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Long-Lived LMCT in a d\(^0\) Vanadium(V) Complex by Internal Conversion to a State of 3d\(_{xy}\) Character

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Supporting Information

ABSTRACT: The exited state dynamics of a d\(^0\) vanadium(V) oxido ligand-to-metal charge transfer (LMCT) complex, VOL\(^{2+}\), were investigated via a combination of static optical and X-ray absorption (XAS) spectroscopy, transient optical absorption spectroscopy, and time-dependent density functional theory (TD-DFT). Upon excitation of the LMCT in the visible region, transient absorption data reveal that internal conversion traps the excited carrier population into a long-lived charge transfer state of 3d\(_{xy}\) electron character, S\(_1\)(d\(_{xy}\)). The internal conversion is substantiated by an isosbestic point in the transient absorption data, two nearby charge transfer states that couple well by TD-DFT, multiple rates in the ground state recovery, and the decay kinetics of an excited state absorption with the energy of a d-d transition in O K-edge XAS spectra. The long lifetime (~420 ps) of S\(_1\)(d\(_{xy}\)) can be ascribed to its poor optical and vibrational coupling to a distorted ground state (S\(_0\)) via a negligible electronic dipole transition in TD-DFT. The lack of luminescence or an identifiable triplet state also suggests attributing the lifetime to electronic contributions. In conjunction with its strong visible absorption and reduction potential, the long-lived LMCT suggests that molecules such as VOL\(^{2+}\) could have potential utility for energy conversion applications. Moreover, the results show that internal conversion between two nearby charge transfer states, differentiated by their 3d character, can form a long-lived charge transfer excitation, broadly informing the discovery of 3d metal-centered optical absorbers with long-lived charge transfer lifetimes.

INTRODUCTION

Molecules and nanostructures exhibiting long-lived, optically accessible charge transfer excitations are desirable for a number of applications including energy conversion, photocatalysis, and chemical sensing. Ideal chromophores have tunable absorption profiles (e.g., for matching to the solar spectrum) and excited state lifetimes similar to or longer than the characteristic electron transfer rates to catalysts or reactants. For the past half-century, metal-to-ligand charge transfer (MLCT) processes in a vast range of pi-acceptor ligated, low-valent metal oxido\(^{1}\), nitrido\(^{2}\), alkylidyne\(^{3}\), peroxo\(^{4}\), cyclopentadienyl, benzene, cycloheptatrienyl, pyridyl, and phosphine complexes have been an area of extensive study.\(^{1}\) Owing to relatively long, visible light-induced MLCT lifetimes, the archetypal Ru(bpy)\(^{2+}\) (with a lifetime of 890 ns in acetonitrile\(^{5}\)) and derivatives thereof, as well as polypyridyl derivatives of other metals (e.g., Os, Fe, Co, Rh, Pt, and Ir), have been investigated as systems for photophysical studies\(^{6–9}\), photosensitizers in solar energy conversion systems\(^{10}\), and potent excited state single-electron reductants for catalytic photon-driven organic transforma-

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through static optical and X-ray absorption, transient optical spectroscopy, and multiple levels of electronic structure theory. Similar to the Cu-based MLCT chromophores, this 3d electronic complex does not contain purely metal-centered excited states that could shorten the LMCT lifetime due to its empty d-block. The advantage of studying an LMCT-based d0 chromophore is that the excited states are primarily of LMCT character, with single electron occupation of a V d orbital and a hole on the ligand.

The transient optical data at timescales longer than a picosecond reveal an internal conversion between two nearby charge transfer states. Within the LMCT absorption, VOLF has two relevant charge transfer states that can couple to each other, as shown in the scheme of Figure 1, S0(d) and S1(dyz), and S1(dxy). Similarly to the Cu-based MLCT chromophores, this 3d electronic compound has metal-centered excited states that are relatively strong visible absorption, suggests its use as a chromophore for energy conversion applications; particularly applications that exploit the LMCT character where reduction occurs from a strongly reducing metal center.

where the character of the excited electron is denoted to differentiate the states. S2 does not couple well to either state in the relaxed geometry due to strong symmetry considerations, described below. The internal conversion is identified in the transient optical data by an isosbestic point, multiple rates in the ground state recovery, and the decay kinetics of excited state absorption to higher lying LMCT states [S0(d)]. The energy of the transition to the lowest lying S0(d) from the initially excited LMCT are calibrated with XAS of the O K-edge. With the use of time-dependent density functional theory (TD-DFT) and multireference second-order perturbation theory (MRCASPT2), the long lifetime of S1(dyz) is assigned to poor optical and vibrational coupling of the occupied 3d orbital to a distorted ground state orbital. The lack of luminescence in this compound supports identifying the long-lived component to electronic, rather than spin, contributions and differentiates this compound from the luminescent MLCT discussed above. Importantly, the results show that a charge transfer state, nearby to the main LMCT absorption and of different 3d character, that has poor optical and vibrational coupling to the ground state can collect excited 3d electrons and thereby significantly lengthen the charge transfer lifetime in a 3d metal-centered LMCT chromophore. The long lifetime, in conjunction with the strong visible absorption, suggests its use as a chromophore for energy conversion applications; particularly applications that exploit the LMCT character where reduction occurs from a strongly reducing metal center.

