Photoaquation Mechanism of Hexacyanoferrate(II) Ions: Ultrafast 2D UV and Transient Visible and IR Spectroscopies

Marco Reinhard, Gerald Auböck, Nicholas A. Besley, Ian P. Clark, Gregory M. Greetham, Magnus W. D. Hanson-Heine, Raphael Horvath, Thomas S. Murphy, Thomas J. Penfold, Michael Towrie, Michael W. George, and Majed Chergui

†Ecole polytechnique Fédérale de Lausanne, Laboratoire de spectroscopie ultrarapide, ISIC, and Lausanne Centre for Ultrafast Science (LACUS), FSB, Station 6, CH-1015 Lausanne, Switzerland
‡School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom
§Central Laser Facility, Research Complex at Harwell Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, United Kingdom
¶School of Chemistry, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom
∥Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, 199 Taikang East Road, Ningbo 315100, China
*Supporting Information

ABSTRACT: Ferrous iron(II) hexacyanide in aqueous solutions is known to undergo photoionization and photoaquation reactions depending on the excitation wavelength. To investigate this wavelength dependence, we implemented ultrafast two-dimensional UV transient absorption spectroscopy, covering a range from 280 to 370 nm in both excitation and probing, along with UV pump/visible probe or time-resolved infrared (TRIR) transient absorption spectroscopy and density functional theory (DFT) calculations. As far as photoaquation is concerned, we find that excitation of the molecule leads to ultrafast intramolecular relaxation to the lowest triplet state of the [Fe(CN)6]4− complex, followed by its dissociation into CN− and [Fe(CN)5]3− fragments and partial geminate recombination, all within <0.5 ps. The subsequent time evolution is associated with the [Fe(CN)5]3− fragment going from a triplet square pyramidal geometry, to the lowest triplet trigonal bipyramidal state in 3−4 ps. This is the precursor to aquation, which occurs in ∼20 ps in H2O and D2O solutions, forming the [Fe(CN)5(H2O/D2O)]3− species, although some aquation also occurs during the 3−4 ps time scale. The aquated complex is observed to be stable up to the microsecond time scale. For excitation below 310 nm, the dominant channel is photooxidation with a minor aquation channel. The photoaquation reaction shows no excitation wavelength dependence up to 310 nm, that is, it reflects a Kasha Rule behavior. In contrast, the photooxidation yield increases with decreasing excitation wavelength. The various intermediates that appear in the TRIR experiments are identified with the help of DFT calculations. These results provide a clear example of the energy dependence of various reactive pathways and of the role of spin-states in the reactivity of metal complexes.

INTRODUCTION

Most of natural and preparative (bio)chemistry occurs in the liquid phase. The solvent molecules are by no means spectators as they affect the outcome of the reactions in different ways, either dynamically by influencing the course of the reaction, for example, hindering it as in the so-called cage effect1 or accelerating it offering a driving force to the escape of fragments into the solvents,2,3 or statically by introducing relative energy shifts of the reactive potential surfaces on which the reactions (including photochemical ones) occur, according to the nature (covalent, charge transfer or, even Rydberg) of the states.

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involved.4 For many years now, since the historical work by Frank and Rabinowitsch,1 the physical effects of the solvent cage on photochemical reactions have been intensely studied by steady-state4–8 and time-resolved methods3,6–8 on a wide class of systems. Less studied are the chemical pathways of the solution phase where intermediates react with solvent species, as discussed in a recent review.3 The complexity of such processes arises from the fact that either the excited solute or a nascent product sees a complex potential surface in its interaction with solvent molecules, which no longer just provide a barrier or a funnel to it but participate in the chemical reaction depending on several aspects such as the nature of the reactants, their translational kinetic energy, their internal (electronic, vibrational, rotational) energy, their orientation, etc.

In attempting to describe liquid phase photochemistry, fundamental questions arise, which concern (a) the role of the initially excited state, (b) the interplay between intramolecular relaxation (electronic or vibrational) in the solute and intermediates and the subsequent reactivity with solvent molecules, (c) the role of spin states of both educts and products, and (d) the role of the excess energy dependence of the photochemical reactions. While a larger excess of kinetic energy of the fragments allows overcoming “physical” solvent cage barriers,5,9 the question remains open for the case of chemical reactions.

In addressing these questions, ligand substitution reactions and redox decomposition processes of metal complexes have been the topic of several mechanistic studies in coordination chemistry because of the fundamental role these reactions play in various chemical, biological, and catalytic processes.10,11 In such systems, ultrafast intramolecular energy relaxation processes, such as internal conversion (IC), intersystem crossings (ISC), and intramolecular vibrational energy redistribution (IVR) in the solute may precede the reaction or be concurrent to it. These processes may also occur in the products if these are formed in excited states. In addition, intermolecular processes such as solvation dynamics, may take place concurrently with the above intramolecular ones,9 and the spin multiplicity plays a crucial role in the reactions leading to ligand substitution.12

Metal carbonyls have been among the most studied systems, probably because they offer the possibility to compare the photochemistry of the isolated molecule with that in condensed phases. Studies of the latter include UV photolysis in low temperature inert matrices3,13 and several ultrafast spectroscopic studies in solution using transient absorption (TA) in the visible10–19 and in the infrared.20–24 More recently, ultrafast studies on the photochemistry of Fe(CO)5 in solution have been pushed into the X-ray domain with an Fe K-edge X-ray absorption study reported by Rose-Petruck and co-workers,25 while Wernet et al.26,27 implemented femtosecond Fe L3-edge resonant inelastic X-ray scattering (RIXS) at the X-ray Free Electron laser in Stanford. RIXS is a variant of X-ray emission spectroscopy and is a sensitive probe of the spin state of molecular systems. The studies on the photoinduced dynamics of Fe(CO)5 in EtOH suggest formation of the [Fe(CO)4(EtOH)]+ complex, and the role of the spin state of the Fe(CO)5 product is still debated. Wernet et al.26 reported a singlet complex on sub-picosecond time scales, which was ascribed to a barrier-less bimolecular reaction where steric effects such as ethanol reorientation and concomitant hydrogen-bond breaking are absent or can easily be overcome.25 This fast photosubstitution is in line with reports of CO-ligand substitution of [Cr(CO)4(bpy)] by solvent molecules,28–32 from a vibrationally “hot” excited state, alongside relaxation into two lower-lying unreactive states. In this case, dependence on excess energy was observed as the quantum yield of the reaction increased with excitation energy. It was argued that vibrational excitation provides sufficient distortion of the reacting molecule in the direction of the transition state whose structure was described as being similar to that of the undisassociated excited molecule.

