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Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of Fe(CO)₅ to Fe(CO)₄EtOH

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We utilized femtosecond time-resolved resonant inelastic X-ray scattering and ab initio theory to study the transient electronic structure and the photoinduced molecular dynamics of a model metal carbonyl photocatalyst Fe(CO)₅ in ethanol solution. We propose mechanistic explanation for the parallel ultrafast intra-molecular spin crossover and ligation of the Fe(CO)₄ which are observed following a charge transfer photoexcitation of Fe(CO)₅ as reported in our previous study [Wernet et al., Nature 520, 78 (2015)]. We find that branching of the reaction pathway likely happens in the 1A₁ state of Fe(CO)₄. A sub-picosecond time constant of the spin crossover from 1B₂ to 3B₂ is rationalized by the proposed 1B₂ → 1A₁ → 3B₂ mechanism. Ultrafast ligation of the 1B₂ Fe(CO)₄ state is significantly faster than the spin-forbidden and diffusion limited ligation process occurring from the 3B₂ Fe(CO)₄ ground state that has been observed in the previous studies. We propose that the ultrafast ligation occurs via 1B₂ → 1A₁ → 1A' Fe(CO)₄EtOH pathway and

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the time scale of the $^1A_1$ Fe(CO)$_4$ state ligation is governed by the solute-solvent collision frequency. Our study emphasizes the importance of understanding the interaction of molecular excited states with the surrounding environment to explain the relaxation pathways of photoexcited metal carbonyls in solution. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

I. INTRODUCTION

The photochemistry and physics of transition metal coordination compounds reflect a complex array of electronic and nuclear dynamics occurring often on the ultrafast, femto- and picosecond time scales. Investigation of these processes at a molecular level has the potential of enhancing our understanding of chemical reactivity, but generally proves to be experimentally and theoretically challenging. Techniques with sub-picosecond time resolution and high sensitivity and selectivity to the metal center provide an important perspective with which to investigate organometallic photochemical dynamics. In comparison to numerous other spectroscopic methods, x-ray spectroscopy has the advantage of being element selective. Combined with pump-probe schemes, it enables the evolution of the electronic structure to be followed with elemental and site specificity. In recent years, time-resolved x-ray spectroscopy methods have been utilized to probe excited state molecular dynamics with (sub-)picosecond resolution. This advancement has been mostly driven by technological progress in short-pulse x-ray sources and in particular, by recent developments of accelerator based light sources. In particular, femtosecond time-resolved resonant inelastic x-ray scattering (RIXS) experiments have become feasible at x-ray free-electron laser sources (XFELs). We report a femtosecond time-resolved RIXS investigation of the ligand exchange reaction dynamics triggered by the CO photodissociation from the transition metal complex Fe(CO)$_5$ in ethanol solution. The investigation presented here expands upon our earlier publication. We studied the short time-scale dynamics (up to 3.5 ps after the excitation) of the reaction with 300 fs time resolution. Our approach employed RIXS at the Fe L$_3$ absorption edge (705–715 eV) which is selectively sensitive to the Fe 3d character of the valence states (i.e., the Fe electrons primarily involved in the bonding and chemical reactivity). This allowed us to resolve changes in the valence electronic structure of the iron carbonyl complex which relate to the Fe-CO bond dissociation, electronic excited state relaxation, and solvent bonding to the under-coordinated Fe(CO)$_4$ photoproduct. Thereby, we can utilize not only the element-specificity of the x-ray probe to monitor the reaction center but also the ability of RIXS to discriminate different chemical species (coordination) and electronic states to map the evolution of the electronic structure with orbital specificity.

Fe(CO)$_5$ has a trigonal bipyramidal ($D_{3h}$) geometry and a closed shell, singlet $A_1^+$ electronic ground state. The onset of the optical absorption spectrum is at 3.5 eV. The optical absorption cross section is dominated by transitions from orbitals of predominantly Fe 3d character to orbitals of significant CO $2\pi$ character, i.e., metal-to-ligand charge transfer (MLCT) excitations. Absorption of a photon with 4.66 eV energy (266 nm) by Fe(CO)$_5$ is followed by a primary dissociation step which splits off one CO, creating the Fe(CO)$_4$ photofragment with a quantum yield close to unity. In the gas phase, Fe(CO)$_4$ undergoes further fragmentation with high quantum yield. The time constant for this fragmentation was reported to be 3.3 ps. In solution, depending on the excitation wavelength and the solvent, sequential dissociation can be suppressed, but not necessarily eliminated. Within the short time-scales studied here, the Fe(CO)$_4$ fragment is the relevant intermediate which interacts with the solvent and determines the course of the reaction.

