

Femtosecond extreme ultraviolet spectroscopy of an iridium photocatalyst reveals oxidation state and ligand field specific dynamics.

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ABSTRACT: Femtosecond X-ray absorption spectroscopy at the Ir O_{3-} -edge and $N_{6,7}$ -edges is performed on the photocatalyst iridium(III) tris(2-phenylpyridine), Ir(III)(ppy)₃ using a tabletop high-harmonic source. Extreme ultraviolet (XUV) absorption between 44 eV and 72 eV measures transitions from the Ir $5p_{3/2}$ and $4f_{5/2,7/2}$ core to $5d$ valence orbitals, and the position of these spectral features is shown to be sensitive to the oxidation state and ligand field of the metal center. Upon excitation of the singlet metal-to-ligand charge transfer (¹MLCT) band at 400 nm, a shift in the spectra due to the formation of the Ir(IV) center is observed, as is the creation of a new spectral feature corresponding to transitions into the t_{2g} hole. Vibrational cooling of the MLCT state on the 3 ps and 16 ps timescales is measured as changes in the intensity of the transient features. This work establishes XUV spectroscopy as a useful tool for measuring the electronic structure of 3rd row transition metal photosensitizers and catalysts at ultrafast timescales.

Introduction

Table-top extreme ultraviolet (XUV) spectroscopy in the 40-100 eV energy range has been shown to be a powerful technique for probing the ultrafast photophysics of 1st row transition metal coordination complexes.¹⁻¹⁰ The $M_{2,3}$ -edge, corresponding to $3p \rightarrow 3d$ transitions, is sensitive to oxidation state, ligand field, and spin-state, providing direct insight into key changes at the metal center.⁹ This technique has been used to examine excited state dynamics at various 1st row transition metal centers, such as nickel,^{2,4,6,11} iron,^{2,7,8,12-14} & cobalt,^{4,5,15,16} for photocatalysts and other molecular systems.

Far less attention has been paid to the potential for XUV spectroscopy of 3rd-row metals. This energy range contains the $O_{2,3-}$ and $N_{6,7}$ -edges of 5d metals: the $O_{2,3}$ -edges corresponds to $5p_{1/2,3/2}$ to valence orbital transitions, while the $N_{6,7}$ -edges corresponds to $4f_{5/2,7/2}$ to valence orbital transitions. Prior work has generally been limited to metallic samples or atomic vapors of 3rd row transition metals in the XUV region. Sonntag, Kunz, and coworkers first performed systematic acquisition of the 40-200 eV region for metallic 2nd and 3rd row transition metals in the 1960s, observing the suite of edges that included proposed $O_{2,3-}$ and $N_{6,7}$ -edges between 40-120 eV for tungsten through gold.¹⁷ Later studies using the dual laser-produced plasma technique more closely examined plasmonic vapors of platinum and tungsten identifying specific transitions and interactions observed for the $O_{2,3}$ and $N_{6,7}$ -edges and examining correlation and relativistic effects.^{18,19} More recent work has examined the photoabsorption spectra of gold,²⁰ iridium,²¹ and other 3rd row metals²² in the XUV region towards calculating and fitting the transitions, finding the edges were dominated by a great number of lines from $4f$ -to- $[5d,6s]$ and $5p$ -to- $[5d,6s]$ transitions. Leone and coworkers recently used transient XUV to examine carrier dynamics in WS_2 at the tungsten O_{3-} and $N_{6,7}$ -edges.²³ However, to our knowledge the spectroscopy of molecular 5d coordination complexes in this energy region is completely unexplored.

In this work, we develop an understanding of excited state dynamics at the O_{3-} and $N_{6,7}$ -edges of 3rd row transition metal coordination complexes, specifically with iridium(III) centers, using XUV spectroscopy. Cyclometalated iridium(III) complexes are ubiquitous photocatalysts and sensitizers, with wide use in photoredox chemistry.²⁴⁻³² They are also common dopants in organic light-emitting diodes (OLEDs).³³⁻³⁵ These complexes generally have strong molar absorptivity ($\sim 10,000 \text{ M}^{-1}\text{cm}^{-1}$) in the UV-Vis spectral region, allowing for excitation at accessible single wavelengths or ambient light sources.^{26,33,34,36-42} Common ligand scaffolds, such as bipyridine (bpy) and 2-phenylpyridine (ppy), are modifiable through ligand exchange or substitutions at select positions, allowing for easy tuning of the charge transfer bands and dynamics.^{29,30,37,41} Their excited state redox potentials are well-suited for transferring electrons in a variety of transformations.^{28,41,43-45} Finally, these triplet states are generally long-lived (ns- μ s) due to the forbidden transition to return to the singlet ground state, allowing for sufficient time to transfer the energy into the desired process.⁴⁵⁻⁴⁷ The strong spin-orbit couplings (SOC) of iridium facilitates efficient intersystem crossing (ISC) between singlet and triplet states, which give high quantum emission yields from the triplet state.

In this work, we performed transient O_{3-} & $N_{6,7}$ -edge XANES on Ir(III)(ppy)₃, showing that metal-based photodynamics can be tracked at this edge akin to synchrotron-based transient $L_{2,3}$ -edge XANES. The ³MLCT excited state is clearly identified by the appearance of a new core-to-valence $5d$ t_{2g} transition and a blue shift in the core-to-valence $5d$ e_g transition. This result provides a foundation for future studies examining the photochemistry of late 3rd row coordination complexes using XUV spectroscopy.

Methods

Iridium(III) tris(2-phenylpyridine) (Ir(III)(ppy)₃) and sodium hexachloroiridate(III) ($Na_3Ir(III)Cl_6$) were purchased from Sigma Aldrich. Thin film samples were prepared through sublimation using a house-build thermal evaporator or dropcast onto 50 or 100 nm Si_3N_4 substrate; specific details are given below. Static UV-Vis spectra were

acquired to confirm sample identity and to check for degradation pre- and post-experiments. Ir(III)(ppy)₃ samples (~114 nm thickness) were deposited onto 50 and 100 nm Si₃N₄ membranes using thermal evaporation (or on glass for the UV/Visible spectrum) and stored in the dark underneath dinitrogen atmosphere in a drybox. Na₃Ir(III)Cl₆ samples were prepared by taking a concentrated, filtered solution of the target complex in dimethylformamide (DMF) and drop-casting onto 100 nm Si₃N₄ membranes.

The tabletop XUV probe was generated through the process of high-harmonic generation (HHG) as described in prior work.¹³ In brief, the 1 kHz, 35 fs, 800 nm pulse of a NIR driving laser is focused into a semi-infinite gas cell containing approximately 100 Torr of neon or 50 Torr of argon gas to generate approximately 20 fs XUV pulses in the energy range from 55–80 eV or 35–60 eV, respectively. The residual NIR pulses were filtered using a 100 nm (Ne) or 200 nm (Ar) thick Al foil and creating a flux of ~10⁵ photons per pulse per 0.1 eV at 64.7 eV (Ne) or 53.5 (Ar) at the sample position. The spectrometer resolution is measured using the absorption lines of Kr⁺ and Xe⁺ and averaged ~0.4 eV (Ne) and 0.33 eV (Ar) FWHM for these experiments. A secondary output from the same laser source was sent through an α-BBO crystal to generate the 400 nm, ~50 fs pump pulse via second harmonic generation. Transient absorption of a thin film of α-Fe₂O₃ is used to determine time zero (t₀) and the instrument response function (IRF) of 90 fs FWHM for Ne conditions, while PbI₂ was used for Ar conditions to determine t₀ and the IRF of 123 fs FWHM. These IRF values are dominated by timing drift over the course of the experiment, and not by the duration of the individual pulses. The pump fluence of 1.7 mJ/cm² at 400 nm for Ne conditions corresponds to an average excitation fraction of 14% per iridium center, while 1.1 mJ/cm² at 400 nm for Ar conditions corresponds to an average excitation fraction of 9% per iridium center. To avoid sample damage during transient data collection, samples are raster scanned, gas cooled using N₂,⁴⁸ and regularly checked for damage by re-taking the ground-state XUV spectrum.