Photoaquation is a particular case of the broader class of ligand substitution reactions in solutions and its understanding is particularly relevant to biology.10,33 It was recently studied in the case of cis-[Ru(bpy)3(CH3CN)2]Cl2 in water, showing the stepwise replacement of each CH3CN ligand by an H2O molecule,34 with the formation of the monoqua cis-[Ru(bpy)3(CH3CN)(H2O)]2+ taking place in <100 ps. Some of the earliest examples of studies on photoaquation concern metal cyanide systems,35–38 such as the [FeII(CN)6]4− ion, whose absorption spectrum is shown in Figure 1. The peculiarity of this system stems from the fact that it is a highly charged ion that has a strong interaction with the solvent.39,40 Both oxidation (eq 1) and aquation (eq 2) processes have been reported upon irradiation in the UV–visible range:41,42

$$\text{[Fe(CN)6]}^{3+} \rightarrow [\text{Fe(CN)6}]^{3-} + e_{\text{aq}}$$

(1)

$$\text{[Fe(CN)6]}^{3+} + \text{H}_{2}\text{O} \rightarrow [\text{Fe(CN)6(H2O)}]^{3-} + \text{CN}^-$$

(2)

With the advent of ultrafast laser techniques, detailed femto- and picosecond TA studies of the photooxidation reaction (eq 1) have been performed.43–46 It is generally believed that this reaction is a consequence of direct or indirect population of the charge-transfer-to-solvent (CTTS) state (Figure 1).41 A tentative assignment of the very short-lived (≈60 fs) CTTS state, absorbing around 490 nm upon 267 nm excitation was made by ultrafast transient absorption (TA),42 but it was assumed that the initially populated 1T2g-state relaxes into the CTTS state, and therefore, the authors could not unambiguously distinguish between these two states. Ultrafast fluorescence up-conversion also failed to detect the CTTS...
state of $[\text{Fe(CN)}_6]^3^−$, contrary to the case of aqueous iodide.\textsuperscript{47}

Anderson et al.\textsuperscript{46} investigated the ionization process upon 266 nm excitation using time-resolved infrared (TRIR) spectroscopy. Their transient spectra in the $\nu(\text{CN})$ region in D$_2$O show a significant baseline offset, which they attributed to a direct precursor of the presolvated electron generated by excitation of the CTTS state. Furthermore, they observed a short-lived absorption peak red-shifted by ca. 2 cm$^−1$ from the parent ion (at 2038 cm$^−1$) as well as a band at 2114 cm$^−1$ due to the photoionized product $[\text{Fe(CN)}_5]^3^−$. The appearance of the latter at the earliest time delays indicates electron ejection in less than 200 fs.\textsuperscript{45}

The photoaquation reaction (eq 2) is less well understood. It is triggered by excitation of weak Laporte-forbidden ligand-field (LF or metal-centered) states ($\epsilon < 400$ M$^−1$cm$^−1$) for $\lambda > 300$ nm\textsuperscript{40} or, with a lower yield, in the ~245–300 nm range, where the CTTS and LF bands overlap (Figure 1). Using flash photolysis, Shirom and Stein\textsuperscript{42} identified the photoaquated complex. The latter undergoes conformational changes predominantly prior to binding of a water molecule. Further details about the experimental and computational setups and procedures as well as the data treatment are given in the Supporting Information (SI).

## EXPERIMENTAL SECTION

### Time-Resolved Infrared (TRIR) Spectroscopy

TRIR spectroscopy was carried out using the ULTRA facility located at the Rutherford Appleton Laboratory, using time-resolved multiple probe spectroscopy (TR$^\text{MPS}$) on the ULTRA and LIFETIME instruments. Detailed descriptions of the experimental setups have been published previously.\textsuperscript{40,59} Briefly, the TR$^\text{MPS}$ experiment utilizes a pump–probe–probe–probe... recording scheme afforded by synchronizing two oscillators with the pump laser tuned to 320 or 266 nm by optical parametric amplification (OPA) while the mid-IR probe is generated using OPAs with difference-frequency mixing units. The pump–probe time delay is controlled using a combination of electronic and optical delays, which allows time delays from picoseconds to milliseconds to be achieved in a single experiment. The instrument response (TRIR) is approximately 300–400 fs. The pump pulse was set to ca. 1 µJ/pulse at the sample using a neutral density filter. Pump and probe beam polarizations were set at the magic angle. Where necessary, a portion of the probe beam was dispersed onto an MCT detector as a reference, while the remainder was passed through the sample, dispersed by grating monochromators and detected by 128-channel linear MCT detectors. Pump and probe beam intensities were set at the magic angle. Where necessary, a portion of the probe beam was dispersed onto an MCT detector as a reference, while the remainder was passed through the sample, dispersed by grating monochromators and detected by 128-channel linear MCT array detectors. $[\text{Fe(CN)}_5]^3^−$ samples were measured in unbuffered H$_2$O and D$_2$O (18 mM) and were circulated in a closed flow system attached to a Harrick solution cell with CaF$_2$ windows, spaced by 100 µm with Teflon spacers. The sample cells were rastered in the two dimensions orthogonal to the direction of beam propagation in order to minimize sample breakdown and localized heating. The spectral resolution is ca. 1.5 cm$^−1$.

### Two-Dimensional Ultraviolet (2D-UV) Spectroscopy

A detailed description of the setup was recently published.\textsuperscript{55,57} Laser pulses from a cryogenically cooled Ti:sapphire amplifier (Wyvern, KM Laboratories) running at 20 kHz pump a noncollinear optical parametric amplifier (NOPA, TOPAS white, Light Conversion) whose output serves as primary light source of the experiment. One third of the generated visible light passes a motorized delay line and subsequently an achromatic frequency doubling stage, which delivers

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Table 1. IR, UV, and Visible Bands and Their Kinetics upon 320 nm Excitation of [Fe(CN)6]4− in H2O (D2O)4