It is well known that singlet Fe(CO)$_4$ is highly reactive and capable of ligand addition with a number of common organic compounds: alkanes, alkenes, alcohols, alkylphosphines, and alkylsilanes. This reactivity arises from the fact that Fe(CO)$_4$ has an electron
deficiency at the Fe center; the 16 valence electrons do not fulfill the 18 electron rule. Furthermore, the Fe center is sterically free to interact with the solvent, making it a strong electrophile. The question thus arises whether the reactivity of Fe(CO)$_4$ towards solution modifies the exited-state relaxation pathways. As reported in our earlier publication, we concluded that after photodissociation of Fe(CO)$_5$, the reactive species Fe(CO)$_4$ converts from an excited singlet state to the triplet ground state and, in a parallel pathway, combines with an ethanol solvent molecule to form Fe(CO)$_4$EtOH or geminately with CO to reform Fe(CO)$_5$ on a time scale of 200–300 fs. The aim of the present investigation is to detail these findings with particular emphasis on the mechanistic details of the reaction pathways.

An important aspect of Fe(CO)$_4$ reactivity relates to the spin state of the complex. While singlet Fe(CO)$_4$ is highly reactive, the electronic ground state of Fe(CO)$_4$ does not coordinate with solvent. The occurrence of $^3\text{B}_2$ electronic state of Fe(CO)$_4$ is established in several solutions, but the mechanistic details of its creation had remained unresolved. It was stated in the gas phase electron diffraction experiments by Ihee et al. and Trushin et al., transient ionization experiment that Fe(CO)$_4$ is created initially in a singlet state and that spin crossover (SC) must take at least several hundreds of picoseconds (according to Ryther et al. IR-absorption experiments even more than 200 ns (Refs. 28 and 29)). This interpretation of the gas phase studies differs significantly from the results of solution phase time-resolved IR-absorption studies, in which Snee et al. concluded that they observed triplet Fe(CO)$_4$ creation in less than 10 ps.

The solvent environment can influence excited state dynamics in a variety of manners. Solvent polarity-dependent state shifts, solvent cage effects (geminate recombination), solvent assisted internal vibrational energy redistribution, and vibrational cooling (energy transfer to the solvent) can all play a significant role. Here, we focus our main attention on the additional aspect of chemically specific coordination, namely, the coordination of ethanol to Fe(CO)$_4$, creating Fe(CO)$_4$L ($L =$ ligand, EtOH in case of ethanol solution). As mentioned earlier, Snee et al. performed a series of experiments in different alcohol solutions and they observed ultrafast (<10 ps) formation of a hot triplet Fe(CO)$_4$ species, which is coordinated through a diffusive mechanism on the 42–340 ps time scale. Intriguingly, in contrast to other alcohol solutions, Snee et al. did not detect triplet Fe(CO)$_4$ in methanol solution (EtOH solution was not measured), possibly due to the difficulty in assigning the transient spectra to specific electronic states before the photoproducts have cooled vibrationally and the similar rate of solvent coordination and vibrational cooling in methanol. They speculated that in contrast to other alcohols, in methanol, Fe(CO)$_4$ could solvate at a faster rate and the observed 42 ps time constant could actually correspond to a cooling process. Recently, in a study by the same group, it was reported that the triplet Fe(CO)$_4$ intermediate was observed in methanol. Specifically addressing Fe(CO)$_5$ photodissociation in ethanol using time-resolved Fe K-edge X-ray absorption spectroscopy, Ahr et al. proposed that the electronic ground state interaction between ethanol and Fe(CO)$_5$ influences the excited state dynamics of Fe(CO)$_5$, making the removal of CO and the addition of EtOH as concerted processes. Creation of Fe(CO)$_5$EtOH was not resolved with the time resolution of the experiment of 3 ps, but they deduced a 14 ps cooling rate. They did not discuss the spin state of the photofragment and assumed it to be a singlet throughout the process. Their model was supported with the argument that in solution a weak Fe(CO)$_5$-EtOH complex is formed.

It is evident that a number of questions related to the mechanism of Fe(CO)$_5$ photodissociation in solution and in particular, the related ligand substitution reactions remain unresolved despite extensive prior study. What is the pathway leading to triplet Fe(CO)$_4$ in solution? What are the mechanistic details of the Fe(CO)$_4$ ligand addition reaction and how can we explain the timescale? How in detail can the findings for the short sub-ps time scale be reconciled with the results for longer time scales? We aim to address these questions below.

II. METHODS

A. Experimental details

The experiment was conducted at the LCLS Soft X-ray Materials Science (SXR) beamline with the Liquid Jet Endstation. A detailed description of the endstation can be found...
The experiment was performed on a 1M Fe(CO)$_5$ ethanol solution. The third harmonic of a Ti:sapphire laser system at 266 nm (4.66 eV) was used for the initiation of the photoreaction. The laser pulse length was 100 fs and estimated pulse energy was $\sim 5 \mu$J (peak fluence $\sim 1.25 \times 10^{11}$ W/cm$^2$). We found the total time resolution of the experiment to be 300 fs full width at half maximum (FWHM) mainly determined by the relative time-of-arrival jitter between the optical laser and the FEL x-ray pulses (deduced from the experimental time traces) and the x-ray pulse length of 160 fs. RIXS spectra were measured at the Fe L$_3$-edge (705–715 eV) with an excitation bandwidth of 0.5 eV. Resolution of the RIXS spectra, defined by the diameter of the jet (20 $\mu$m) in the “slitless” mode, was 1.0 eV. The average peak incident fluence of the x-ray beam was $2 \times 10^{11}$ W/cm$^2$ ($1.6 \times 10^{10}$ photons per pulse). Further details can be found in Ref. 1.