Results

Ground-State XUV Spectroscopy. The spectrum of the O₃- and N_{6,7}-edge XANES of Ir(III)(ppy)₃ is shown in Figure 1A. The O₃-edge appear as a broad feature with a peak at 54.1 eV. The N_{6,7}-edges appear at higher energy than the O₃-edge as narrower peaks at 64.4 (N₇) and 67.4 eV (N₆). The 3.0 eV split between N-edges arises from spin-orbit coupling (SOC) induced by the heavy metal center and is consistent with free ion XUV examples and observed 4f_{7/2}/4f_{5/2} binding energy in XPS.^{49,21} This split is consistent regardless of oxidation or ligand field as it derives from the SOC of the core hole.

Significant edge shifts occur in the O and N-edges of iridium as a function of the ligand field strength. In comparing Na₃Ir(III)Cl₆ with Ir(III)(ppy)₃, the N_{6,7}- and O₃-edges blueshift by approximately 2 eV when going from Ir(III)Cl₆³⁻ to Ir(III)(ppy)₃ (N_{6,7}-edges shown in Fig. 1B; O₃-edges in Fig. S2). This is attributed to the stronger ligand field of the latter complex. Cl⁻ is a weaker sigma donor

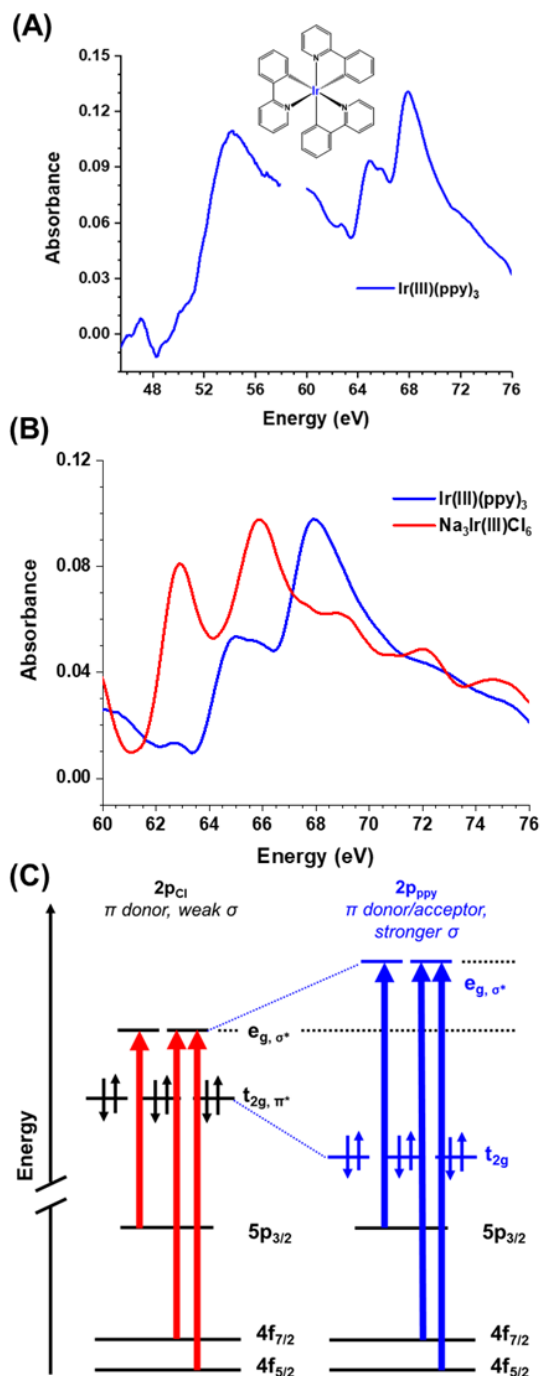


Figure 1 (A) Static O₃- and N_{6,7}-edge XANES of Ir(III)(ppy)₃, measured using Ar as an HHG medium from 45–58 eV and Ne from 60–66 eV. (B) N_{6,7}-edge XANES overlay of Ir(III)(ppy)₃ (blue) and Na₃Ir(III)Cl₆ (red). (C) Simplified octahedral orbital diagram of changes in the Ir(III) 5d-orbital manifold from chloride to 2-phenylpyridine (ppy) ligands.

compared to 2-phenylpyridine's N_{py} and C⁻; the ppy ligand will result in higher energies for the empty e_g d-orbitals compared to the chloride ligand and is consistent with the significant blue edge shift for both edges (Fig. 1C). Similar shifts based on ligand field strengths have also been noted at the L_{2,3}-edges for 3rd row metals; a recent example with platinum macrocyclic compounds showed that exchanging

weaker field ligands (porphyrin, chloride) for stronger field ligands (corrole, pyridine, alkyl) in octahedral Pt(IV) compounds resulted in a 0.4 eV blue shift of the Pt L₃-edge.⁵⁰ This shift was caused by the corresponding rise in the d-orbital manifold due to the strengthened ligand interactions. While the shift observed in this work between the iridium(III) species is larger (2 eV vs 0.4 eV), this can be attributed to the more dramatic ligand field strength difference of six chloride ligands versus three bidentate 2-phenylpyridine ligands. This shift shows that O₃- and N_{6,7}-edges can be used to track changes in ligand field on the metal center, both as a result of ligand substitution and after photoexcitation (as shown below).