<table>
<thead>
<tr>
<th>frequency (cm−1)</th>
<th>vibrational bands in H2O (D2O)</th>
<th>electronic bands in H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tsize (ps)</td>
<td>tdecay (ps)</td>
</tr>
<tr>
<td>2038 (bleach)</td>
<td>&lt;0.5 (&lt;0.5)</td>
<td>rIR,IR ≈ 2117 &lt;0.5 (&lt;0.5)</td>
</tr>
<tr>
<td>2050−2090</td>
<td>&lt;0.5 (&lt;0.5)</td>
<td>rIR,IR ≈ 2090 &lt;0.5 (&lt;0.5)</td>
</tr>
<tr>
<td>2086</td>
<td>&lt;1 (&lt;1)</td>
<td>26 ± 4,6 (22 ± 4)</td>
</tr>
<tr>
<td>2090</td>
<td>r = 4 ± 2 (3 ± 2)</td>
<td>rIR,IR ≈ 2090 &lt;0.5 (&lt;0.5)</td>
</tr>
<tr>
<td>2060</td>
<td>r = 4 ± 2 (3 ± 2)</td>
<td>rIR,IR ≈ 2090 &lt;0.5 (&lt;0.5)</td>
</tr>
<tr>
<td>2026, 2049, 2088</td>
<td>r = 19 ± 4 (23 ± 5)</td>
<td>rIR,IR ≈ 2090 &lt;0.5 (&lt;0.5)</td>
</tr>
<tr>
<td>2117</td>
<td>&lt;0.5 ≈ rIR,IR</td>
<td>rIR,IR ≈ 2090 &lt;0.5 (&lt;0.5)</td>
</tr>
</tbody>
</table>

“SP stands for square pyramidal, TBP stands for Trigonal bipyramidal. 6An additional <1 ps contribution is observed, which can be attributed to overlap with the CN− band (see Figures 7 and S8). The time scale is affected by overlap with the 2090 cm−1 band of the TBP species. 7It is difficult to resolve the experimental band at 2026 cm−1 due to overlap with the parent bleach. The assignment is done on the basis of band-fitting, DFT calculations (Table S2), and previous work. 45 An additional 4 ps transient is observed.

The photochemistry [Fe(CN)6]4− in aqueous solutions had previously been reported11,42 for only a few fixed excitation wavelengths. In addition, the ultrafast visible44 and IR45 studies carried out so far only considered excitation into the CTTS states of [Fe(CN)6]3− at 266 nm (Figure 1 and eq 1). Here we complement these studies by covering the excitation range from 280 to 330 nm, using two-dimensional UV transient absorption spectroscopy in H2O and O and focus on specific excitation wavelengths using TRIR in H2O and D2O. Given the scarcity of ultrafast studies, it is important to benchmark our TRIR experiments against those previously reported under 266 nm excitation. 43

TRIR spectra of [Fe(CN)6]4− in H2O and D2O at fixed time delays following excitation at a pump wavelength (λpump) of 266 nm are shown in Figures S1 and S2. There is a significant baseline offset at early times, in agreement with previous studies that assigned the change in the baseline to the precursor of the presolvated electron. The parent band (2038 cm−1) is bleached, and a new transient peak at 2117 cm−1 is visible within ~1 ps, with the earlier times obscured by the baseline offset mentioned above. The band at 2117 cm−1 is due to formation of the ferricyanide ion, [Fe(CN)6]3−, consistent with ref 45. The parent band of [Fe(CN)6]4− and 3−, consistent with ref 45. The kinetic traces of significant bands for the sample in H2O are shown in Figure S3 and are similar in the case of D2O. There is a partial recovery of the parent with a concomitant partial decrease of the intensity of the 2117 cm−1 band observed on the nanosecond time scale, fully consistent with the partial recombination of the solvated electron with [Fe(CN)6]3−. The [Fe(CN)6]3− band then persists up to the longest time delays in our experiment (Figure S2). At early times (Figure S3a), an apparent partial recovery of the parent bleach band at 2038 cm−1 occurs on a time scale of t = 20 ± 5 ps. The band frequencies and their time scales are summarized in Table 1. A band is also observed at ~2088 cm−1 at early times, whose decay seems to be independent of the
[Fe(CN)₆]³⁻ band at 2117 cm⁻¹. We will come back to it later.

In order to disentangle contributions from different photochemical channels, we now turn to 2D UV TA spectroscopy. Figure 2 shows the 2D UV TA spectra (ΔA) of aqueous [Fe(CN)₆]⁴⁻ as a function of pump (λ_pump) and probe (λ_probe) wavelengths at selected delays (Δt = 0.5, 1, 4, and 50 ps). After 50 ps, there is only little change in the observed transient signals, which remain stable up to the limit of our temporal window (∼780 ps). Two main trends characterize the time and spectral evolution of the system as a function of λ_pump: one below ∼310 nm, and the other above. There is a clear dependence of the appearance of spectral features on λ_pump.

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Upon excitation into the CTTS region (ca. 290 nm), the transient ground state [Fe(CN)₆]³⁻ absorption bands can be identified, resulting from photooxidation (dashed red line in 50 ps window). The [Fe(CN)₆]³⁻ band is formed within our time resolution (∼150 fs) and partially decays due to recombination with the photoejected electrons.

At lower energy, in the region of the ¹T₁g absorption (blue line in Figure 2), a <1 ps-lived positive signal appears, which is most pronounced in the highest-energy part of the probe range (<280 nm). At λ_probe < 340 nm, this signal decays and becomes negative such that by ∼50 ps, it resembles the inverted static [Fe(CN)₆]⁴⁻ absorption spectrum (Figure 2, 50 ps window, red line), reflecting a long-lived ground state bleach. At λ_probe > 340 nm, the signal remains positive, indicating a long-lived
absorption band. Therefore, direct excitation of the $^1T_{1g}$ state yields long-lived species, which are not explained in terms of a photooxidized product, [Fe(CN)$_6$]$^{3+}$. In the following, we will mainly focus on results obtained at $\lambda_{\text{pump}} = 284$ nm and $\lambda_{\text{probe}} = 320$ nm, which are representative of the processes described by eqs 1 and 2.

As discussed before, previous time-resolved optical and X-ray studies, showed that photoaquation is the favored process after $^1T_{1g}$ excitation (320 nm), while the signal upon <300 nm excitation is predominantly due to photooxidation. Figures 3a,c compare the transient spectra at 284 and 320 nm excitation, at different integrated pump–probe delay windows. Relatively large temporal integration ranges are chosen for enhanced clarity, but all conclusions are confirmed by averages over smaller ranges (Figures S4 and S5). Both figures show a dominant absorption in the blue most part (<300 nm) of the probe range, which quickly disappears (within 1–2 ps), leaving the transient with a profile that does not evolve much thereafter. In Figure 3a, the transients at later times are dominated by the broad absorption (from about 285 to 355 nm) of the $^2T_{2g} \rightarrow ^2T_{2u} (t_2gπ \rightarrow t_2gσ)$ ligand to metal charge transfer (LMCT) band of [Fe(CN)$_5$(H$_2$O)]$^{3+}$ and the solvated electron (as demonstrated below). In Figure 3c, the transients show weak negative (bleach) and positive signals, which we discuss hereafter.