B. Computational details

Accurate simulations of L-edge x-ray spectra require inclusion of relativistic effects and a balanced treatment of many core- and valence-excited states. For these reasons, theoretical x-ray spectra were derived from restricted active space self-consistent field (RASSCF) calculations. The active space in the RASSCF calculations included 14 electrons in 14 orbitals; the 2p in the RAS1 space with at most one hole, four 3d in the RAS2 space and in RAS3 seven orbitals, including the nominally empty 3d orbital and the lowest unoccupied $e'$, $e''$ and $e'$ orbitals depicted in Fig. 1, with at most 2 electrons. Recently, also Suljoti et al. applied the RASSCF method to Fe(CO)$_5$. Further computational details can be found in Ref. 1.

RIXS spectra were simulated using the Kramers-Heisenberg formula. Spectra were calculated for an ensemble of randomly oriented molecules excited by linearly polarized light and detected in the plane of polarization. Interference effects were excluded. To account for intermediate state lifetime broadening at the L$_3$ and L$_2$ edges, the values of 0.3 eV and 0.6 eV (FWHM) were used, respectively. The bandwidth of the incident photons was 0.5 eV FWHM.

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FIG. 1. Qualitative valence molecular-orbital (MO) diagram of Fe(CO)$_5$. Displayed is the subset of Fe(CO)$_5$ MOs which are derived from Fe 3d and CO 5$r$ and 2$p$ orbitals. For the sake of clarity, the MOs with mostly Fe 4$s$, 4$p$, and CO 1$p$ character are not shown (depicted for completeness in gray). The labels for the respective symmetry adapted orbitals in the $D_{3h}$ point group are given in the parentheses after the Fe and CO orbital labels. MOs contributing most to Fe-CO bonding are additionally combined in four groups and labeled based on their symmetry with respect to the Fe-CO bond and the metal/ligand character (bold labels). Photoexcitation initiated by the 266 nm (4.66 eV) laser photons corresponds to MLCT transitions between occupied $d_e$ and unoccupied 2$p^*$ MOs (red arrow). The inset shows the Fe(CO)$_5$ ground state geometry (atoms are colored accordingly: blue—Fe, gray—C, and red—O).
Gaussian). RIXS spectra were also broadened with the spectrometer resolution (1 eV FWHM, Gaussian). Finally, a 0.5 eV Gaussian broadening was applied for both intermediate and final states to account for additional broadening observed in the experiment, most likely due to inhomogeneous broadening from solvent environment and vibrational effects. Ab initio Car-Parrinello molecular dynamics (CPMD) simulation within the periodic density functional framework were performed for 25 ps (7 ps equilibration) on the Fe(CO)₅ complex solvated by 100 ethanol at a density of 0.785 g/cm³ and ambient temperature, obtained through the Nose-Hoover thermostat coupling at 3000 cm⁻¹. The system was deuterated and a time-step of 0.1 fs was used in combination with a fictitious electron mass of 300 a.u. in the Car-Parrinello dynamics. The CPMD simulation was initialized from a 1 ns long classical MD simulation (MDynaMix) using a rigid solute with the Charmm force field and the OPLS-AA force field for ethanol. We used the Perdew-Burke-Ernzerhof (PBE) functional augmented with empirical van der Waal interactions and a 85 Ry kinetic energy cut-off of the plane-wave expansion. We employed norm-conserving pseudo-potentials derived for the PBE functional.

III. RESULTS

The results of the time-resolved RIXS (tr-RIXS) measurements are summarized in Fig. 2. Panel (a) displays the pumped-unpumped difference RIXS map. One notices a decrease in the (2p₃/2)⁻¹(2π⁺)¹ resonance at 711.5 eV, a small increase of (2p₃/2)⁻¹(d⁺*³)¹ resonance at 709.5 eV, and a larger increase from 706 to 709 eV where the Fe(CO)₅ ground state has no absorption. Different from Ref. 1, we define in Fig. 2(a) five spectral regions (1, 2, 2b, 3, and 4) and not four (1, 2, 3, and 4). We use delay scans taken in these regions (Fig. 2) to investigate the dynamical pathway of the reaction.