Transient XUV Spectroscopy. Transient O₃-edge and N_{6,7}-edge XANES were used to investigate the excited-state dynamics of Ir(III)(ppy)₃ upon singlet metal-to-ligand charge transfer (¹MLCT) band excitation at 400 nm. Ir(III)(ppy)₃ serves as an excellent initial target for transient XUV spectroscopy due to its well-studied photochemistry,^{34,35,39,40,42,46,51-61} applicability as a dopant for OLEDs,^{33,35,62} and common use as a photosensitizer and catalyst in organic transformations.^{24-26,29} Examining the UV-Vis spectrum of Ir(III)(ppy)₃ (Fig. 2), three main bands are present: one below than 300 nm that corresponds to singlet π - π^* transitions from the 2-phenylpyridine ligand, a broad band centered at 375 nm that corresponds to a ¹MLCT (d- π^*) transition, and lower intensity triplet MLCT (³MLCT) bands clustered between 430-500 nm.^{39,40,46} Prior studies have found that for Ir(III)(ppy)₃, the lowest excited state is a triplet metal-to-ligand charge transfer (³MLCT) corresponding to electron transfer from occupied Ir 5d to unoccupied ppy- π^* orbitals, with an emission lifetime on the order of microseconds (μ s).^{40,46,56} Previous optical transient absorption (OTA) and photoluminescence (PL) decay studies have shown that after 400 nm excitation, the ¹MLCT state rapidly (≤ 70 fs) undergoes intersystem crossing (ISC) to the ³MLCT state manifold; this triplet state undergoes intramolecular vibrational relaxation (IVR) and vibrational cooling on the order of 200 fs to 5 ps, before slowly relaxing back down to the singlet ground state on the order of nano- to microseconds.^{33,39,40,46,47,51,55,56,63} Transient L_{2,3}-edge XANES of Ir(III)(ppy)₃ with ~ 100 ps time resolution has been performed in the 11.2-11.3 (L₃) and 12.8-13.0 (L₂) keV region at a synchrotron light source, revealing two key features: a lower energy absorption arising from the core electrons into the photoinduced 5d vacancy for the L₃-edge and a blue-shifted positive absorption corresponding to an oxidation state increase at the iridium center at both L₃- and L₂-edges.^{60,64} The authors assigned these features to the ³MLCT state and derived an excited state $10D_q$ of $\sim 6.45 \pm 0.20$ eV. However, this work primarily focused on this emitting triplet state rather than the early relaxation. Nanosecond transient L₃ XANES of [Ir(Chp)₂(ddtbbpy)]⁺, picosecond transient L₃ X-ray absorption of Ir(III)(ppy)₂(bpy)⁺, and femtosecond X-ray transient absorption spectroscopy of Ir(III)(ppy)₂(ppz) at a free-electron laser showed similar spectral features for the triplet MLCT states.⁶⁵⁻⁶⁷

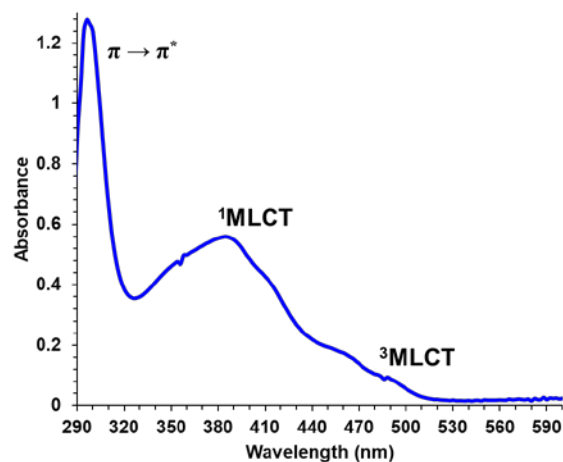


Figure 2 UV-Visible spectrum of a 114-nm thick film of Ir(III)(ppy)₃ on glass.

In the current work, transient absorption spectroscopy was performed using Ar as a HHG medium for the O₃-edge and Ne for the N_{6,7} edges. We performed transient O₃-edge XANES of Ir(III)(ppy)₃ using 400 nm excitation, with an excitation fraction of $\sim 9\%$. Time zero and the IRF of 123 fs for these experiments were independently measured by transient XANES of PbI₂ at the iodine N_{4,5}-edge. Figure 3A shows averaged spectral slices at select delay times from -250 fs to 100 ps overlaid on the static O₃-edge spectrum of Ir(III)(ppy)₃. Upon excitation, a positive feature centered at 48.3 eV appears, along with minor bleach features below 43 eV and weaker higher energy features between 50-57 eV. Within the first few hundred femtoseconds these features have reached their maxima and start to decay (Fig. S5, S7). By 10 ps, all these features have flattened out and are still present at 100 ps, the longest delay time probed.

Transient N_{6,7}-edge XANES spectra of Ir(III)(ppy)₃ are shown in Figure 3B, overlaid with the ground-state spectrum. Upon excitation, negative features appear at 64.5 and 67.5 eV along with a positive feature at 60.1 eV, with additional weak positive features centered at ~ 66 eV and 68-70 eV. Within the first few hundred femtoseconds these features have reached their maxima and start to decrease (Fig. S6, S8). By 10 ps, all these features have flattened and remain so through the later delay times (up to 50 ps).

Single-energy kinetic analysis at three key transient N_{6,7}-edge features (60.1 eV absorption, and 64.5 & 67.5 eV bleaches) were undertaken, and the traces are shown in Figure 3C (early delay times shown in Fig. S8). Due to low signal-to-noise for the approximately 66 and 69 eV absorptions, reliable kinetic analysis could not be completed. For the three features tracked, each could be fit as an exponential decay with a shelf that corresponds to the 1.5μ s⁴⁰ ³MLCT lifetime. The lifetimes of the exponential decay component are tabulated in Table 1. Single energy kinetic analysis of the positive feature from transient O₃-edge at 48.3 eV was also performed, and the trace is shown in Figure 3D (early delay times shown in Fig. S7). This was fitted to an exponential decay with a long-time shelf shown in Table 1.