The solvated electron is characterized by an extinction coefficient that is much larger than that of all other photoproducts as can be seen in Figure S6. This induces a significant offset of the signals at all time delays. In order to identify the spectral features in Figures 3a,c, the extinction coefficients ($\epsilon$) of the expected photoproducts were used to simulate the final transient spectra. For the transient obtained under 284 nm excitation, the extinction coefficient is calculated as $\epsilon_{284nm} = 8 \times 10^{-7}(\epsilon_{[\text{Fe(CN)}_6]^{3+}} + \epsilon_{[\text{Fe(CN)}_6]^{4+}} - \epsilon_{[\text{Fe(CN)}_6]^{4-}})$. The coefficients $\epsilon_{[\text{Fe(CN)}_6]^{3+}}$, $\epsilon_{[\text{Fe(CN)}_6]^{4-}}$, and $\epsilon_{[\text{Fe(CN)}_6]^{4+}}$ are known from the literature (Figure S6). The resulting $\epsilon_{284nm}$ is shown as a black dashed line in Figure 3a, and it overall agrees with the transient spectrum at the longest time delays (purple trace) despite some deviations between 295 and 330 nm.

In the case of 320 nm excitation, the most likely final product is the aquated species. We therefore calculate $\epsilon_{320nm} = 8 \times 10^{-7}(\epsilon_{[\text{Fe(CN)}_6(H_2O)]^{4+}} - \epsilon_{[\text{Fe(CN)}_6]^{4+}})$, where the value of $\epsilon_{[\text{Fe(CN)}_6(H_2O)]^{4+}}$ is taken from literature. The result is shown as a black dashed line in Figure 3c, and it nicely reproduces the shape of the longest time delay transient, confirming the presence of the photoaquated species [Fe(CN)$_5$(H$_2$O)]$^{3+}$. The rising signal in the low energy part of the spectrum therefore likely reflects the tail of the $^1A_1 \rightarrow ^1E(1)$ absorption band of [Fe(CN)$_5$(H$_2$O)]$^{3+}$, which is centered around 440 nm in the static absorption spectrum.

This is confirmed by probing at lower energies, in the 380–480 nm region, and Figure 4a shows the TA spectra in this region, averaged over different temporal windows. Absorption features appear within ~0.7 ps with maxima at ~0.4 and >470 nm. After a fast initial decay, further evolution of the transient occurs with minor changes around 410 nm. At times >1 ps, the TA spectrum (dark blue and purple traces) converges to the static difference spectrum of the [Fe(CN)$_5$(H$_2$O)]$^{3+}$ ($^1A_1 \rightarrow ^1E(1)$ transition) and [Fe(CN)$_6$]$^{4-}$ absorption ($\epsilon_{320nm}$ black dashed trace).

In order to gain a quantitative understanding of the 2D UV data, a global fit (GF) was carried out. Four exponential time scales are required in the photoaquation regime (320 nm excitation, see below). For both 284 and 320 nm excitation, transient spectra at ~50 ps delay still show small changes (Figures 3, S4, and S5), presumably due to slow, nonexponential recombination kinetics of the corresponding photochemical species; these changes are not properly captured by our multiexponential kinetic model. Therefore, the inclusion of an additional time scale is avoided in favor of a more stable fit model. This strategy and the extracted time constants are fully confirmed by the IR results presented below. Fitting the initial decay requires two exponential time scales ($\tau_1 = 0.5$ ps, $\tau_2 = 4$ ps), a stretched exponential fit was attempted, but it poorly reproduced the data. An additional time constant of ~16 ps ($\tau_3$) is needed to capture the intermediate times. Representative kinetic traces for 284 and 320 nm excitation are shown in Figure 3b,d, together with their fits. The time constant for the longest process obtained from the GF of the 2D UV data set is $\tau_4 \approx 7$ ns ($\tau_4$), but this value should be considered as an order of magnitude due to the limited range of the data set. The fitted time constants are summarized in Table 1.

To disentangle the spectral components making up the full 2D UV data set, we also applied a singular value decomposition (SVD) as described in refs S7 and S6 and in section S4. The SVD analysis of the 2D UV data set yields 2D decay associated dispersed action spectra (DADAS) corresponding to the four decay constants ($\tau_1 = 0.5 \pm 0.1$ ps, $\tau_2 = 4 \pm 2$ ps, $\tau_3 = 16 \pm 3$ ps, $\tau_4 \approx 7$ ns). All spectra are subsequently corrected for the photolysis yield (section S2) in order to obtain signal magnitudes, which are directly comparable with quantum yields. The extracted four DADAS are plotted in Figure S7 and their detailed description is given in section S4.2. The consistency of the extracted parameters is confirmed by a fit of the kinetic traces integrated over the spectral regions 380–410 and 410–470 nm. The choice of these regions is justified by the spectral evolution shown in Figure 4a. Assuming that the above four time scales of the UV-probe experiment also occur in the visible-probe region, we obtain a satisfactory fit of the kinetics, notwithstanding the poor signal-to-noise ratio (Figure 4b). Since the visible probe measurements were limited by an IRF of $\tau_{\text{IRF,visible}} \approx 690$ fs (see Experimental Section), we left out the fastest component in this analysis. The ~7 ns component appears in the analysis of both the 284 nm and
the 320 nm excitation data. As already mentioned, this time scale is much longer than the time range of the measurements and is, therefore, only indicative of slow processes that reflect the long-lived species upon 320 nm excitation or the electron–ferricyanide recombination upon 284 nm excitation.