Identification and assignments of the species observed in the experiment are based on a comparison of the experimental tr-RIXS data (Fig. 2) with the RIXS maps calculated for various possible geometries and electronic states (Fig. 3 and Figs. S4–S13). As detailed in our previous publication, minimally three distinct photoproducts are required to explain the experimental intensities. Here, this assignment is briefly summarized because the following discussions and analyses are based on it. The three species identified in Ref. 1 are labeled as E, T, and L. E stands for a “hot” singlet excited state of the Fe(CO)₄ photoproduct, T for vibrationally “hot” lowest triplet state (¹B₂) Fe(CO)₄, and L for “hot” ligated singlet (¹A₁) Fe(CO)₄EtOH (species C) and Fe(CO)₅ (species H). Extending our previous assignments, we discuss below the involvement of an additional species S, a vibrationally “hot” singlet state Fe(CO)₄. Descriptions and assignments of the species E, T, S, C, H, and L are summarized in Table I. Further details on the assignments of the photoproducts can be found in the supplementary material. We construct two consistent rate models that describe the observed experimental intensities in the five regions defined in Fig. 2. Relative intensities (contrasts) of the species in all five regions were extracted from the calculated RIXS map in Fig. 3 and kept fixed during the fitting procedure. (The details about the rate model can be found in the supplementary material.)

First kinetic rate model is same as in Ref. 1. (The results of this rate model are displayed in Fig. 2(b).) This kinetic rate model includes two parallel reaction pathways, E → T and E → L. This is the simplest rate model which can show reasonable agreement with the experiment (Fig. 2(b)). However, in the gas phase, it has been shown that the ¹B₂ state of Fe(CO)₄ (species E) relaxes ultrafast to the singlet closed shell ¹A₁ state (species S). In addition, species S is reactive towards ligand addition, which, as we will argue below, provides possible explanation to ultrafast appearance of species L. Therefore, we will consider here a second kinetic rate model which includes E → S relaxation, followed by parallel S → T and S → L pathways. Fit of the corresponding rate model is shown in Fig. 2(c). Similarly to the first rate model, it is able to fit the experimental delay scans with a good accuracy. The extracted time constants for both kinetic rate models are listed in Table II. We would like to emphasize that the two models are not

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contradictory. Both models describe the branching of species E to T and L; however, the second model introduced here elaborates the “minimal” model applied in Ref. 1 by including a new intermediate species S. Below we turn to a detailed discussion of the proposed reaction pathways with a particular emphasize on the possible participation of species S, a singlet closed shell singlet state of Fe(CO)₄.

IV. DISCUSSION

Fig. 4 summarizes schematically the relevant potential energy surfaces (PESs) and pathways of Fe(CO)₅ photoreaction in ethanol. The relative energies of particular molecular geometries and electronic states are calculated using RASSCF and CASPT2 methods (Table S3). The qualitative PESs in Fig. 4 are constructed based on the previous studies. Based on
these PESs, we proceed with discussing the mechanistic details of the experimentally observed dynamical pathways.

### A. Fe(CO)$_5$ photodissociation

Based on the previous studies, it is known that Fe(CO)$_5$ dissociates on an ultrafast (<100 fs) time scale$^{25,26,31}$ The effectively instantaneous (within our 300 fs time resolution) appearance of the ligand field (LF) $^1$B$_2$ excited state Fe(CO)$_4$ (species E) after the photoexcitation of Fe(CO)$_5$.

**TABLE I.** Assignment of species and definitions based on the calculations. For further details, see the supplementary material. Calculated RIXS maps of the species are displayed in Fig. 3.

| Species | Description | Geometry and electronic state | Regions with significant intensity |
|---------|-------------|-------------------------------|----------------------------------|
| E       | “Hot” singlet excited state Fe(CO)$_4$ | Fe(CO)$_4$T, $^1$B$_2$ (LF) Fe(CO)$_4$S, $^1$B$_2$ (LF) Fe(CO)$_4$E $^1$B$_2$ (LF) | 1, 2, 3, 4 |
| T       | “Hot” lowest triplet state Fe(CO)$_4$ | Fe(CO)$_4$T, $^3$B$_2$ (LF) Fe(CO)$_4$S, $^3$B$_2$ (LF) Fe(CO)$_4$E $^3$B$_2$ (LF) | 2, 2b, 4 |
| S       | “Hot” lowest singlet state Fe(CO)$_4$ | Fe(CO)$_4$T, $^1$A$_1$ (GS) Fe(CO)$_4$S, $^1$A$_1$ (GS) Fe(CO)$_4$E $^1$A$_1$ (GS) | 2b, 4 |
| C       | “Hot” singlet ground state Fe(CO)$_4$EtOH complex | Fe(CO)$_4$EtOH-B, $^1$A$'$ (GS) Fe(CO)$_4$EtOH-C, $^1$A$'$ (GS) | 3, 4 |
| H       | “Hot” singlet ground state Fe(CO)$_5$ | Fe(CO)$_5$, $^1$A$_1$ (GS) Fe(CO)$_5$C$_2$90, $^1$A$_1$ (GS) Fe(CO)$_5$C$_4$120, $^1$A$_1$ (GS) Fe(CO)$_5$C$_4$180, $^1$A$_1$ (GS) | 3, 4 |
| L       | “Hot” singlet ground state ligated Fe(CO)$_4$ | C, H | 3, 4 |
Fe(CO)$_5$ to the MLCT states is a result of several very fast internal conversion (IC) processes which also include dissociation of a CO. Such ultrafast excited-state dynamics in Fe(CO)$_5$ is facilitated by the many energetically close lying states and the Jahn-Teller effect present in states with E$^0$ orbital symmetry (Fig. 4). Trushin et al. deduced from their gas phase experiment three time constants leading to excited singlet Fe(CO)$_4$. Two time constants before the dissociation, 21 fs and 15 fs, were interpreted as electronic relaxations in MLCT and LF manifolds (summarized as a single electron back-transfer process in Fig. 4) which are then followed by the dissociation on 1B$_2$ surface within 30 fs. These time scales are consistent with the effectively instantaneous appearance of the excited Fe(CO)$_4$ (species E) in our experiment. In addition, our observation of the 1B$_2$ state is consistent with the dissociation in the singlet manifold. However, given our data quality and time-resolution, we cannot completely exclude alternative dissociation pathways, e.g., dissociation in the triplet manifold. Also, we find it possible that the dissociation happens directly from some MLCT state. Similarly to ligand field 1E$^0$ states, the dipole allowed MLCT 1E$^0$ states are subject to a Jahn-Teller effect. Such a dissociation pathway would lead to the respective Fe(CO)$_4$ MLCT state(s), which would then internally relax to the LF 1B$_2$ state. Distinguishing between LF and MLCT dissociation pathways requires improved experimental time resolution.