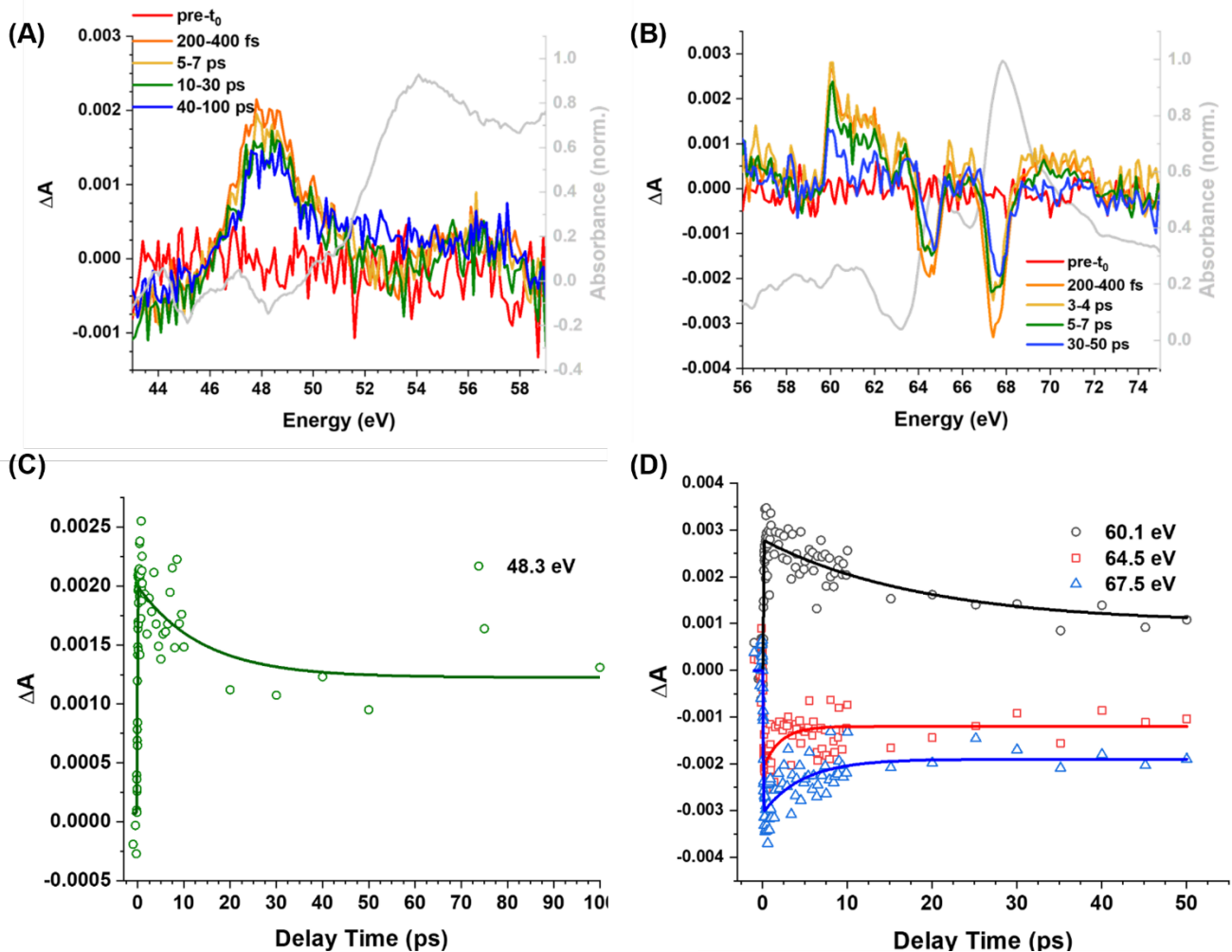


Figure 3 Transient O₃₋ (A) and N_{6,7}-edge (B) XANES spectra of Ir(III)(ppy)₃ at select averaged time delays with 400 nm excitation. The static ground state for the respective O₃₋ and N_{6,7}-edges are overlaid as the grey traces. Kinetic traces (circles) of transient O₃₋ and N_{6,7}-edge XANES features with fit as (solid) line. (C) 48.3 eV positive feature from transient O₃₋ spectra; (D) 60.1 eV positive feature (black, circles) and 64.5 (red, squares) & 67.5 eV (blue, triangles) negative features from transient N_{6,7}-edge spectra.

Discussion

Figure 4A displays the transitions that occur in the ground state compared to the MLCT excited state for Ir(III)(ppy)₃ in a simplified orbital diagram. For 3rd row metals, the observed transitions primarily arise due to dipole-allowed transitions of core electrons to empty bound states with selection rules of $\Delta L = \pm 1$ and $\Delta J = 0, \pm 1$, where L and J are the orbital and total angular momentum, respectively. The core-hole with spin $S=1/2$ couples to the respective core orbital with L character to give $J = |L \pm S|$ states. The 4f core orbital with $L=3$ will produce the spin-orbit-coupled $4f_{5/2}$ ($J=L-S$) and $4f_{7/2}$ ($J=L+S$) states, and the 5p core ($L=1$) is split into $5p_{1/2}$ and $5p_{3/2}$. The 5d orbitals ($L=2$) will split into either $5d_{3/2}$ or $5d_{5/2}$ states. Ir(III)(ppy)₃ is C₃ symmetric, leading to the 5d orbital manifold depicted in Figure S9, but can generally be simplified to pseudo-octahedral (O_h) due to the large crystal field splitting.⁶⁴ Given the presence of both spin-orbit coupling (SOC) and an approximately octahedral ligand field, the 5d orbital manifold will result in predominantly $J = 5/2$ states for the empty e_g set of orbitals and two sublevels from the t_{2g} set where $J =$

$5/2$ for the upper state and $J = 3/2$ for the doubly-degenerate lower state shown in Figure 4. This molecular orbital diagram is described in more detail in references⁶⁸ (generally for Ir cubic system) and⁶⁴ (specifically for C₃-symmetric systems).

The O₂-edge ($5p_{1/2} \rightarrow 5d$) is not evident in our experimental data for either Ir(III)(ppy)₃ or Na₃Ir(III)Cl₆. Transitions from the $5p_{1/2}$ are only allowed when an available 5d orbital has $J = 3/2$ character, as the other potential transition ($5p_{1/2}$ to $5d_{5/2}$) is forbidden due to $\Delta j = +2$. Additionally, due to the Ir 5p SOC of ~ 15 eV as derived from XPS,⁶⁹ any

Energy (eV)	τ (ps)
48.3	14 ± 6
60.1	19 ± 3
64.5	2.0 ± 0.7
67.5	4.8 ± 0.9

Table 1 Lifetimes at key energies from transient O₃₋ and N_{6,7}-edge XANES spectra.

O₂ transitions would at least be partially overlapped with transitions from the N_{6,7}-edges. Indeed, a prior photoionization experiment with atomic Ir in the XUV energy range showed very weak 5p_{1/2}-based transitions nearly overlapped with strong 4f_{7/2,5/2}-based transitions.²¹ It has also been noted that the theoretical cross-section ratio between the 5p_{1/2} and 4f peaks yields at most 2% for XPS photon energies, and XPS fitting for Ir 4f binding energies generally ignore 5p_{1/2} contributions.^{49,69,70} We expect that the Ir O₂-edge is much weaker than the other edges in this region and likely subsumed within the N_{6,7} transitions, and is thus not directly observed here. In an appropriate system that furnishes available 5d_{1/2} states, the O₂-edge for a 3rd row transition metal coordination complex can be observed; see the supporting information for a platinum(II) example where a weak O₂-edge is present. However, transitions from the 5p_{3/2}, 4f_{7/2}, and 4f_{5/2} core orbitals are allowed to either 5d_{5/2} or 5d_{3/2} empty orbitals, resulting in the observed O₃, N₇, and N₆-edges for Ir(III)(ppy)₃, respectively, shown in Figure 4.

In the MLCT excited state, a hole is generated in the occupied t_{2g} orbital, resulting in new allowed transitions from the core orbitals to this vacancy. Transient L_{2,3}-edge XANES of Ir(III)(ppy)₃ indicated that the 5d vacancy is J = 5/2, as a lower energy positive feature appears in transient L₃-edge (2p_{3/2}, Δj = +1) that is not present by transient L₂-edge XANES (2p_{1/2}, Δj = +2).⁶⁴ The same selection rules hold for the 5p → t_{2g} transitions in this work, with 5p_{1/2} → 5d_{t_{2g}} forbidden and 5p_{3/2} → 5d_{t_{2g}} allowed. The latter is observed as the positive transient feature centered at 48.3 eV. Transitions from both 4f_{7/2} and 4f_{5/2} to the 5d_{5/2} t_{2g} vacancy are allowed, resulting in the transient set of doublet-like features at 60.1 and 63.1 eV for transient N_{6,7}-edge XANES.

The effective oxidation state change from Ir(III) to Ir(IV) lowers the energy of the core orbitals, which will result in a blueshift of the core → e_g transitions. For the N_{6,7} edge,

this shift manifests as the derivative-shaped features between 63 and 74 eV. The negative features are more intense than the positive features due to the asymmetry of the ground-state peaks, with a sharper rise on the low-energy side. In the case of the O₃-edge, the ground-state 5p → 5d feature is broad, and the expected negative feature around 52 eV is likely obscured by the broad 5p_{3/2} → 5d_{t_{2g}} absorption. A weak blueshifted absorption between 53-58 eV can be seen in the 2D contour plot in Figure S5.

The XUV spectra selectively probes the Ir d-orbital manifold and is therefore not expected to distinguish between the initial ¹MLCT excited state and the ³MLCT state that forms in tens of femtoseconds. The resulting transient features thus arise from the ³MLCT manifold and relaxation dynamics within or from this manifold. The transient O₃ positive feature is ~5.8-6.0 eV from the ground-state edge, in agreement with the ~5.9 eV energy difference between the analogous features in transient L₃-edge XANES and consistent with an excited state ¹⁰D_q value of 6.5 eV predicted from density functional theory computations.^{52,60,64} There is only a weak bleach feature and blue-shifted positive absorption by transient O₃-edge, likely arising from distribution of the depletion over the broad O₃-edge in the GS convoluted with potential blue shift of the O₃-edge in the oxidized excited state (see Figure S5 for a 2D transient O₃-edge plot at early delay times) at 53.5-54 eV and 54-57 eV, respectively.