With these elements in hand, we then extract the DAS in the combined UV–visible probe range for 320 nm excitation, which are shown in Figure S5b, while Figure 5a shows the steady state spectra of \([\text{Fe(CN)}_6]^{4-}\) and of the aquated form. The 0.5 ps \((\tau_1)\) DAS is only constructed for the UV range due to the limited time resolution in the visible range, and it essentially shows the fast decay of the induced absorption peaking below 280 nm. In the visible range, an absorption band centered at \(\lambda_{\text{probe}} \approx 460\) nm also appears within the time resolution of the experiment (see Figure 4a). The 4 ps \((\tau_2)\) DAS reflects a second, slower decay component of the induced UV (<320 nm) absorption and some spectral intensity redistribution from 410–480 nm to 380–410 nm of the absorption in the visible range. The 16 ps \((\tau_3)\) DAS displays a ground state bleach recovery below 320 nm, and it mirrors the 4 ps DAS above 330 nm, pointing to an intensity redistribution back from 380–410 nm to 410–480 nm. The prominent negative feature of the 16 ps DAS in the 410–480 nm region reflects the rise of the \(\sim 7\) ns \((\tau_4)\) DAS that has a broad and intense absorption covering the 380–480 nm range. The \(\sim 7\) ns DAS is nicely reproduced by \(\varepsilon_{320\text{nm}}\) (see above), and it can therefore be assigned predominantly to the \([\text{Fe(CN)}_5(H_2O)]^{3-}\) complex. As seen from the scaling factor in Figure 4a, the photolysis yield is considerably lower in the visible probe experiments. This is consistent with calculated excitation yields (see section S2) and the larger sample thickness in the latter experiment, which is expected to enhance absorption effects. Therefore, the dynamics in the \(\lambda_{\text{probe}} < 320\) nm range point to the decay of a single photoinduced species in 0.5 and 4 ps, while the range \(\lambda_{\text{probe}} > 320\) nm shows a 4 ps band splitting/broadening process, followed by band merging/narrowing in 16 ps, which is indicative of structural and symmetry changes. The appearance of features assigned to \([\text{Fe(CN)}_5(H_2O)]^{3-}\) is \(\sim 16\) ps, while the nature of the absorption bands present at the earliest times and their subsequent spectral evolution is discussed below.

We also estimated quantum yields as a function of excitation wavelength of the photoproducts \([\text{Fe(CN)}_6]^{3-}\) and \([\text{Fe(CN)}_5(H_2O)]^{3-}\). As their extinction coefficients are known, the differences with respect to the \([\text{Fe(CN)}_6]^{4-}\) ground state extinction coefficient can be scaled to match the measured transient difference spectra, and quantum yields can be estimated from the resulting scaling factors. This procedure is described in detail in section S2. The extracted quantum yields for photoaquation \((\phi_{\text{aq}})\) and photooxidation \((\phi_{\text{ox}})\), along with those previously reported,\textsuperscript{41,42} are shown in Figure 6 and they exhibit rather large uncertainties as they involve estimating the fraction of photoexcited molecules, \(f_{\text{exc}}\) for which we assumed an uncertainty of 100% to be conservative. However, the observed trends agree with the previously reported values.\textsuperscript{41,42,46}

From Figure 6, we can draw the following conclusions: First, \(\phi_{\text{aq}}\) shows no wavelength dependence between 360 and 310 nm, pointing to a Kasha-type behavior for this photochemical channel, that is, internal conversion processes lead to a relaxation to the lowest-energy state(s) that is (are) the doorway to the aquation reaction. Second, \(\phi_{\text{aq}}\) decreases from \(\sim 20\%\) to \(\sim 10\%\) between 310 and 250 nm. This can be explained by the fact that \(\phi_{\text{aq}}\) increases with increasing energy in this same range. Third, the total yield \((\phi_{\text{aq}} + \phi_{\text{ox}})\) also increases with increasing excitation energy, pointing to the increased photochemical decomposition via photooxidation with increasing excitation energy. Last, \((\phi_{\text{aq}} + \phi_{\text{ox}}) < 1\) (typically \(\sim 0.5\) at 285 nm and \(\sim 0.2\) at 310 nm), suggesting that either not all molecules are decomposed or a substantial part reform.

Although photoaquation is observed, when we directly excite the lowest lying singlet state \(^1\text{T}_{1g}\) the intermediate states
leading to [Fe(CN)₆(H₂O)]³⁻ remain unidentified. In order to complement the above analysis, we also carried out TRIR spectroscopy exciting at 320 nm, that is, into the ¹T₁g state.

Figure 7 shows the TRIR transient spectra for [Fe(CN)₆]³⁻ in H₂O. The corresponding kinetic traces are shown Figure S8,

and additional transient spectra for H₂O are compared in Figure S9 with those for D₂O. The spectra appear similar for H₂O and D₂O, and they contain more spectral features than those obtained upon 266 nm excitation. A very weak band due to [Fe(CN)₆]³⁻ appears at 2117 cm⁻¹ (inset in Figure 7). This is consistent with the 2D UV TA results (Figures 3c, 5, and 6), which show a weak contribution of photoionization at 320 nm.

From the earliest times, Figure 7 shows a depletion near the parent band at 2038 cm⁻¹ along with a broad absorption band at ca. 2060–2090 cm⁻¹. The latter decays rapidly (τ₁ < 1 ps), concomitant with a partial recovery of the parent band (Figures S8a,c). The initial recovery corresponds to ~40% of the excited molecules, and it can tentatively be assigned to geminate recombination of the CN⁻ radical with the pentacoordinated species formed by irradiation at 320 nm. The IR absorption bands of the aqueous cyanide ion have been reported at 2079 cm⁻¹ with a bandwidth of 16–18 cm⁻¹.⁶ The 2055–2090 cm⁻¹ band probably reflects this contribution, but additional ones may be present as will be discussed later. Under 320 nm excitation, the TRIR spectrum obtained 2 ps after photolysis shows absorption bands near 2060 and ~2090 cm⁻¹ (Figure 7). The 2060 cm⁻¹ band is clearly distinguishable from the initial broad 2055–2090 cm⁻¹ signal at early times as it grows in τ₂ = 4 ± 2 ps and decays in τ₀ = 23 ± 4 ps (Figure S8c), giving rise to a new band at 2049 cm⁻¹ that grows on a similar time scale (19 ± 4 ps, Figure S8b). It partially overlaps the parent bleach band. The 2049 cm⁻¹ band is the IR band of the photoaquated species.⁶⁵ The parent bleach band exhibits an additional recovery in 23 ± 4 ps (Figure S8a). A similar behavior is observed in D₂O.