| Time constant (fs) | Time constant (fs) |
|-------------------|-------------------|
| E → T 300 ± 100 | E → S 200 ± 100 |
| E → L 200 ± 100 | S → T 400 ± 100 |
|                | S → L 300 ± 100 |

FIG. 4. Schematic pathways of Fe(CO)$_5$ photoreaction in ethanol. Illustrative MOs populated by the “active” electron for each state are shown next to the state label. Relative state energies of the displayed geometries are from RASSCF/CASPT2 calculations. Shown potential energy surfaces (PESs) are qualitative. Charge back-transfer (CT) and dissociation processes are not directly observed in this work and therefore depicted with gray arrows. Geminate recombination is a minority channel and thus represented by a dashed arrow.
Due to insufficient time resolution, we can neither confirm nor exclude the influence of the solvent before or during the dissociation of CO, corresponding to the recently proposed concerted CO dissociation and EtOH addition mechanism by Ahr et al.8 Our kinetic rate model analysis (Table II) demonstrates that the experimental findings are consistent with all photodissociated molecules converting to the four-coordinated \(^{1}B_2\) state of Fe(CO)\(_4\) (species E), consistent with the interpretation of the gas phase measurements of Trushin et al.31 However, our observation of subsequent ultrafast ligation of species E agrees with the claimed ultrafast appearance of Fe(CO)\(_4\)EtOH complex by Ahr et al.,8 although the observation of four-coordinated \(^{1}B_2\) intermediates by us requires an EtOH addition mechanism which is not concerted with CO dissociation. Below we therefore discuss in detail the possible mechanisms of ultrafast ligation of species E which are sequential to CO dissociation and which do not require a presence of six-coordinate Fe(CO)\(_5\)EtOH complexes prior to photoexcitation. However, we will show below that physical mechanism of ultrafast ligation requires the presence of the species S (Fig. 2(c)), augmenting the model introduced in Ref. 1 that does not include the species S (Fig. 2(b)).

B. Fe(CO)\(_4\) spin crossover

Decay of the \(^{1}B_2\) Fe(CO)\(_4\) state (species E) to the \(^{3}B_2\) triplet ground state (species T) takes \(\sim 300\) fs.1 Such fast SC time scales has now been observed in variety of coordination and organometallic complexes and appears to be the rule, rather than the exception for metal complexes.75–78 To the best of our knowledge, this reported time scale for the intramolecular SC in Fe(CO)\(_4\) has not been measured before, although the (ultra)fast appearance of triplet intermediates in these systems has been previously detected.35,40,41

Our experimental data are consistent with two SC mechanisms: direct SC from \(^{1}B_2\) to \(^{3}B_2\) (E \(\rightarrow\) T) or IC from \(^{1}B_2\) to \(^{1}A_1\) followed by SC from \(^{1}A_1\) to \(^{3}B_2\) (E \(\rightarrow\) S \(\rightarrow\) T). The first option, corresponding to the first rate model used in Ref. 1, would correspond to a spin-flip transition without a change in orbital character. This direct SC is, however, unlikely because it violates the energy gap rule (see also respective PESs in Fig. 4). In addition, according to Trushin et al., the IC from \(^{1}B_2\) to \(^{1}A_1\) takes only 50 fs, reasonably agreeing with the extracted time constant 200 \(\pm 100\) fs. Besora et al. calculated the \(^{3}B_2\) to \(^{1}A_1\) hopping probability to be 1/13 resulting from the spin-orbit coupling of these states.36 Given that spin allowed surface hopping from \(^{1}B_2\) to \(^{1}A_1\) is 50 fs,31 it is thus reasonable to conclude that the spin-forbidden surface hopping (SC) from \(^{1}A_1\) to \(^{3}B_2\) is on the order of \(\sim 500\) fs, therefore, rationalizing the experimentally observed 400 fs time scale. Therefore, we find that the presence of ultrafast SC can be explained by evoking the intermediate S as in the second kinetic rate model (Fig. 2(c) and Table II). The population of an intermediate \(^{1}A_1\) state (i.e., species S) also matches with the observed ultrafast ligand addition pathway, as we will argue below. Further studies of the Fe(CO)\(_4\) potential energy surfaces and the determination of the minimum energy crossing points between the \(^{1}B_2\), \(^{1}A_1\), and \(^{3}B_2\) surfaces could give additional valuable insight to the proposed SC pathway.

