have approximately the same intensity as the signal assigned to state **B** (corresponding to an average of states **B** and **C** as described here), and would thus be consistent with the interpretation that **D** represents a lower-energy, longer-lived state on the LMCT manifold.

CONCLUSIONS

Once one accounts for the difference in noise level and in instrument response function of the different experiments, it becomes apparent that all of the ultrafast measurements of FeTPPCl are consistent with a model in which the initially excited $\pi\pi^*$ state **A** relaxes very quickly (<100 fs) to form a sequence of three excited states, with lifetimes of 0.4-0.6 ps (**B**), 1.4-2.3 ps (**C**), and 13-19 ps (**D**). All of the measurements originally agreed that **C** is best assigned as a LMCT state. **B**, which was not resolved in the fsXUV measurements and was originally interpreted as a $\pi\pi^*$ state in the optical TA, is now shown to be best described as a short-lived LMCT state (thus explaining its inability to be distinguished from **C** in the fsXUV studies). The XAS data is consistent with a model where the initial charge transfer is into a σ^* (Fe $d_{z^2}/Cl p_z$) orbital forming state **B** followed by relaxation into a π^* (Fe $d_{xz}/Cl p_x$, Fe $d_{yz}/Cl p_y$) orbital forming state **C**. While **C** has been proposed to decay either to a vibrationally hot ground state or to a metal centered state, neither of these proposals is consistent with the present data. However, a model in which **C** branches between ~ 70 (+15, -10%) GS and ~ 30 (-15, +10%) formation of a third LMCT state would explain all of the available spectroscopy and would in addition explain the observation that

at low-temperature, a long-lived FeTPPCL excited state can absorb a second photon, leading to formation of an FeTPPCL-toluene exciplex.¹⁰ The decay pathway that has been revealed by this combined spectroscopic study is illustrated schematically in Figure 15. Only through the application of all of these methods (UV-visible, M_{2,3}-edge XUV, K-edge pre-edge, K-edge XANES, XSS, and resonance Raman spectroscopy) is it possible to fully define the excited state evolution of this molecule. As a final note, one initial concern about the M-edge experiments was the sample environment – solvation dynamics can affect intramolecular electron transfer rates⁴² and it was not obvious that the dynamics of FeTPPCL in thin films were relevant to those in solution. In the present case at least, it is possible to reconcile all of the experimental data without invoking differences in solvation environments.

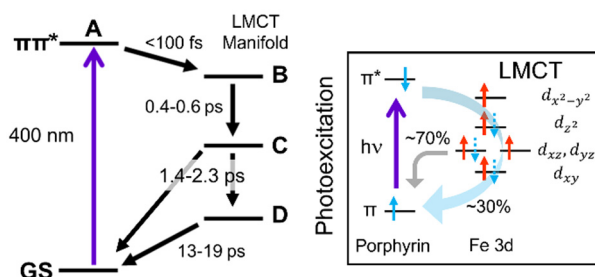


Figure 15. Schematic diagram of the relaxation pathway following excitation of FeTPPCL in the Soret band. Initial excitation populates a $\pi\pi^*$ state (A). This state decays on a time scale <100 fs to a LMCT state, first the $\pi\sigma^*$ (Fe $d_{z^2}/\text{Cl } p_z$) (B) followed by $\pi\pi^*$ (Fe $d_{xz}/\text{Cl } p_x$, Fe $d_{yz}/\text{Cl } p_y$) (C). Population in this LMCT state branches between ground state recovery, 70% (+15, -10%) and formation of a third LMCT state (D), likely a π Fe d_{xy} state, 30% (+10, -15%).

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DATA AVAILABILITY STATEMENT

The processed data used to produce the figures shown in the manuscript and Supporting Information are available from DeepBlue (DOI: 10.7302/pzk0-ff86).

SUPPORTING INFORMATION

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/to be determined>.

Details of the data analysis, additional data figures, FDMNES simulations as a function of structure, representative input files for calculations. (PDF)

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