RESULTS: SYNTHESIS, CHARACTERIZATION, AND PHOTOLUMINESCENCE

Figure 2 shows the X-ray crystal structure of the vanadium(V) oxido chelate, VOLF, under study supported by the fluorinated tetradentate aminophenol ligand (L2F). Although similar ligands to H4L2F have been prepared via thermal Mannich condensation using relatively electron-rich phenols,21 we found that this method resulted in only a trace yield of the electron-poor fluorinated ligand even after several weeks of reaction time. In contrast, we found that microwave heating of 4-fluoro-2-methylphenol, ethanalamine, and formaldehyde in 1-butanol at 110 °C for 5 h resulted in an overall yield of 50% for H4L2F. VOLF was obtained as a burgundy powder in excellent yield (98%) through the dropwise addition of oxidovanadium triisopropoxide into a solution of H4L2F in toluene.22 Red block crystals of VOLF suitable for XRD crystallography were obtained by vapor diffusion of cyclohexane into m-xylene (Figure 2). Full synthetic details for H4L2F and VOLF are given in the Supporting Information.

By definition, LMCT results in metal-centered excited states where reduction photochemistry can be controlled by shifting the redox properties of the metal through either ligand modification and/or metal substitution. As a result, tuning of LMCT excited state energetics should be possible over a wide range. Electrochemistry of VOLF shows that an irreversible V(IV/V) redox couple at −1.01 V versusFc/Fc’ (Figure S17 of the Supporting Information), which suggests that this class of compounds has metal-centered excited states that are relatively strong reductants. VOLF therefore has the thermodynamic potential to photochemically drive the reduction of protons to form dihydrogen in solar energy-to-fuels applications or to mediate organic transformations such as quinone reduction.24

Unlike the MLCT compounds discussed above, there is no observed static photoluminescence. Static photoluminescence was measured on an Edinburgh Photonics FLS920 spectrometer. Samples of 1 μM VOLF were prepared in nitrogen-sparged spectroscopic grade THF (Sigma-Aldrich). The spectrum of VOLF was recorded with excitation and emission bandwidths of 4.0 nm, 1 nm step, and a 1s dwell time; for comparison, the reported sensitivity of 6000:1 at the Raman band of water was...
collected at 350 nm excitation, 5 nm spectral bandwidth, and 1 s integration time. Three spectra were averaged. Upon excitation with 405 nm light, no photoluminescence from the VOL sample was detected between 415 and 750 nm. A more concentrated, 1 mM solution of VOL in THF was also prepared. Static photoluminescence measurements of this 1 mM solution (excitation/emission bandwidths of 5 nm, 1 nm step size, 0.1 s dwell time) also showed no photoluminescence between 415 and 750 nm.

The absence of photoluminescence suggests that the long-lived charge transfer state is not easily ascribed to triplet formation. Another way to identify triplet formation is to estimate the energy barrier for ground state recovery and compare it to previously measured singlet–triplet ISC activation barriers that lead to long-lived states. In order to determine the upper limit for the energy barrier to ground state recovery, a simple Arrhenius model was applied to the measured decay rate at room temperature (423 ps) in the ultrafast optical experiments below and the rate at ~80 °C. At ~80 °C, we were unable to observe any transient absorption signal on the nanosecond timescale (experimental details for the nanosecond measurements are in the Supporting Information). The time-resolution of the nanosecond transient absorption measurement, and therefore the upper bound for the lifetime of this transition at ~80 °C, is ~2 ns. Using these two data points, we conclude that the energy barrier is less than 50 meV. This 50 meV maximum barrier is significantly lower than the precedent set for ISC by rubrene in sucrose octaacetate matrix, which is on the order of 160 meV.25

RESULTS: STATIC OPTICAL/X-RAY SPECTRA AND TD-DFT CALCULATIONS

Optically exciting VOL in the visible region (400–500 nm) gives the LMCT absorption spectrum shown in Figure 3a). Using TD-DFT, we are able to reproduce and decompose this spectrum. There are four bright transitions that make up the absorption, hereafter labeled as S1–S4. These excited states are shown in Figure 4, where yellow denotes an electron and blue is the corresponding hole. Electron–hole distributions are shown both for the ground state geometry and at the relaxed minima of each excited state potential energy surface. Each excited state is clearly of LMCT character, involving charge transfer from one or both of the ligands to the metal center (unoccupied V d orbitals). We label the two frontier (HOMO−1 and HOMO) donating orbitals involved in these excitations as πx and πy, respectively (Figure 3b).