A surprising result of the kinetic fitting is the difference in decay times between features corresponding to the t_{2g} hole (the positive features at 48.3 eV and 60.1 eV) and those corresponding to the e_g orbitals (the derivative-shaped features from ~63-72 eV). The t_{2g} features decay with a lifetime of ~16 ps before reaching their plateaus, while the e_g features relax in only ~3-4 ps before plateauing. The difference in lifetimes between these two types of features indicates that they report on different relaxation

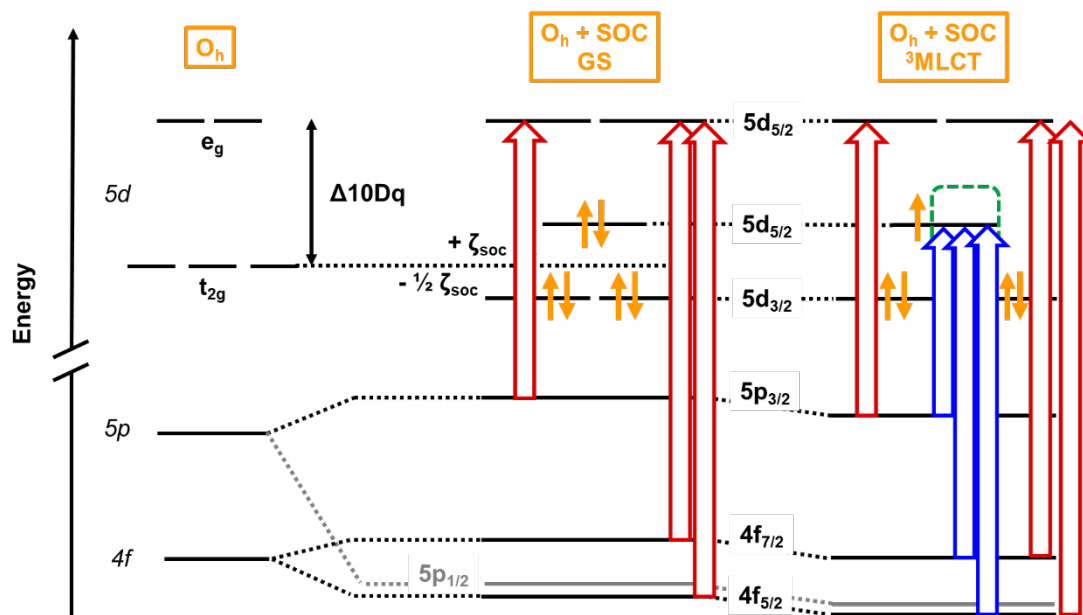


Figure 4 Simplified orbital diagram for allowed XUV transitions from the core 5p and 4f orbitals to valence 5d orbitals in the ground state versus excited MLCT state in Ir(III)(ppy)₃.

modes. Prior computational work has shown changes in the Ir-C_{ppy}/N_{ppy} bonds in the ³MLCT excited state compared to the ground state Ir(III)(ppy)₃,^{51,52,58,59,61} indicating a geometric distortion in the triplet state that could be coupled to different vibrational modes.^{52,61} Transient optical and luminescence absorption of Ir(III)(ppy)₃ in THF also observed a decay with a ~3 ps lifetime which was assigned to vibrational cooling to the surrounding matrix.^{49,46,55} This likely corresponds to the 3-4 ps decay components of the e_g features. The derivative-shaped transient results from a blueshift of the 4f → 5d transition in the excited state vs the ground state. There are therefore two plausible explanations for the ~30% loss of intensity of the negative features over on this timescale. As the metal-ligand bonds expand, the ligand field splitting 10Dq will be reduced, lowering the energy of the e_g orbitals. Alternatively (or perhaps concurrently), this geometric relaxation may redistribute partial charge back onto the Ir, making it more Ir(III)-like and raising the 4f orbital energies.

A different explanation must be invoked for the ~16 ps loss of intensity of the core → t_{2g} hole features, as these are induced absorption features that are not present in the ground state. The intensity change is therefore not caused by a shift in the energy of the new absorption but must instead be due to either a loss of population in the excited state or a decrease in the oscillator strength of the transition. As there is no evidence from optical transient absorption spectroscopy of a 30% loss of the ³MLCT state at early times, we therefore postulate that the ligand twist noted in calculations of the ³MLCT state geometry^{51,52,58,59,61} reduces the 4f,5p → t_{2g} overlap and therefore weakens the transition. Ab initio calculations of the core to valence transitions along the excited state trajectory will be necessary to confirm these hypotheses. The RASSCF method was used successfully in the picosecond hard X-ray studies of a similar cyclometalated Ir(III) complex to rationalize the excited-state spectra,⁶⁶ and can be combined with molecular dynamics calculations of the ³MLCT relaxation.

It is somewhat surprising that the magnitude of the ~16 ps decay at both the 5p → t_{2g} and 4f → t_{2g} are nearly identical: in each case ~40% of the peak intensity is lost on this timescale. The 4f orbitals are significantly more localized than the 5p orbitals, so we originally expected the 4f → t_{2g} transition to be less sensitive to the ligand field strength and symmetry. Leone and coworkers noted that the tungsten O₃- and N_{6,7}-edges showed different dynamics in their transient XUV investigation of WS₂, and proposed that the more localized 4f core led to a strong core-exciton spectrum that was not as apparent for the 5p core-hole.²³ We did not observe significant differences between the t_{2g} features in the present work, although there was a slightly delayed rise of this signal at the O₃ edge (see Supporting Information for details).

The schematic potential energy surface in Figure 5 summarizes the Ir(ppy)₃ dynamics observed in this work. Overall, the combined transient XUV spectroscopy at the O₃- and N_{6,7}-edges are in good agreement with known dynamics for 400 nm excitation of the ¹MLCT band. Upon 400 nm excitation, there is ultrafast ISC (<90 fs) from the singlet

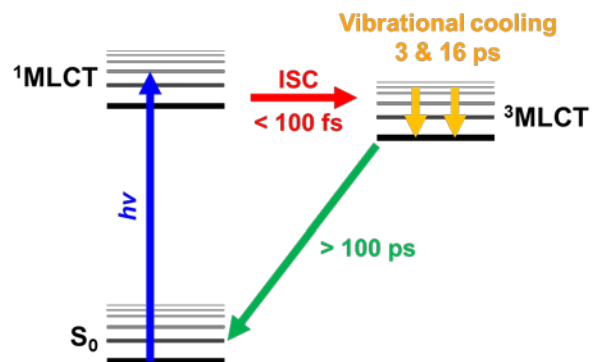


Figure 5. Diagram of Ir(ppy)₃ dynamics upon 400 nm excitation derived from transient O₃- and N_{6,7} XANES.

MLCT state to the triplet MLCT state. There is then vibrational relaxation by various modes to the equilibrium ³MLCT state on the order of 200 fs to 15 ps. The final ³MLCT state slowly decays back to the ground state, lasting several orders of magnitude than the delay times collected (up to 100 ps). These results match well to prior ultrafast optical & photoluminescent work examining the manifold, showing that time-resolved XUV be used for tracking metal-based dynamics in iridium complexes.