C. Ultrafast ligation of Fe(CO)\(_4\)

The surprisingly fast time scale for the solvent addition of 200–300 fs demonstrates the high reactivity of Fe(CO)\(_4\). In order to understand this high bimolecular reaction rate, we consider two factors: the collision frequency and the ratio of reactive/non-reactive collisions. The time constant of ligation is on the same order of magnitude as the average solute-solvent collision frequency of \(\sim 500\) fs, indicating that effectively every collision with the solvent is reactive. The collision frequency was deduced by assuming a collision radius of 2 Å for both Fe(CO)\(_5\) and EtOH at room temperature (kT = 0.0257 eV). Additionally, 500 fs is also the time it takes to travel 2 Å with an average relative solute-solvent velocity at room temperature. 2 Å is the distance molecules need to move to form a Fe(CO)\(_4\)EtOH complex: The distance from the Fe center to oxygen or carbon of an EtOH molecule in the first solvation shell is \(\sim 4\) Å and \(\sim 5\) Å (Fig. 5), respectively, and the corresponding bond length in a hydroxyl bound Fe(CO)\(_4\)EtOH complex is \(\sim 2\) Å and in an alkyl bound Fe(CO)\(_4\)EtOH complex is \(\sim 3\) Å.74
Although the observed ligation time constant matches well, within the experimental errors, with the room temperature collision frequency of 500 fs, it is important to consider if a considerable excess of vibrational energy in the Fe(CO)$_4$ fragment could have an effect on the ligation time constant because there is an obvious square root dependence between the speed of a molecule and the kinetic energy. From gas phase studies, it is known that Fe(CO)$_4$ has to accommodate about 2.2 eV excess vibrational energy directly after dissociation (depending on the exact electronic state). However, at such early time delays, it is difficult to estimate the amount of vibrational energy in modes relevant for the ligation because there has not been enough time for thermalization of the energy through internal energy redistribution processes. At so early times, a considerable fraction of the 2.2 eV energy is carried by CO-Fe-CO bending motions that are strongly coupled to CO dissociation coordinate. It is nevertheless evident that even if a small fraction of this energy is deposited to the Fe(CO)$_4$ translational degrees of freedom, the ligation time constant could shorten considerably. Given the experimentally observed time constant, one could quantify that the translational energy of Fe(CO)$_4$ is in the order of 0.1 eV or less.

Ligation at the rate of the collision frequency is only possible if all of the Fe(CO)$_4$ collisions with the solvent are reactive, resulting in the formation of the complex effectively during a first collision. It follows that there must be no hindrance of the ligation neither due to slower dynamics of ethanol reorientation and/or hydrogen-bond network rearrangements nor due to IC from the open shell $^1 \text{B}_2$ state to the closed shell $^1 \text{A}_1$ (or $^1 \text{A}'$ in C$_s$ symmetry) state. We shall discuss these two aspects in more detail.

IC to $^1 \text{A}_1$ Fe(CO)$_4$ state is necessary for the ligand addition reaction because only the $^1 \text{A}_1$ state is reactive with respect to ligation (i.e., $^1 \text{A}_1$ potential energy surface is barrierless and attractive, Fig. 4). This is distinctive from the open shell $^1 \text{B}_2$ LF states which are repulsive
(Fig. 4). The latter can be explained by the fact that the low-energy anti-bonding \( d_{x^2} \) orbital which strongly hybridizes with the occupied orbitals of the incoming ligand is unoccupied in \( 1A_1 \) in contrast to \( 1,3B_2 \) states.\(^1\) Addressing a possible hindrance of ligation due to IC from the \( 1B_2 \) surface to the \( 1A_1 \) surface, it is important to discuss the location of surface hopping. We consider it unlikely that the hopping takes place along the Fe-EtOH distance coordinate because the \( 1A_1 \) and \( 1B_2 \) surfaces do not cross along this coordinate (Fig. 4). Most likely, it is the very energetic internal CO-Fe-CO bending modes that are active in IC from \( 1B_2 \) to \( 1A_1 \) (Fig. 4). The surface hopping could take place at a tetrahedral Fe(CO)\(_4\) geometry where \( 1B_2 \) and \( 1A_1 \) states are degenerate.\(^3\) The high internal energy contained by the CO-Fe-CO bending modes allows the molecule to access the crossing seams between \( 1B_2 \) and \( 1A_1 \) promptly. As mentioned before, Trushin et al. measured a time constant of 50 fs for this process, and therefore Fe(CO)\(_4\) molecules convert to reactive \( 1A_1 \) state already before colliding with the solvent.\(^3\) Therefore, we find that ultrafast ligation can be present only if the Fe(CO)\(_4\) converts ultrafast to intermediate \( S \) species, again favoring the second kinetic rate model (Fig. 2(c)) in contrast to the first kinetic rate model introduced in Ref. 1 (Fig. 2(b)).