In the ground state geometry (indicated with a *), S2*–S6 are made up of contributions from V d orbitals and both phenyl rings (πx and πy). S2* is an even combination of πx and πy, while S6* and S4* have slightly more weight on the πy side. For clarity, we label all excited states by their largest d component. Figure 3b shows the largest d component of S2* as dyz, since the transition is 60% πx → 3dyz. The lowest energy excitation, S2*(d2yz−), has the hole localized to one ligand; this state has only πy character.

In the transient optical spectroscopy discussed below, the LMCT is excited at 400 nm (Figure 3a). Since S2*(d2yz) and S2*(d2xy) are close in energy, both states are initially populated due to Franck–Condon broadening. After excitation, the wave packet will evolve along the potential energy surface of each of the electronic states. Importantly, electron–hole dynamics differ along each excited state surface. As the wavepacket moves along the potential energy surface, S4(d2yz) and S4(d2xy) lose their πy character; the hole becomes localized on πx. The largest d component of S4 changes from d2yz to d2xy. As a consequence

![Figure 3](image3.png)

Figure 3. (a) Optical absorption of VOL. The broad absorption peak occurring for wavelengths longer than 400 nm is due to a charge transfer excitation from the ligand-to-metal center (LMCT). (b) Single particle orbitals contributing to the main transition (peak at 425 nm) into S2*, Vertical lines denote TD-DFT transition energies and oscillator strengths.

![Figure 4](image4.png)

Figure 4. Electron–hole distribution for the first four excited states in the visible region. The hole is shown in blue and electron in yellow. This color scheme distinguishes the states from the single particle orbitals shown in Figures 3 and 5.
to these changes, $S_1(d_{xy})$ and $S_4(d_{yz})$ essentially have the same character in the relaxed geometry (Figure 4).

$S_3(d_{yz})$ exhibits the opposite trend; relaxation along the excited state potential causes the hole to localize on $\pi_-$. The mismatch in hole localization ($\pi_-$ vs $\pi_+$) between $S_3(d_{yz})$ and $S_4(d_{yz})$ suggests that internal conversion (IC) between these states is symmetry forbidden and unlikely.

Conversely, the character of $S_3(d_{yz})$ is unaffected by relaxation. The hole remains localized on $\pi_-$, and therefore, IC from either $S_3(d_{yz})$ or $S_4(d_{yz})$ to $S_1(d_{xy})$ is possible. Since $S_1(d_{xy})$ and $S_4(d_{yz})$ are so similar in character, we excite both with our pump at 400 nm, and the $S_3(d_{yz})$ initially excited state is significantly brighter, we adopt $S_3(d_{yz})$ as the higher energy state in a two-state model of the low energy, relaxed charge transfer states. $S_1(d_{xy})$, the lowest energy excited state and the only one that can couple to either $S_3$ or $S_4$, is the lower energy state.

We also compute the excited state absorption spectra explored through our probe. We find that there is more coupling optically (through the dipole matrix element) between $S_1(d_{xy})$ and higher states than from $S_1(d_{xy})$ (see Figure S3 of the Supporting Information). The majority of the higher lying states within 3.0 eV are of LMCT character. From $S_3(d_{yz})$ up, ~60% of states are pure LMCT, while the remaining 40% are mixed (not pure LMCT, MLCT, or ligand-to-ligand charge transfer). Similarly, $S_3(d_{yz})$ has ~65% pure LMCT and 35% mixed.

To calibrate where the nearest higher-lying LMCT states are, denoted by $S_n(d)$ in Figure 1, we have done X-ray absorption spectroscopy of the O K-edge (1s absorption) of the molecule (Figure 5). Since LMCT states all have the electron primarily

![Figure 5. X-ray absorption spectrum of powder VOL in PFY mode. Scheme shows the DFT d orbital (dashed lines) splitting based on observed transition energies from XAS.](image)

on vanadium, the energy differences between V LUMO orbitals, or the $d^1$ absorptions, are indicative of the level splitting between LMCT states. The level alignment of the LUMO is informed by the pre-edge region of the O K-edge that comprises three lower energy (529–535 eV) bands, each a mixture of oxygen 2p orbitals with vanadium 3d states.26–29 Previous work has shown that for tetrahedral compounds of $e$ and $t_2g$ symmetries,28,29 the peak separation of these bands in the O K-edge reproduces observed d-d transitions fairly well.26,28 Therefore, the energy separation between the lower two peaks in the XAS spectrum, 2.2 eV, is assigned to the level splitting between the lowest LUMO orbitals (two degenerate pairs, LUMO/LUMO+1, and LUMO+2/LUMO+3), indicative of excited state absorption from the initial LMCT to the next higher LMCT state.30–34