Finally, we note that the high absorption cross section of the 4f,5p → valence transitions is attractive for pump-probe spectroscopy. A comparison of Figure 1A and Figure 2 reveals that the O₃- and N_{6,7}-edge peaks are ~20% as intense as the ¹MLCT visible-light transition. The attenuation length of a visible pump and XUV probe are therefore well matched, which simplifies experiment design.

Conclusion

X-ray absorption spectroscopy is a powerful tool for measuring the element-specific electronic structure of complex molecules, and developments in the past two decades have extended its reach to femtosecond timescales and tabletop sources. We now show that O₃- and N_{6,7}-edge XANES spectroscopy can be performed on 3rd-row transition metal complexes with a high-harmonic source, and that the resulting spectra are diagnostic of the ligand field strength and oxidation state of the metal center. Transient absorption spectroscopy of Ir(III)(ppy)₃ performed with ~100 fs time resolution shows both the initial formation of an MLCT state and the subsequent vibrational relaxation. This work opens up the possibility of femtosecond O₃- and N_{6,7}-edge XANES as a routine spectroscopic technique for the study of molecular complexes relevant to light harvesting and catalysis.

ASSOCIATED CONTENT

Supporting Information. Details of instrumental methods, data processing, and analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>

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ACKNOWLEDGMENT

The transient XUV instrument, including the nonlinear optical parametric amplifier, was built with partial funding from the Air Force Office of Scientific Research under AFOSR Awards No. FA9550-14-1-0314 and FA9550-18-1-0293. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0018904. We are grateful to Dr. Frank de Groot for discussion on analysis.

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Femtosecond extreme ultraviolet spectroscopy of an iridium photocatalyst reveals oxidation state and ligand field specific dynamics.

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Static XUV

All ground state spectra shown in this work are presented after subtraction of a power-law baseline that accounts for photoionization of the valence electrons. The raw absorption spectrum is shown in Figure S1.

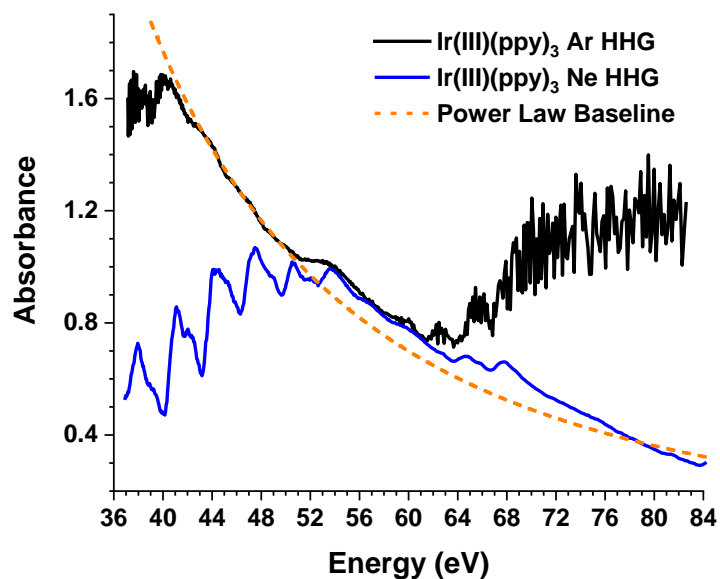


Figure S1. Raw absorption spectra of Ir(ppy)₃ using argon HHG conditions for O₃-edge XANES (black line) and neon HHG conditions for N_{6,7}-edge XANES (blue line) with the powerbase line (dotted orange line).

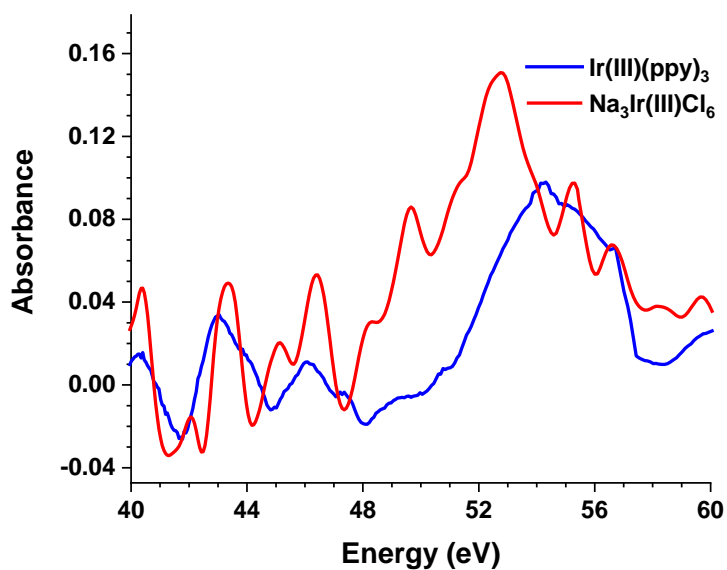


Figure S2. O₃-edge XANES overlay of Ir(III)(ppy)₃ (blue) and Na₃Ir(III)Cl₆ (red).

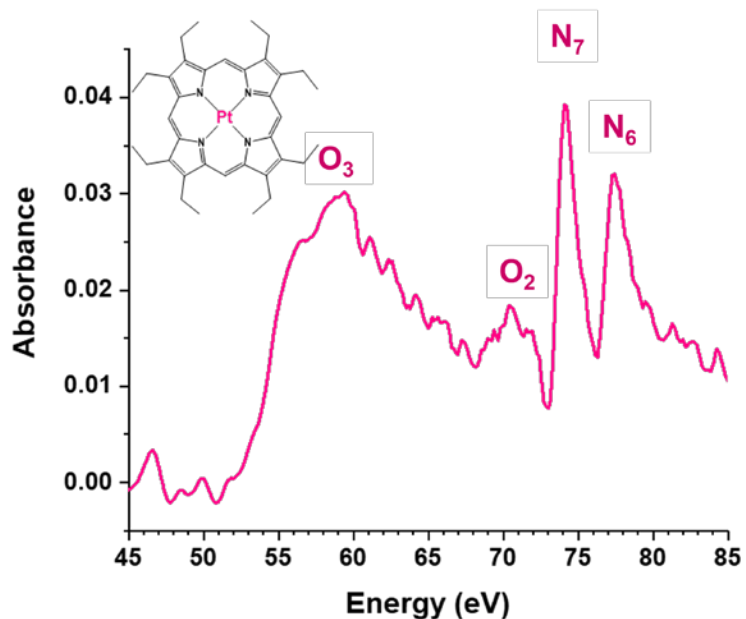


Figure S3. O_{2,3}- & N_{6,7}-edge XANES of Pt(II)OEP.