Experimental and computational studies have shown that (equilibrium) reorientational dynamics in bulk ethanol occur on time scales on the order of 10–100 ps.\(^80\)–\(^82\) Efficient ligation of \( 1A_1 \) Fe(CO)\(_4\) species can therefore be possible only if the ethanol molecules in the first solvation shell of Fe(CO)\(_5\) are “pre-aligned” to a favorable configuration for the reaction (i.e., with hydroxyl groups towards Fe(CO)\(_5\)) or if the ligation is not sensitive to the orientation of ethanol molecules. In a recent study, it was found that in Fe(CO)\(_5\) ethanol solution a Fe(CO)\(_5\)EtOH complex can be formed.\(^6\) Our calculations failed to find a stable Fe(CO)\(_5\)EtOH complex, but we confirmed the presence of an ordered first solvation shell with ethanol molecules oriented towards Fe(CO)\(_5\) with their hydroxyl groups (Fig. S20).\(^7\) The presence of pre-oriented solvent molecules is favorable for ultrafast ethanol addition reaction. Alternatively, our time resolved RIXS spectra do not distinguish between hydroxyl and alkyl coordinated ethanol molecules. Therefore, based on the current experiment, we cannot conclude on how important the ordering of the solvation shell is for the ligation. However, we find that pre-orientation is not necessary to explain our experimental observables. Highly reactive \( 1A_1 \) Fe(CO)\(_4\) species can also react with alkyl groups,\(^35\),\(^83\) creating an agostic-type of bond\(^84\) with the methyl group of ethanol. Thus, we assume that both hydroxyl and alkyl solvated complexes are created in the process (species C was defined before as 1:1 mixture of hydroxyl and alkyl solvated Fe(CO)\(_2\)EtOH complexes). The fact that reorientation of the solvent molecules or a disruption of the hydrogen-bond network does not seem necessary thus explains why ligation of \( 1A_1 \) Fe(CO)\(_4\) molecules (species \( S \)) with the solvent is so fast.

We performed two CPMD simulations to investigate the solvation of Fe(CO)\(_4\). Simulations were performed by removing one CO ligand at \( t = 0 \) from a Fe(CO)\(_5\) molecule in \( 1A_1 \) closed shell ground state (Fig. 6). Therefore, different from the situation in the experiment, there is no excess vibrational energy deposited to Fe(CO)\(_4\) moiety. Note that in both simulations the EtOH molecule which eventually binds with the Fe(CO)\(_4\) comes from a second solvation shell. This could be one reason why in these two simulated cases the ligand addition takes \( \sim 4 \) ps, i.e., significantly more than observed in the experiment. Although these simulations do not directly confirm the experimental findings, they nevertheless show that the reduction of Fe-O(EtOH) distance by 2 Å can happen with less than 1 ps even in case of cold Fe(CO)\(_4\), therefore supporting our argument based on the solute-solvent collision frequency.

The ultrafast ligand addition mechanism proposed here is qualitatively similar to solvation of Cr(CO)\(_5\) after photodissociation of Cr(CO)\(_6\) in alcohol solution. First observed by Simon et al. with UV/Vis transient absorption spectroscopy, in methanol solution, a Cr(CO)\(_5\)MeOH is created with \( \sim 2.5 \) ps.\(^85\) Joly et al. carried out measurements in a selection of alcohols (including ethanol) and found a rather solvent independent 1.6 ps solvation time constant which is preceded by 350 fs dissociation.\(^86\),\(^87\) The initially created Cr(CO)\(_5\)ROH species are mostly alkyl coordinated, rearrangement to thermodynamically stable hydroxyl coordinated species takes 80–200 ps, depending on the solvent.\(^88\)–\(^90\) Note that, in contrast to Fe(CO)\(_4\), the ground state of
Cr(CO)\textsubscript{5} is a singlet and therefore the Cr(CO)\textsubscript{5} species follow the ultrafast ligation pathways without any competing branching to a triplet state. The slower time scale of Cr(CO)\textsubscript{5} ligation compared with Fe(CO)\textsubscript{4} could be related to the additional CO ligand which sterically hinders the reaction.