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### RESULTS: TRANSIENT OPTICAL SPECTROSCOPY AND TD-DFT CALCULATIONS

Excitation of VOL at 400 nm leads to the transient spectrum, probed from 400–700 nm, shown in Figure 6. This spectral

![Figure 6. Transient spectra of VOL in THF taken (a) at early times and (b) at later times. Arrows show the direction of signal growth (decay) as time delay increases. Early contributions from solvent response are removed at times before 200 fs. The isosbestic point occurring at intermediate times is demarcated by a black box. The maximum of the ESA (2.3 eV) is highlighted in gray.](image)

region comprises the LMCT excitation into the initial charge transfer states (~400–525 nm) and excited state absorptions (~500–600 nm). Transient spectra were collected at both short time delays (100–500 fs, Figure 6a) and longer time delays (1–500 ps, Figure 6b). To aid assignment of the transient signals, the transient spectra are compared to the static UV–vis LMCT spectrum in each time window, at 100 fs and at 36 ps. In the region of 400–525 nm, the transient spectra exhibit a ~ΔmOD associated with a ground state bleach (GSB) and stimulated emission (SE). An excited state absorption predominates in the region beyond 525 nm for times faster than 36 ps. After 36 ps, the ESA has decayed substantially, and the transient spectrum largely follows the UV–vis LMCT spectrum (Figure 6b).

Importantly, the transient spectrum contains an isosbestic point for the time window 1 to 36 ps where the ΔmOD is time independent (Figure 6b). For the isosbestic point to appear, there must be negligible back electron transfer to the ground state. This suggests that at these timescales there is a concentration of total excited carriers that is constant over the entire spectral region but whose contribution exchanges between two different excited electronic populations that both contribute to the spectrum.35–37 $S_1(d_{xy})$ and $S_3(d_{yz})$ described in the two-state model for VOL can account for these two populations. An isosbestic point would result from internal

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conversion (IC) between them. We will return to a detailed description of the isosbestic point after describing its involvement in the kinetic components of the spectral signals. For our kinetic analysis, we applied a sum of single exponential functions, each convolved with the Gaussian instrument response function (IRF) of our system (fwhm 100 fs), as the fitting function for the kinetic traces in most spectral regions (eq 1). The excepted region (540–590 nm, centered about the peak of the ESA) was modeled with a slight variation on the general summation to account for a small rising component (eq 2). Time constants were extracted from global fits of multiple kinetic traces within a particular spectral region.

\[
\Delta mOD = \sum_{i=0}^{n} A_e^{-t/\tau} \otimes \text{IRF}
\]

\[
= \sum_{i=0}^{n} A_{rise} e^{-t/\tau_{rise}} \left[ 1 + \text{erf} \left( \frac{t}{\sigma \sqrt{2}} - \frac{\sigma}{\tau_{rise} \sqrt{2}} \right) \right]
\]

\[
\Delta mOD = \left[ A_{rise} e^{-t/\tau_{rise}} + \sum_{i=0}^{n} A_i (e^{-t/\tau} - e^{-t/\tau_{time}}) \right] \otimes \text{IRF}
\]

The kinetics probed by the GSB/SE transition are shown in Figure 7a and Figure S9 of the Supporting Information. Kinetic traces reveal rapid relaxation of the initial state and then a much slower decay. The kinetics are well-represented by a triexponential function composed of fast 0.180 ps ± 0.005 ps (\( \tau_{\text{rise}} \)), intermediate 7.27 ps ± 0.32 (\( \tau_1 \)), and slow 455 ps ± 30 (\( \tau_2 \)) time constants. The expected amplitude of the transient signal at time zero based on the concentration of VOL\(^{fi} \) in solution, the pump power, and interpreting the signal as a GSB of the LMCT transition with an extinction coefficient derived from static UV-vis is ~100 \( \Delta mOD \), while here ~80 \( \Delta mOD \) is observed. There are at least two physical phenomena that could be attributed to the 0.18 ps time constant: singlet-to-triplet intersystem crossing (ISC) and intra- and inter vibrational relaxation (IVR). Generally in the MLCT compounds studied previously, a fast 0.02–0.1 ps ISC is observed as first as a stimulated emission signal from the singlet state significantly red-shifted from the GSB and then a much weaker, further red-shifted emission signal of the triplet state. An SE contribution related to ISC may be less important in VOL\(^{fi} \) since no long-lived emission is observed; the 0.18 ps time constant is observed in the region of the GSB rather than in a red-shifted spectrum, and there is gross agreement of the signal magnitude with expectations from a GSB. However, it may also be the case that the SE in VOL\(^{fi} \) is not significantly red-shifted from the GSB or that the ESA contribution masks the true SE signal. IVR of the initially excited Franck–Condon state to a relaxed state less well-coupled to the ground state geometry will certainly be present and can also account for the 0.18 ps time constant. Given the TD-DFT description where the hole localizes to \( \pi_e \) and the d-electron undergoes symmetry changes (Figure 4), this IVR could be quite large; this is further indicated by the 90% reduction in the transition dipole back to \( S_0 \) for \( S_0 \) (Table S2 of the Supporting Information). Therefore, for now, the time constant of 0.18 ps is attributed to a combination of ISC and IVR (\( \tau_{\text{ISC-IVR}} \)) and we focus on the longer timescale kinetics and transient spectrum. Resolution of the ISC and IVR contribution to \( \tau_{\text{ISC-IVR}} \) through separate ultrafast fluorescence studies that would directly detect SE\(^{38,39} \) is set aside for later experiments.