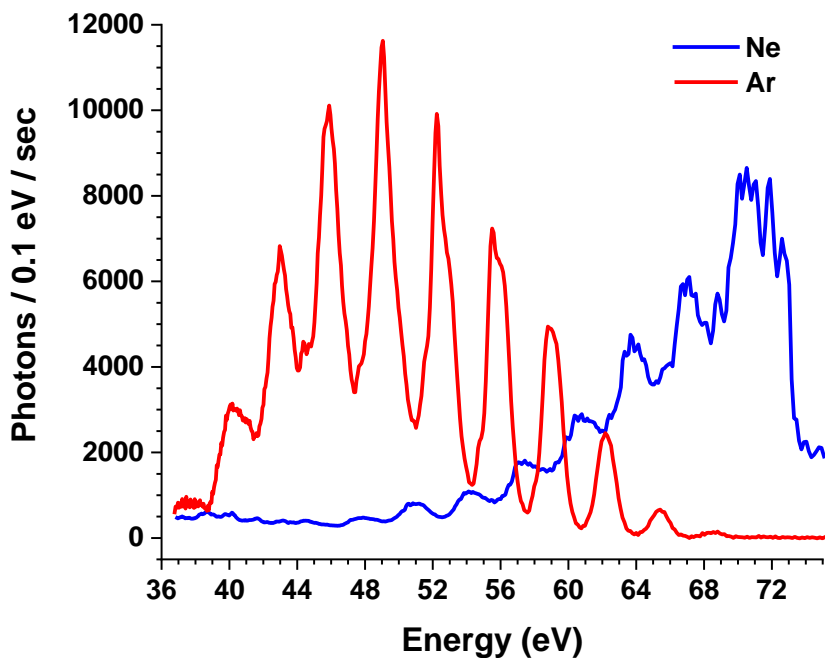


Figure S4. Overlay of HHG XUV harmonic flux (photons/0.1 eV/sec) using Ar (red) and Ne (blue) gas medium through the same thin film Ir(III)(ppy)₃ for the static XANES, showing the ~58-59.9 eV energy range provide low continuum flux for ground state experiments.

Transient XUV – 2D Plots

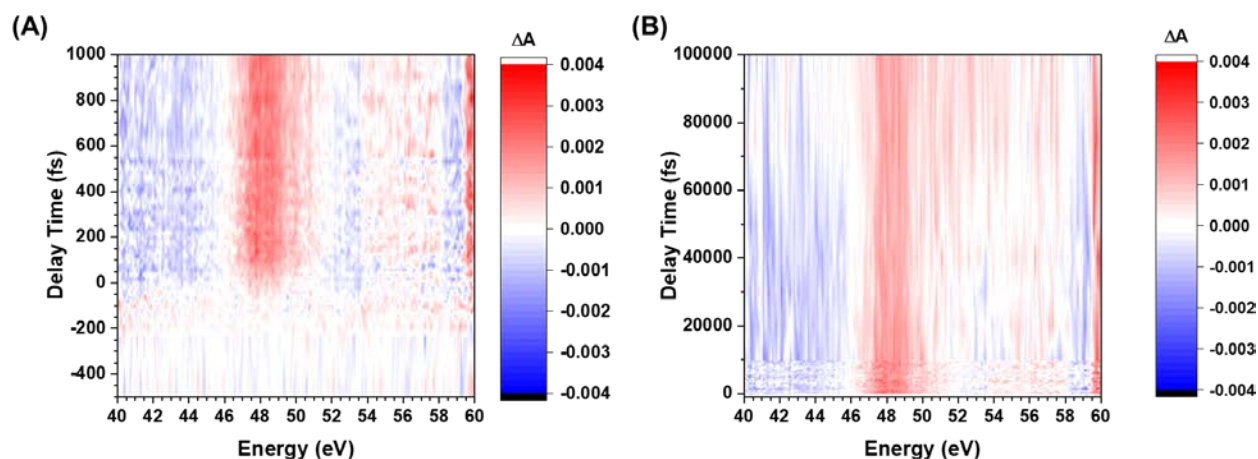


Figure S5. 2D transient O₃-edge XANES of Ir(III)(ppy)₃ with 400 nm excitation at early (A) and late (B) delay times.

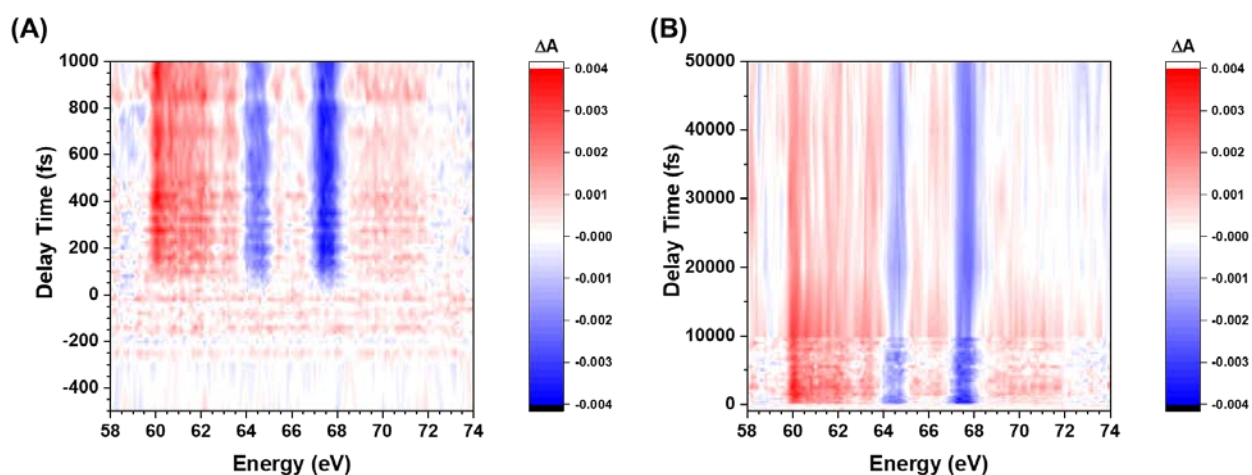


Figure S6. 2D transient N_{6,7}-edge XANES of Ir(III)(ppy)₃ with 400 nm excitation at early (A) and late (B) delay times.

Transient XUV – Kinetics

Both mono- and bi-exponential sequential decays with a long-time shelf were attempted when performing kinetic analysis at the positive transient O₃ feature at 48.3 eV. A sequential bi-exponential decay using the experimental IRF of 123 fs was attempted to fit the 48.3 eV kinetic data (tabulated in Table S1), but the earlier short time component has a lifetime on the order of the experimental IRF and a standard error nearly as large as the lifetime itself. This suggested while there is potentially an early, short-lived feature on a similar timescale as the ~120 fs IRF, this is convoluted with the IRF rise. This led us to primarily analyze the kinetic data using the mono-exponential decay function as described

in the main text. The kinetic of the transient O₃-edge positive feature match well to the transient N_{6,7}-edge positive feature, with the O₃-edge ~16 ps decay component within error of the N_{6,7}-edge decay component. No satisfactory bi-exponential kinetic model was found for the transient N_{6,7}-edge features, nor was there a delayed rise in these features.