The $\text{E} \rightarrow \text{L}$ reaction can thus be summarized in two steps (Fig. 4). First, intra-molecular $1\text{B}_2$ to $1\text{A}_1$ IC facilitated by the very energetic CO-Fe-CO bending modes, which is followed by a single collision with the solvent on an attractive $1\text{A}_1$ ($1\text{A}_1$ in C\textsubscript{s} symmetry) surface with an approximately room temperature solute-solvent collision speed (Fig. 4). We therefore propose that branching of the Fe(CO)\textsubscript{4} relaxation pathway takes place in the four-coordinated $1\text{A}_1$ state. Which pathway a particular molecule takes depends on what happens before: reactive collision with the solute or SC to $3\text{B}_2$ driven by highly energetic CO-Fe-CO bending motions. In Section II B, we proposed a mechanism for SC which explains why the latter has a similar time scale to the solute-solvent collision frequency, therefore rationalizing our experimental observation that both SC and ligation are relevant channels.

Snee et al. studied slower time scale kinetics (up to 700 ps) of the Fe(CO)\textsubscript{5} photoreaction in methanol and they observed the appearance of CO stretch peaks of the thermally relaxed Fe(CO)\textsubscript{4}MeOH complex with a time constant of 42 ps.\textsuperscript{41} We believe that such slow formation of the final reaction product is consistent with the ultrafast ligand capture process observed here. As noted by Snee et al., the slow time scale is related to cooling of the Fe(CO)\textsubscript{4} moiety, diffusional reorientation motions of the solvent molecules, and reaction of the remaining triplet Fe(CO)\textsubscript{4} species with ethanol. This could also include relaxation of alkyl solvated Fe(CO)\textsubscript{4}EtOH complexes to hydroxyl bound configurations, similar to Cr(CO)\textsubscript{5}ROH. Consistently, vibrational relaxation of the CO-Fe-CO bending modes has been independently measured to take 10–20 ps, depending on the solvent.\textsuperscript{8,91,92} We would therefore emphasize that the ultrafast ligation process identified here does not lead to a formation of stable Fe(CO)\textsubscript{4}EtOH complex with a single clearly defined structure corresponding to the minimum energy geometry. Instead, the observed spectroscopic signature of the complex indicates that a solvent molecule has moved to the first coordination shell of iron. The formed solvent complex thus samples likely a wide range of geometries that have a solvent molecule in proximity to iron.

V. SUMMARY AND OUTLOOK

Our study complements and details our earlier publication on the excited-state dynamics of Fe(CO)\textsubscript{4} after CO photodissociation of Fe(CO)\textsubscript{5} in ethanol solution.\textsuperscript{1} By analyzing in detail the experimental results and corresponding quantum-chemical calculations, we reveal that chemical interaction between Fe(CO)\textsubscript{4} and the surrounding environment significantly modifies the excited state...
state relaxation pathways on the sub-picosecond time scales. This is manifested by the parallel appearance of four-coordinated triplet and five-coordinated (ligated) singlet photoproducts. Based on an extensive kinetic rate model analysis, we propose the following reaction pathways. Photodissociation of Fe(CO)$_5$ yields the Fe(CO)$_4$ photoproduct in a ligand-field excited state ($^1B_2$). Relaxation of this state follows two competing pathways: Approximately half of the Fe(CO)$_4$ molecules undergo a spin crossover to the $^3B_2$ state, while the other half relaxes via the formation of a solute-solvent complex, Fe(CO)$_4$EtOH in the $^1A'$ ground electronic state, or recombines with the CO to form Fe(CO)$_5$. We propose that both SC and ligation happen via four-coordinated $^1A_1$ state that is populated ultrafast due to highly energetic CO-Fe-CO bending motions. The branching of the reaction pathway happens in the $^1A_1$ state: it can convert into non-reactive $^3B_2$ state, facilitated again by the CO-Fe-CO bending motions, or it can collide with a solvent molecule and form a Fe(CO)$_4$EtOH complex. Due to the extremely high reactivity of the Fe(CO)$_4$ $^1A_1$ state, ligation does not require considerable reorientation of solvent molecules and therefore Fe(CO)$_4$ in the $^1A_1$ state becomes effectively ligated during its first collision with the solvent. The branching ratio between spin crossover and ligation pathways is thus determined by the time of intra-molecular $^1A_1$ to $^3B_2$ SC with respect to solute-solvent collision frequency.

In conclusion, we would like to emphasize that further experimental studies are needed in order to fully understand the Fe(CO)$_4$ ligand exchange dynamics. These experiments should be able to clearly distinguish between different spin ($^1A_1$ vs. $^3B_2$) and coordination (complexed vs. uncomplexed) state of Fe(CO)$_4$. Femtosecond Fe L$_3$-edge RIXS technique utilized in the current study has this ability; however, a better time-resolution (<100 fs) and an improved signal-to-noise ratio are needed. Alternatively, recently developed combined ultrafast X-ray emission spectroscopy and diffuse X-ray scattering should also have this capability. Additional difficulty related with the interpretation of these ultrafast, highly non-equilibrium processes is the fact that a relaxation to species with well-defined geometries and energy barriers has not yet taken place. This renders kinetic modeling of these processes approximate and it is thus anticipated that the analysis of the future improved experiments needs to consider the actual dynamical nature of these processes by taking into account the broad time-dependent distribution of structures the molecules are sampling.

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