We now turn to the two longer time constants of the GSB/SE spectrum [7.27 ps (\( \tau_1 \)), 455 ps (\( \tau_2 \))]. Since IVR and ISC are expected to occur at faster timescales, these later time constants should come from electronic contributions of excited populations. The observation of two long timescale contributions to the GSB decay is unlike that seen in the canonical Ru(bpy)\(^3+ \) or recent Fe(bpy)\(^3+ \) where fast ISC, IVR, and IC are followed by a single long time constant identified by GSB traces, attributed to a fluorescent, charge transfer state in Ru(bpy)\(^3+ \) and the high spin metal-centered state in Fe(bpy)\(^3+ \). Indeed, VOL\(^{fi} \) has two closely spaced charge transfer states that could both contribute significantly to the GSB spectral decay (Figure 3a, Figure 4). The clear resolution of the two timescales in the GSB traces in VOL\(^{fi} \) could be a result of a population exchange between the initially excited \( S_1 \) population and the lower energy \( S_2 \) population (i.e., a series pathway that comes from internal conversion between the two CT states). On the other hand, the resolution of the two timescales could result from a parallel pathway, in which both \( S_1 \) and \( S_2 \) decay back to the ground state with different time constants. DFT calculations that reproduce the LMCT UV-vis spectrum do show that the relaxed geometry of \( S_1(d_{yz}) \) has a finite transition dipole to the ground state \( |S_0(d_{yz}) \rightarrow S_0(S) \rangle \), while \( S_1(d_{yz}) \rightarrow S_0 \) is significantly smaller; this would effect how each transition contributes to the GSB and their decay, in either a series or parallel model. The transition dipoles of these two transitions are shown in Table S2 of the Supporting Information.

Figure 7. Kinetic traces of VOL\(^{fi} \) at variable probe wavelengths of (a) 425, (b) 550, and (c) 500 nm with corresponding fits in black. The transitions contributing to the traces at each wavelength are indicated. The Gaussian IRF (100 fs fwhm, red dotted) is plotted in (a) to compare with the GSB/SE dynamics, and the 425 nm kinetic trace is reproduced (gold dashed) in (b) to highlight the rise component in the ESA trace.
The decay kinetics probed by the ESA spectrum, shown in Figure 7b and Figure S8 of the Supporting Information, can be fit with a triexponential function containing one rise component and two decaying components (eq 2) having time constants of 0.188 ps ± 0.024 (τ_{rise, ESA}), 0.602 ps ± 0.054 (τ_0), and 6.63 ps ± 0.12 (τ_1), respectively, in the region of the maximum of the ESA (2.3 eV, 540–590 nm). The similarity of τ_1 with the intermediate timescale observed in the GSB traces (7 ps) ties the decay of the ESA to the same state involved in the GSB decay. If a series pathway/internal conversion between the two charge transfer states is involved then the ESA decay would report uniquely on the decay of S_2. In a parallel pathway of S_1 and S_2 to the ground state, the ESA would report on one or the other. The isosbestic point that we observe between 1 and 36 ps, in the same timeframe that the IC would be expected for the ESA of S_1 to the ground state, is what primarily points to a series pathway with IC at 400 nm, ∼0.3 eV away from the poorly absorbing S_2 state. Therefore, S_1 is unlikely to be substantially excited initially such that it could account for the rather large 20 ΔmOD ESA at early times. Internal conversion, on the other hand, could significantly populate the S_1 state. The time constant τ_0 ∼ 0.602 ps is tied to τ_1, 6.63 ps, occurring exclusively together as will be discussed further below; it likely comes from IVR within S_0. The rise time of 0.188 ps is determined by the inclusion of a negative amplitude exponential to modulate the amplitude of subsequent decay (eq 2). Since it is similar to the fast 0.18 ps τ_0 of the LMCT GSB, it likely results from an overlapping −ΔmOD and therefore could be related to IVR or ISC. Finally, we note that the large ESA observed also invalidates attributing 6.63 ps τ_1 or 0.6 ps τ_2 to an ISC, since excited state absorptions will primarily be determined by the electronic structure, regardless of whether the initial state is a singlet or triplet with respect to the ground state.