The assignment of the 2060 cm⁻¹ and the ~2090 cm⁻¹ bands is now discussed. Close inspection of the profile of the ~2090 cm⁻¹ band shows that it is composed of more than one contribution (Figure S10): (a) its width is significantly broader than the spectral resolution of the instrument (ca. 1.5 cm⁻¹); (b) there are clear shoulders on its high- and low-energy wings; (c) the kinetic traces at the wings (Figure S8d) and at the maximum of the band (Figure S8e) confirm its composite nature. At 2088 cm⁻¹, the intensity decays in τ₁ = 23 ± 4 ps; at 2090 cm⁻¹, it grows in τ₂ = 4 ± 2 ps and decays in τ₁ = 23 ± 4 ps. At ~2086 cm⁻¹, it first rapidly decays, likely due to overlap with the broad CN⁻ band at early times, and then undergoes a longer decay in 23 ± 4 ps. These various trends are further confirmed by the global analysis (section S5) of the data set in H₂O, which provides the decay associated spectra (DAS) plotted in Figure 8. Four time components emerge from this analysis: (i) The τ₁ = 0.5 ps DAS reflects quite well the early time transient observed in Figures 7 and S8, with the bleach band at 2038 cm⁻¹ having a long tail to the red, and the broad positive band in the 2055–2090 cm⁻¹ range. (ii) The τ₂ = 3.5 ps DAS shows, along with the bleach band, a weak positive feature around 2020–2030 cm⁻¹, while it is close to zero around ~2086 cm⁻¹ presumably due to overlap of a positive (decaying) feature with the negative contribution of a growing band at 2090 cm⁻¹. The long blue tail of the bleach may be a rising component of the band that appears at 2060 cm⁻¹ in the 23 ps DAS and also contains a partial rise of the band characteristic for the aquated species (see below). (iii) The τ₁ = 23 ps DAS shows two new positive features at 2060 and ~2090 cm⁻¹. The distinction between the different bands making up the latter (Figure S10) is no longer as clear as seen in the time traces in Figure S8. However, all decay with τ₂ = 23 ps which is consistent with the corresponding DAS. Finally, the DAS at infinite time exhibits three positive features: weak ones around 2026 cm⁻¹ and at 2088 cm⁻¹ and a prominent one at ~2049 cm⁻¹. All three are characteristic of the aquated form as discussed below (Table 1).

Figure 7. TRIR spectra of 18 mM [Fe(CN)₆]³⁻ acquired in H₂O at several time delays after photolysis at 320 nm. The inset shows the expanded region of the 2117 cm⁻¹ ferricyanide stretch.

Figure 8. Decay associated spectra (DAS) obtained from the singular value decomposition of the transient IR data sets in H₂O (τ₁ = 0.5 ps, τ₂ = 3.5 ps, τ₀ = 23 ps, τ₄ = infinity).
Under 266 nm excitation, the ∼2088 cm⁻¹ band was significantly weaker, and any subsequently formed species was not clear. However, spectral fitting of the parent bleach is consistent with formation of a band at 2049 cm⁻¹, which is formed at a similar rate as the decay of the ∼2088 cm⁻¹ species. Therefore, the TRIR results support photoaquation under excitation both 266 and 320 nm, but the quantum yield for the former is lower, consistent with the 2D-UV TA experiments. Most importantly, at both pump wavelengths, the various IR features exhibit kinetic behaviors that parallel those reported in the 2D UV and the visible TA spectra. Therefore, in Table 1, we have grouped these bands according to their time scales, and we discuss their assignment below.

In order to aid the latter, we performed calculations of the electronic and vibrational energies using density functional theory (DFT, see section S6). We first calculate the νCN vibrational frequencies and structural parameters of the hexacoordinated complexes with an explicit unconstrained water solvent model (Figure S11), which is supported by previously published calculations of the spin-state energetics of [Fe(H₂O)₆]³⁺ using a similar approach. For the [Fe(CN)₆]⁴⁻ complex in its ground state, the calculations give a frequency of 2040 cm⁻¹ for the νCN band (Table S2), consistent with the experimental value of 2038 cm⁻¹. For the T₃ state of the complex, calculations predict bands at 2058, 2067, and 2079 cm⁻¹, with the first and last being the most intense ones. The calculated structure for this state in water shows a significant distortion: a large elongation (by about 20%) of the axial Fe–C bond (Table S3), found to be 2.40 Å compared to 1.92 Å in the ground state, while the equatorial bond lengths are 1.95 and 2.00 Å in the triplet state. The molecular orbitals (MOs) show that formation of the T₃ state involves the population of an antibonding dₓ²−y²-like orbital (Figures S12 and S13), and consistent with the calculated axial elongation, this is expected to induce a Jahn–Teller distortion. The elongation of the axial Fe–C bonds is significantly larger than what was measured for Fe(II)-polypyridine complexes in their quintet states, which is identical for all six Fe–N bonds. However, the reported values are consistent with optimized triplet state calculations of Ru(II)-polypyridines, where two opposing Ru–N bonds of [Ru(tap)]²⁺ (tap = 1,4,5,8-tetraazaphenanthrene) have been calculated to elongate from 2.104 Å in the ground state to 2.516 Å in the triplet ligand field state. Indeed, several computational studies on the photodissociation of Ru(II)-polypyridines have noted the dissociative nature of 3LF states involving the population of orbitals with a high degree of σ-antibonding character between the axial CN ligands and the metal. Our DFT calculations find the excitation energy for the lowest triplet state to be 2.86 eV, which is lower in energy than the predicted lowest quintet state (4.66 eV above the ground state), suggesting that the latter is less likely to be formed (Table S4).

Next, we consider the pentacoordinated complex: DFT geometry optimization and frequency calculations have been performed in vacuo and with a polarized continuum model (CPCM) of the solvent for a range of possible pentacoordinated intermediates. The results are summarized in Table S5. The calculations with or without solvent predict a similar energy hierarchy of states: the triplet trigonal bipyramidal (TBP) structure being the lowest energy form, followed by the singlet square pyramidal (SP) and the triplet square pyramidal (TSP). We note that the prediction of accurate singlet–triplet splittings is a challenging problem and can be sensitive to the nature of the exchange–correlation functional. Calculations using the B3LYP* functional, which is parametrized with this in mind, lead to a lowering of the singlet state energy, bringing the 1SP structure within 2 kJ/mol of the 3TBP configuration. Furthermore, the calculated C-PCM frequencies for the 3TBP form show two strong bands separated by over 20 cm⁻¹, consistent with the 23 ps-lived 2060 and 2090 cm⁻¹ bands observed in the experiment, although the calculated frequencies are somewhat higher. The singlet spin square pyramidal structure has two bands split by less than 10 cm⁻¹.

**DISCUSSION**

**Assignment of Bands.** We first identify the IR bands. Under 266 nm excitation and as stated above, the 2117 cm⁻¹ band is due to the oxidized product [Fe(CN)₆]³⁻, formed within the time resolution of our experiments. This band partially decays on the time scale of tens of nanoseconds due to recombination with the photoproduced solvated electron (Figure S3b). Under 320 nm excitation, some of the formed IR features are also easily identifiable, such as the [Fe(CN)₆]³⁻−2117 cm⁻¹ band and the photoproduced species [Fe(CN)₆(H₂O)]⁻ band at 2049 cm⁻¹ (reported at 2043 ± 10 cm⁻¹ in ref 65, Table S2). In addition to the latter band, the DAS also revealed the weaker bands at ca. 2026 and 2088 cm⁻¹ that also belong to the aquated species. The calculations indeed predict two weaker bands at 2037 and 2068 cm⁻¹, which we believe are associated with the former two (Table S2).