The potential presence of an early, short-lived feature by transient O₃-edge XANES that is not present in transient N_{6,7}-edge XANES points to different information gained about the dynamics at each edge. Given that the main difference between the O₃- and N_{6,7}-edges are the starting core orbitals, it is likely that the potential short-lived state involves changes in iridium 5p orbital interactions in this state. A recent report by Chang *et. al.* noted that the tungsten O₃- and N_{6,7}-edges showed different behavior of core-exciton transitions at the N_{6,7}-edge compared to core-to-band transitions at the O₃-edge when tracking the dynamics of photoexcited carriers in WS₂; they postulate that these differences occur based on the difference in degree of localization of the core orbitals.¹

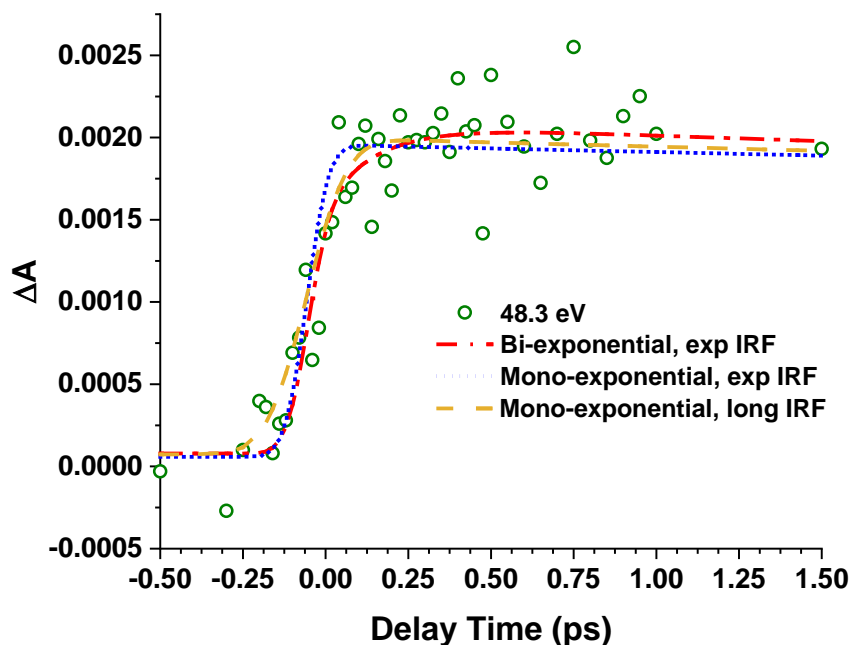


Figure S7. Transient O₃-edge XANES of Ir(III)(ppy)₃ with 400 nm excitation show to 1.5 ps delay time – kinetic analysis at 48.3 eV at early times with three different sequential exponential models attempted: bi-exponential with the experimental 123 fs IRF, mono-exponential with the experimental IRF, and mono-exponential allowing the IRF to drift, all with a long-time shelf.

Table S1. Summary of transient O₃-edge kinetic analysis at 48.3 eV using three different sequential exponential decay models with a long-time shelf.

Fit	IRF (fs)	τ_1 (ps)	τ_2 (ps)	Shelf (mÅ)
Mono-exponential	123	-	16 ± 8	+ 1.2
Mono-exponential	245	-	14 ± 6	+ 1.2
Bi-exponential	123	0.16 ± 0.11	11 ± 3	+ 1.2

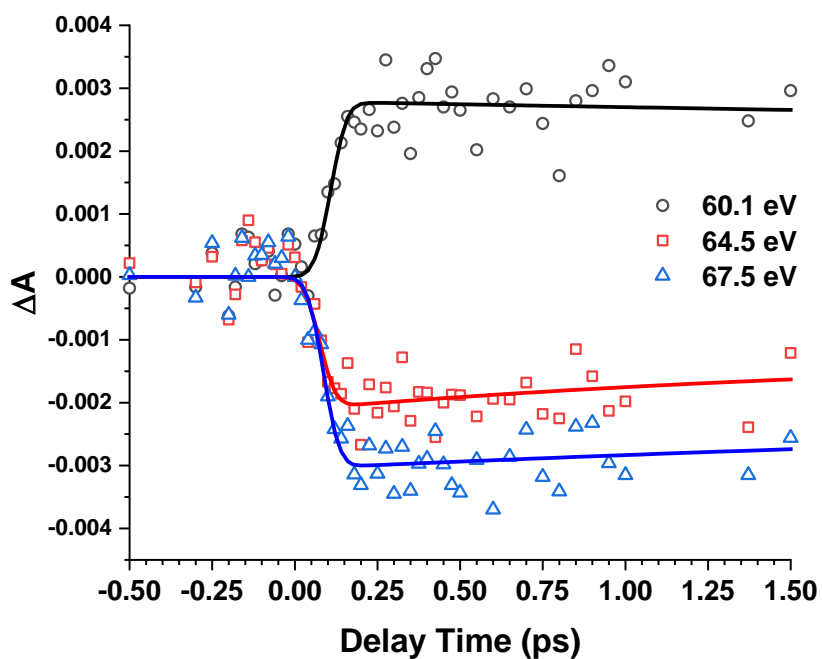


Figure S8. Transient N_{6,7}-edge XANES of Ir(III)(ppy)₃ with 400 nm excitation at early delay times (to 1.5 ps) – kinetic analysis at 60.1 (black, circles), 64.4 (red, squares), and 67.4 eV (blue, triangles).

Orbital Manifolds – O_h vs C_3

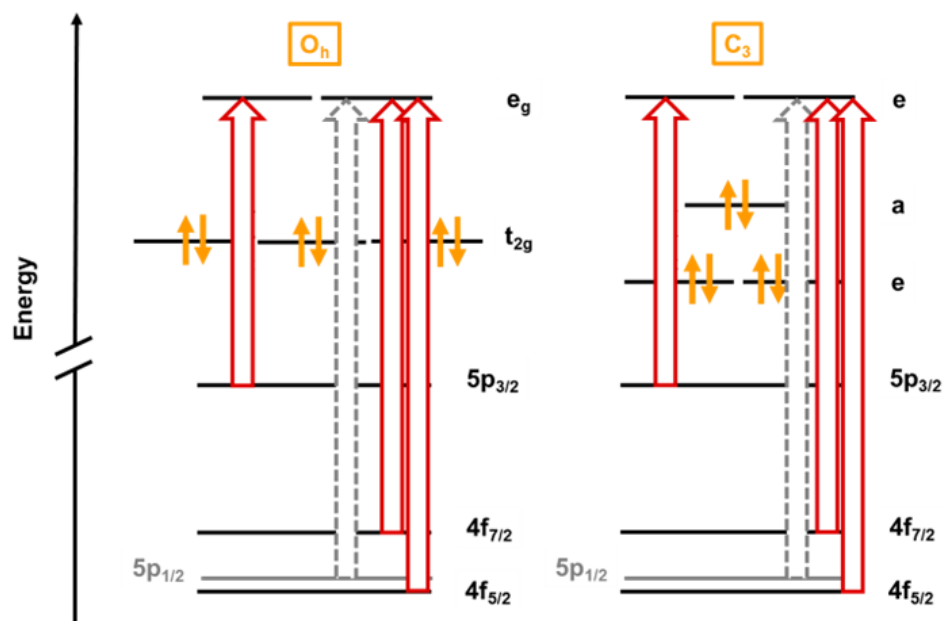


Figure S9. Simplified orbital manifold shown for an octahedral (A) or C_3 -symmetric iridium(III) (d^6) center with allowed transitions as red arrows and unobserved $5p_{1/2}$ to valence trans in dotted grey arrows.

References

- (1) Chang, H. T.; Guggenmos, A.; Chen, C. T.; Oh, J.; Géneaux, R.; Chuang, Y. De; Schwartzberg, A. M.; Aloni, S.; Neumark, D. M.; Leone, S. R. Coupled Valence Carrier and Core-Exciton Dynamics in WS_2 Probed by Few-Femtosecond Extreme Ultraviolet Transient Absorption Spectroscopy. *Phys. Rev. B* **2021**, *104* (6), 1–14. <https://doi.org/10.1103/PhysRevB.104.064309>.