To model the kinetics at probe wavelengths (500 nm) where the ESA and GSB/SE overlap, the amplitudes of four exponentials with fixed time constants determined above (0.18, 0.60, 6.63, and 455 ps) were fit to each trace. As seen in Figure 7c and Figure S10 of the Supporting Information, these fixed time constants generate curves that match the data well, suggesting that these are the main time constants involved. The contributions of each can be clearly illustrated by the changes in sign of the transient signal. Immediately after excitation, the GSB/SE (−ΔmOD) is the most prominent, decaying within 0.18 ps. After the picosecond, the GSB/SE signal has decayed enough such that the signal is dominated by the ESA which lasts for 6.63 ps. The decay of the ESA results in a second sign change and the reemergence of the longer lived, 455 ps GSB (−ΔmOD) as the dominant signal. Given the long time constant of τ_2, we can safely associate it with a pure GSB decay rather than SE signal. The decay kinetics in this region of spectral overlap show that a separate time constant to account for the ESA of S_1 is not required to fit the traces. This suggests that the ESA of S_1 decays concomitantly with its associated GSB, or the 455 ps τ_2 time constant. While for S_2 there are spectral regions where the ESA dominates leading to a separately measured time constant in the GSB and ESA, for S_1 the GSB dominates the spectrum throughout.

Having given some of the evidence for IC between two charge transfer states through the kinetics of the GSB/SE and the ESA, we now turn to the assignment of the ESA spectrum. Since DFT calculations show that the majority of the higher lying excited states to which there could be an absorption are of LMCT character (Figures S3 and S4 of the Supporting Information), the contributions to the ESA from S_2(d) are likely. A positive assignment of the ESA to higher-lying LMCT states comes from the energy of d transitions obtained by XAS of the O K-edge (Figure 5). The ESA peaked at 550 nm (2.3 eV) (Figure 6b) comes very close to the splitting (2.2 eV) of the two lowest pre-edge peaks in the XAS spectrum, uniquely assignable to d-d transitions with significant O 2p character and discussed above. A 2.2 eV absorption also agrees with d transitions in vanadium(IV) compounds in the literature.

While a positive assignment can be made based on the energy of the ESA and the XAS data, there are in principle, three other possible transitions that could account for the ESA: MLCT, dication LMCT, and intraligand transitions. A dication LMCT transition is the least likely candidate as removal of a second electron from the ligand to create a dication is highly unfavorable and such a transition is expected to appear significantly blue-shifted from the LMCT. An excited state MLCT transition could come from excitation of the electron in V d LUMO orbitals to a higher-lying ligand LUMO orbital. However, in our TD-DFT calculations, we do not see any pure MLCT transitions up to 3.0 eV away from the relaxed states. The intraligand hole excitation to lower-lying HOMO orbitals is the only real alternative to a higher-lying LMCT state as an assignment of the ESA. Ideally, one would perform spectroelectrochemical measurements of the ligand to determine the UV–vis spectrum of the ligand cation. Unfortunately, electron or hole transfer by electrochemistry decomposes the ligand. In the measurements done, the tail of a new UV absorption near 375 nm is observed with no accompanying absorptions above 400 nm. Oxidative and reductive spectroelectrochemistry of VOL reveals complex decomposition without discernable formation of redox products by optical absorption spectroscopy. Furthermore, subtraction of the normalized absorption spectrum of VOL from the one-electron reduced or oxidized VOL does not furnish meaningful data. Indeed, cyclic voltammetry of VOL in THF shows irreversible one-electron redox couples (see the Supporting Information for cyclic voltammetry of VOL and spectroelectrochemical characterization of VOL and H_2L^2 in Figures S17 and S18 of the Supporting Information.)

In order to clarify the roles of the ligand hole and S_2(d) to the ESA, singular value decomposition (SVD) transformation of our transient data was carried out, and a global analysis subsequently applied (refer to the Supporting Information for details). For our global analysis, we applied the general model (eq 1) used in our earlier fits to the resultant SVD kinetic basis vectors and extracted the global time constants associated with the excited state without regard to particular spectral regions (Figure S13a of the Supporting Information). The best fit for the global analysis was obtained from a tetraexponential function, producing decays of 141 and 777 fs and 6.85 and 423 ps, in good agreement with the parameters obtained from our prior fits. The corresponding normalized decay-associated spectra (DAS) (refer to the Supporting Information), reflective of the relative spectral contributions for each time constant, are shown in Figure 8.