As mentioned above, the broad <1 ps IR band that appears in the 2055−2090 cm⁻¹ region can be assigned to the CN⁻ ion (in a singlet X ¹Σ⁻ state, Table S2). However, since according to the calculations (Table S2), the [Fe(CN)₆]⁴⁻ complex also has bands in the same region, we cannot exclude that both [Fe(CN)₆]⁴⁻ and CN⁻ species are observed within the time resolution of the experiment. This early time IR absorption decays, concomitantly with the partial early time recovery of the parent. It is related to the τ₁ = 0.5 ps process that appears in the UV (Figures 5 and S7) with maximum absorption <280 nm, which we assign to the [Fe(CN)₆]⁴⁻ fragment, as the CN⁻ fragment has no known absorption bands in this region. Thus, the initial sub-picosecond decay of these IR and UV bands reflects the transient lifetime of the 3[Fe(CN)₆]⁴⁻ state and the geminate recombination of [Fe(CN)₆]⁴⁻ with CN⁻.

Just as for the IR, the UV and visible transitions belonging to [Fe(CN)₆]³⁻, [Fe(CN)₆]²⁻, and [Fe(CN)₅(H₂O)]⁻ are easily identifiable, and Table 1 shows their assignments and lifetimes. Note that for the pentacoordinated complex, the predicted IR frequencies are higher than the experimental ones but lie within the expected level of accuracy for an open-shell transition metal complex and given the approximate nature of the solvent model.

**Mechanism of Photoaquation.** From the body of ultrafast studies on electronically excited metal complexes, electronic relaxation proceeds at extremely fast time scales of a few tens of femtoseconds, to reach the lowest electronically excited state, in line with the Kasha rule. This also applies to chemical reactions. Indeed, the constant photoaquation yield for excitation wavelengths between 310 and 365 nm reflects this behavior (the red most wavelength corresponds to the absorption threshold). It is therefore reasonable to assume that the relaxation cascade reaches the lowest triplet state prior to proceeding to dissociation. In addition, ϕₘ + ϕₘ ≤ 0.5 down to 260 nm excitation (Figure 7), which implies that there is a substantial recovery of ground state [Fe(CN)₆]⁴⁻ on an ultrafast time scale.
Photoexcitation at 320 nm into the $^{1}\text{T}_{1g}$ state is followed by Jahn–Teller distortion, due to the degeneracy of the excited state electronic configuration, and ISC into the lower triplet $^{3}\text{T}_{1g}$ state, leading to dissociation of the molecule into $[\text{Fe(CN)}_5]^{3-}$ and CN$^-$. As explained above, the triplet state is characterized by the transfer of one electron from the bonding $t_{2g}$ orbital to the antibonding $e_g$ orbital (Figure S12), and a significant elongation of some of the Fe–CN bonds (Table S3), which may favor dissociation in the solvent.

Therefore, given that from the earliest probed times in our experiments, we have formed an $[\text{Fe(CN)}_5]^{3-}$ species, the subsequent UV, visible, and IR spectral changes reflect electronic/structural relaxation of this species. The CN$^-$ ion is in a singlet state, and we assume that dissociation proceeds via a triplet state producing the nascent $[\text{Fe(CN)}_5]^{3-}$ in a triplet state, which can adopt either a trigonal bipyramidal (TBP) or a square pyramidal (SP) form. Furthermore, as described above (Table S5), the energies of the calculated states follow the order $^{3}\text{TBP} < ^{3}\text{SP} < ^{1}\text{SP}$ and the $^{1}\text{SP}$ form ($52$ kJ/mol higher than $^{3}\text{TBP}$) is the most likely to be generated by dissociation and can undergo a further rearrangement. $\tau_f$ is reflected in a $3.5$–$4$ ps rise of the bands at $2090$ and $2060$ cm$^{-1}$ and the decay of the $2086$ cm$^{-1}$ band (Figure S8c,d) and corresponds to the production of $^{3}\text{TBP}$. This process can either be associated with the $^{3}\text{SP}$ form undergoing a conformational change to the $^{3}\text{TBP}$ form, or a spin and conformational relaxation which would include a passage via the intermediate $^{1}\text{SP}$ form, and both SP species are predicted to exhibit two bands. The involvement of a singlet $[\text{Fe(CN)}_5]^{3-}$ moiety in the kinetic processes on the $4$–$20$ ps time scale is very unlikely as similar singlet $16$-electron intermediates have been shown to coordinate to very weakly coordinating solvents on the femtosecond time scale. For example, solvation by alkanes of $\text{Cr(CO)}_6$ formed by photoejection of CO from $\text{Cr(CO)}_6$ occurs in $\sim$1 ps. $^{26}$ Similar behavior is observed for many metal carbonyl species in these weakly coordinating solvents.$^{16,77}$ H$_2$O is a much more coordinating solvent to such fragments than alkanes, and it is expected to react at faster time scales.

For the $^{3}\text{TBP}$ form, we have seen that the calculations predict two bands separated by ca. $20$ cm$^{-1}$ with an intensity ratio of $\sim$3:1 between the lower and higher energy bands. This trend is reproduced between the $2060$ and $\sim2090$ cm$^{-1}$ bands, which in addition grow and decay on the same time scales (Figure S8c,f). This leads us to associate the $\sim20$ ps time scale of $\tau_f$ to the decay of the $^{3}\text{TBP}$ complex. Because this is also the time scale for formation of the aquated species, we consider that formation of the latter proceeds from a $^{3}\text{TBP}$ precursor.

The rise-time ($3.5$–$4$ ps, $\tau_f$) and decay ($23$ ps, $\tau_c$) of the $2090$ and $2060$ cm$^{-1}$ bands are similar to those of the signal in the $330$ to $410$ nm region and likewise, the decay time corresponds to the rise of the aquated complex. This, along with the fact that the $\sim4$ and $\sim16$ ps UV–visible bands are clearly correlated (Figure S5) suggests that we are still dealing with the $[\text{Fe(CN)}_5]^{3-}$ intermediate, consistent with the SP to TBP rearrangement.