At early times following excitation, the creation of the initial charge transfer excited state is illustrated by DAS1, consisting of both an LMCT GSB and the ESA (141 fs, Figure 8). Importantly, the 423 ps spectrum, DAS4 is nearly identical to DAS1 in both the LMCT GSB and the ESA. The fact that an
ESA persists at longer timescales and is so similar to the initially excited charge transfer state points to the fact that the long-lived state is indeed of charge transfer character. However, the similarity of the ESA at the two timescales might not at first seem consistent with the involvement of two different charge transfer states, S\(_1\) and S\(_3\). This could be reconciled by an ESA of common origin for the two states agnostic of the excited state electron character, with the most likely candidate being a ligand hole absorption. The similarity in DAS1 and DAS4 likely comes from the fact that, in both, the GSB reports on the unexcited population through the S\(_1\) \(\rightarrow\) S\(_0\) transition, while the ESA reports on the total excited state population through the ligand hole transition. Furthermore, the ESA of DAS1 and DAS4 also occurs in DAS2 and DAS3, and is therefore present throughout the ground state recovery, again indicating an ESA of common origin.

On the other hand, a comparison of the decay-associated spectra at intermediate times (DAS2, 777 fs and DAS3, 6.85 ps) with the early/late DAS reveals an additional ESA. The ESA is slightly blue-shifted from the excited state population after IVR and ISC in the initial picosecond. For the \(\Delta mOD\) to be time independent at 485 nm from 1 to 36 ps, the extinction coefficients must be, at 485 nm, related in the following way: \(-\epsilon^3_{\text{LMCT}} + \epsilon^3_{\text{d-d}} = -\epsilon^3_{\text{LMCT}} + \epsilon^3_{\text{d-d}}\). In order to see if this is viable, we can utilize extinction coefficients for the LMCT back to \(S_0\) and for the ESA transitions to \(S_n(d)\) (summed over 2.0 to 2.5 eV) calculated by TD-DFT for both states (Tables S2 and S3 of the Supporting Information). Since the extinction coefficients reported in the tables indicate an average magnitude, most attributable to the peak energy of the transitions, we scale these first by the amount the extinction coefficient would decrease from the peak energy to 485 nm, a wavelength significantly to the blue of the LMCT transition and to the red of the ESA transition to \(S_n(d)\).

For the LMCT transition, the scaling is 50% from the UV–vis absorption. The ESA transition to \(S_n(d)\) is harder to estimate, but DAS2 and DAS3 suggest that 10% as a higher bound is reasonable. With these considerations, the equation roughly holds, where it is imbalanced by \(\sim4\%\) of the transition dipole for the initial S\(_1\) \(\rightarrow\) S\(_0\) transition. A final note on these extinction coefficients is that the deconvolved spectra (DAS2 and DAS3) and the TD-DFT calculations suggest that \(\epsilon^3_{\text{LMCT}} \sim \epsilon^3_{\text{d-d}}\). While extinction coefficients are generally much weaker for d-d than LMCT transitions, these d-d transitions really involve two LMCT states, which can significantly enhance optical d-d transitions from what one would normally expect in the ground state.\(^{45–47}\)

**DISCUSSION**

Taken together, the results show that a long-lived excited LMCT state is created by internal conversion between two CT states, differentiated by their V d-character: \(S_n(d)\) and \(S_0(d)\). The evidence comes from (1) an isosbestic point at intermediate timescales (from 1 to 36 ps); (2) after the initial picosecond of IVR/ISC, the recovery of the LMCT GSB with two time constants (6.8 and 423 ps); (3) a distinct 6.8 ps decay observed independently in the kinetic traces of the ESA and DAS3, within the time window of the isosbestic point and, therefore, assignable to internal conversion; (4) unique DAS spectra at intermediate timescales (0.78 ps, 6.8 ps), where the energy of the ESA can be assigned to a transition to \(S_n(d)\),
corroborates interpreting the isosbestic point as coming from an internal conversion between different excited electronic states; and (5) a DAS spectrum at 423 ps that still exhibits an ESA, likely related to a ligand hole. Corroborating this evidence are TD-DFT calculations that suggest a two state model where internal conversion between \( S_1(d_{xy}) \) and \( S_1(d_{yz}) \) is likely by symmetry. Further, they suggest a higher transition dipole of \( S_1(d_{xy}) \) to \( S_0(d) \) than for \( S_1(d_{yz}) \), explaining why a 6.8 ps decay related to internal conversion can be isolated from the ESA. Finally, the TD-DFT calculations for the different transition dipoles also show that an isosbestic point is viable.

Figure 9 depicts the kinetic pathway that results from this internal conversion. For the purposes here, we are concerned with the longer timescales associated with this internal conversion rather than the initial ISC/IVR of 0.14 ps found in the LMCT GSB and for the earliest DAS spectra. We note that this time constant, if attributable to IVR, could involve relaxations from both \( S_0^*(d_{yz}) \) and \( S_0^*(d_{xy}) \), until they end up in relaxed states of the same symmetry (Figure 4). Understanding this fast decay fully is set aside for later experiments, as internal conversion is similarly possible from singlet or triplet states. After a combination of IVR and ISC within 0.14 ps, the initial wave packet excited by the pump ends up in a still unthermalized \( S_0^*(d_{yz}) \) state, given that thermalization timescales are usually longer and that there are two time constants associated with \( S_0 \) based on the two DAS spectra (0.78 and 6.82 ps). We assign the 0.78 ps time constant \( (\tau_0) \) to thermalization of \( S_0^*(d_{xy}) \) to \( S_0(d_{xy}) \), though in this case \( S_0^*(d_{yz}) \) is not necessarily the initially excited Franck–Condon state but has unoccupied electron density on \( \pi \) orbitals. Together, the minimal electron weight on the bridging oxygen to \( \pi \) and the \( \pi \) occupation of \( S_0^* \) leads to a very small transition dipole for \( S_0(d_{xy}) \to S_0^* \) [Table S2 of the Supporting Information or ~10% of the initially excited transition to \( S_0^* \)]. Furthermore, Franck–Condon overlap between low energy vibration modes of \( S_1(3d_{yz}) \) with the ground state is negligible (<10^-8). While \( S_0^* \) does lie higher in energy than \( S_0 \), the energy difference is small.

Given the significant distortions in the unoccupied density of \( S_0^* \), with the weight on the \( \pi \) orbital, one could ask whether or not the lifetime of the excited charge transfer state \( S_1(3d_{yz}) \), would also be long if the \( S_1(3d_{yz}) \) state was not available. While the TD-DFT and MSCASPT2 indicate that the overlap of \( S_1(3d_{yz}) \) with the distorted ground state leads to a very small transition dipole, it is still significant for \( S_1(3d_{xy}) \). While the transition dipole between \( S_1(3d_{yz}) \) with the same distorted ground state is indeed reduced, it is still 10% of the initially excited transition to \( S_0^* \), the energy difference is small.

The long lifetime is ascribed to internal conversion from the initially excited state to a nearby charge transfer state, \( S_1(3d_{yz}) \), with poor optical and vibrational overlap to a distorted ground state. In conjunction with no observed photoluminescence, the long lifetime is attributed to a nonradiative transition with little opportunity to release its energy to vibrations. Future work will investigate the universality of this type of long-lived charge transfer in 3d metal-centered compounds by transient absorption and TD-DFT, along with uses for VOL and related compounds containing \( d^0 \) LMCT transitions for driving photochemical reactions.

### CONCLUSION

In conclusion, a long-lived (423 ps) LMCT state is found in a 3d metal-centered compound, VOL. The long lifetime is ascribed to internal conversion from the initially excited state to a nearby charge transfer state, \( S_1(3d_{yz}) \), with poor optical and vibrational overlap to a distorted ground state. In conjunction with no observed photoluminescence, the long lifetime is attributed to a nonradiative transition with little opportunity to release its energy to vibrations. Future work will investigate the universality of this type of long-lived charge transfer in 3d metal-centered compounds by transient absorption and TD-DFT, along with uses for VOL and related compounds containing \( d^0 \) LMCT transitions for driving photochemical reactions.

### ASSOCIATED CONTENT

#### Supporting Information

Synthesis and characterization of \( \text{H}_2\text{L}^3 \) and VOL, and further experimental details for X-ray crystallography (CCDC 1027781), DFT calculations, X-ray absorption measurements,
 ultrafast and nanosecond transient absorption, and photoluminescence measurements. These details include: NMR, FT-IR spectra; a cyclic voltammogram and spectroelectrochemistry of VOL\(^{\#}\) (characterization); unit cell determination and comparison of experiment to theoretical geometries (crystallography); a full molecular orbital diagram and decomposition of the major contributions to the LMCT transition and calculated transition dipoles for ground-state bleaches and excited state absorptions (theory); group velocity dispersion (GVD) correction, singular value decomposition (SVD) spectrally resolved global fits of kinetic traces; as well as global analysis to generate decay-associated spectra (ultrafast transient absorption). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b00513.

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Notes

The authors declare no competing financial interest.

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