Concomitant with the decay of the final $[\text{Fe(CN)}_5]^{3-}$ species, the aquated $[\text{Fe(CN)}_5(\text{H}_2\text{O})]^{3-}$ (at $2049$ cm$^{-1}$ in the IR and ca. $440$ nm in the UV) grows in $\sim20$ ps. This time scale is not uncommon in solutions. For example, photolysis of $\text{Fe(CO)}_5$ produces $^{1}\text{Fe(CO)}_4$ which rapidly converts to $^{3}\text{Fe(CO)}_4$ before the subsequent reaction with solvent species occurs, which is very slow and strongly dependent on the nature of the solvent (ranging from $43$ ps in EtOH$^{21}$ to $13$ ns in heptane$^{2})$. The scenario we propose here is very similar: the reactivity with solvent species is dramatically (typically 2 orders of magnitude) slowed down due to the rapid ISC to the triplet state of the fragment.$^{26,76}$

The recovery of $[\text{Fe(CN)}_5]^{3+}$ occurs on all the above time constants: at the earliest times ($\sim1$ ps), geminate recombination takes places concomitant with the disappearance of the broad IR absorption. This early recombination is estimated to affect $\sim40\%$ of the initially bleached molecules, and given its short time scale, it can only be due to geminate recombination (GR) and/or intramolecular relaxation. The $3$–$4$ ps time constant of the parent bleach recovery reflects further recombination of CN$^-$ fragments with the SP form; however it is much less efficient as it is nongeminate due to its time scale. Indeed, since further recombination occurs over $\sim20$ ps resulting in an overall recombination fraction of $\sim75\%$, the $3$–$4$ ps time constant would barely represent $20\%$ of the latter contribution. The $\sim20$ ps time scale is similar to that for photoaquation, and therefore we conclude that the latter is the rate-determining step for the non-GR of $[\text{Fe(CN)}_5]^{3-}$ and CN$^-$ species (there are more water molecules than CN$^-$ fragments in the environment of the pentacoordinated species).

Based on the above, we propose the following scenario for the photoaquation process, as summarized in Scheme 1: (i)
square pyramidal form in order to accommodate the water molecule. Surely the participation of the latter is needed in order to make this rearrangement possible. Molecular dynamics simulations are needed to further elucidate these details. This being said, the present observations invalidate the mechanism of dissociative interchange between \([\text{Fe(CN)}_6]^{3−}\) and \(\text{H}_2\text{O}\) proposed by Finston and Drickamer.33 Despite indications from 2D IR34,35 and X-ray studies40,78 of a specific interaction of \([\text{Fe(CN)}_6]^{4+}\) with water molecules, the solvent does not seem to play an essential role in the photochemistry of the molecule, except to allow the process of geminate recombination by caging the fragments within the first picoseconds. The lack of an isotope effect on the kinetics of photoaquation is also in line with the relatively long time scales of the reported processes, which are governed by the barrier for conversion of \([\text{Fe(CN)}_6]^{3−}\) into \([\text{Fe(CN)}_6(\text{H}_2\text{O})]^{3−}\).

Other examples of photoaquation reactions of metal cyanides include \([\text{Co(CN)}_6]^{3−}\), which presents an interesting target of investigation as it is isoelectronic to \([\text{Fe(CN)}_6]^{3−}\). \([\text{Co(CN)}_6]^{3−}\) has so far not been investigated by ultrafast methods but earlier studies, based on ligand exchange reactions36 and pressure-dependent quantum yield measurements79 have pointed to a dissociative interchange mechanism for the formation of \([\text{Co(CN)}_6(\text{H}_2\text{O})]^{3−}\). This difference from the ferrocyanide case may be indicative of an increased dissociation energy of the Co–CN bond.

Finally, the increased photoionization yield with increasing energy points to a non-Kasha behavior for this channel, which is logical since electron dynamics are much faster than the nuclear dynamics associated with intramolecular relaxation. This is also reflected in the decrease of the photoaquation quantum yield upon excitation of the CTTS states and consistent with the lack of an ultrafast CTTS fluorescence.

The body of work on ultrafast intramolecular relaxation of complex molecular systems in solution shows that the Kasha Rule is largely verified and exceptions are rare.75,80 Intra-molecular electronic energy redistribution occurs at extremely short time scales, reaching values even shorter than the high frequency vibrational time scales73,81 while ISC events also occur at very short time scales.74 It is therefore expected that the Kasha Rule will also be verified for photochemical reactions, that is, the significant chemistry involves only the lowest states. The only reaction channel that competes in any significant way with intramolecular energy redistribution are photooxidation events, as the release of an electron must occur at significantly shorter time scales than the vibrational ones. This is valid for CTTS dynamics, as in the present case, or interfacial electron injection of a molecular adsorbate on a semiconductor substrate.82−85

**CONCLUSIONS**

We have carried out a detailed investigation of the excitation energy-dependent ultrafast photochemistry of aqueous \([\text{Fe(CN)}_6]^{4+}\). Combining advanced ultrafast spectroscopic tools: 2-dimensional UV spectroscopy, visible and infrared transient absorption spectroscopy, along with quantum chemical calculations, we have elucidated the photoaquation mechanism of \([\text{Fe(CN)}_6]^{4+}\) in water. The initial events are an ultrafast intramolecular relaxation to the lowest triplet state and dissociation of the molecule with release of a \(\text{CN}^−\) fragment. Part of the fragments recombine geminately within the solvent cage. All these events (intramolecular energy redistribution, dissociation, geminate recombination) occur in <0.5 ps. The subsequent observed dynamics is all due to the \([\text{Fe(CN)}_6]^{3−}\) fragment, which is initially formed in the square pyramidal configuration in the triplet state. It then undergoes conformational changes in 3−4 ps to the lower lying triplet state of the trigonal pyramidal form. Binding of water molecules takes place in ~20 ps and shows no isotope effect. This relatively long time scale must reflect a rearrangement of the pentacoordinated trigonal bipyramidal complex to a geometry favoring uptake of a water molecule. Molecular dynamics simulations will be needed to further support this scenario. In addition, ultrafast X-ray spectroscopy provides ideal tools to detect the nuclear, electronic, and spin structure of the intermediate pentacoordinated form,86 and studies are ongoing at X-ray free electron lasers to this purpose.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02769.

Data acquisition and treatment, determination of quantum yields, global analysis, density functional calculations, TRIR spectra, time-integrated UV and visible transient absorption spectra, 2D UV DADAS, kinetic traces of the IR signals, and statistical analysis of the UV, visible, and IR data (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

*Mike.George@nottingham.ac.uk*

**ORCID**

Nicholas A. Besley: 0000-0003-1011-6675

Majed Chergui: 0000-0002-4856-226X

**Present Addresses**

1PULSE Institute for Ultrafast Energy Science, Stanford, CA, USA.

2CTR Carinthian Tech Research AG; Europastrasse 4/1, 9524 Villach/St. Magdalen, Austria.

**Notes**

The authors declare no competing financial interest.

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