Orbital-specific mapping of the ligand exchange dynamics of Fe(CO)₅ in solution

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Transition-metal complexes have long attracted interest for fundamental chemical reactivity studies and possible use in solar energy conversion^{1,2}. Electronic excitation, ligand loss from the metal center, or a combination of both creates charge and spin density changes at the metal site³⁻¹¹, which need to be controlled to optimize complexes for photocatalytic hydrogen production⁸ and selective carbon-hydrogen bond activation⁹⁻¹¹. A molecular-level understanding of how transition-metal complexes catalyze reactions, and in particular of the role of short-lived and reactive intermediate states involved, will be critical for such optimization. However, suitable methods for detailed characterization of electronic excited states have been lacking. Here we use x-ray laser based femtosecond-resolution spectroscopy and advanced quantum chemical theory to probe the reaction dynamics of the benchmark transition-metal complex Fe(CO)₅ in solution. We find that the photo-induced removal of CO generates the 16-electron Fe(CO)₄ species, a homogeneous catalyst^{12,13} with an electron deficiency at the Fe center^{14,15}, in a hitherto unreported excited singlet state that either converts to the triplet ground state or combines with a CO or solvent molecule to regenerate a penta-coordinated Fe species on a sub-picosecond time scale. This finding, which resolves the debate about the relative importance of different spin channels in the photochemistry of Fe(CO)₅^{4,16-20}, is enabled by the ability of femtosecond x-ray spectroscopy to probe frontier-orbital interactions with atom specificity. We anticipate that the method will be broadly applicable in the chemical sciences, and complement approaches that probe structural dynamics in ultrafast processes.

In our experimental set-up (Figure 1a), the valence electronic structure of Fe(CO)₅ is probed with femtosecond-resolution resonant inelastic x-ray scattering (RIXS) at the Fe L₃-edge (Fe L₃-RIXS, illustrated in Fig. 1b). The frontier orbitals of ironpentacarbonyl, Fe(CO)₅, and its photofragments are the Fe-centered d_π and d_σ* orbitals. With an incident photon energy of 710 eV to select the lowest-energy x-ray resonance corresponding to 2p→LUMO(d_σ*)

excitations and scattering inelastically to the valence-excited ligand-field states with $d_{\pi}^7 d_{\sigma}^{*1}$ configuration, we effectively probe $d_{\pi} \rightarrow d_{\sigma}^*$ transitions (note that the single-electron orbital-based assignments can be applied at the level the system is studied here, see the Supplementary Information section 2.b.). The energies of these transitions equal the measured energy transfers (i.e., the difference between incident and scattered photon energies indicated as “In” and “Out” in Fig. 1b), and directly reflect the changes in chemical bonding and ligand coordination. The intensities of the transitions in $\text{Fe}(\text{CO})_5$ are marked in Fig. 1c (top). The main intensity maximum involves $2p \rightarrow 2\pi^*$ excitations at 711.5 eV with excitation to the ligand-centered $2\pi^*$ orbitals and inelastic scattering to $d_{\pi}^7 2\pi^{*1}$ charge-transfer states (Fig. 1c) and is not further analyzed.

The unsaturated carbonyl $\text{Fe}(\text{CO})_4$ was generated in ethanol (EtOH) solution by photodissociation of $\text{Fe}(\text{CO})_5$ with optical (266 nm) femtosecond laser pulses in less than 100 fs. Our experiment consisted of recording Fe L_3 -RIXS intensities versus energy transfer while scanning incident photon energy and pump-probe time delay with a time resolution of 300 fs. The observed bimodal spectral distribution exhibits different intensities for different delays (Fig. 1c, middle and bottom), reflecting changes in $2p \rightarrow \text{LUMO}$ resonance energies within the 706.5 to 710 eV range and changes in $d_{\pi} \rightarrow d_{\sigma}^*$ transition energies within the -1 to 6 eV range. These changes quantify the changes in the frontier-orbital interactions caused by changes in ligand coordination when going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_4$ and during the subsequent excited-state dynamics. Ligand dissociation is expected to create a “localized hole on the metal”¹⁵ with a concomitant decrease in the d_{π} - d_{σ}^* splitting (see the molecular-orbital diagram in the Supplementary Information section 2.e.). This manifests itself in the Fe L_3 -RIXS spectra at time delays of 0-700 fs (Fig. 1c, middle) as a new $2p \rightarrow \text{LUMO}$ resonance at 706.5 eV and as the maximum of the $d_{\pi} \rightarrow d_{\sigma}^*$ transitions shifted to lower energies by -4 eV relative to $\text{Fe}(\text{CO})_5$. Coordinative saturation through ligation with CO or ethanol restores the d_{π} - d_{σ}^* splitting mostly due to σ -bonding between $\text{Fe}(\text{CO})_4$ and CO or ethanol. This could explain the

occurrence of $2p \rightarrow \text{LUMO}$ and $d_\pi \rightarrow d_\sigma^*$ transition energies comparable to $\text{Fe}(\text{CO})_5$ at late delays of 0.7-3.5 ps (at 709.5 and 3 eV, Fig. 1c, bottom).

To substantiate this and quantitatively analyze the time-resolved data in Figure 2a, we performed ab initio Fe L_3 -RIXS calculations for selected structures. The calculated spectra of the three lowest electronic states of $\text{Fe}(\text{CO})_4$, of the lowest states of $\text{Fe}(\text{CO})_4\text{-EtOH}$ complexes and of $\text{Fe}(\text{CO})_5$ in optimized and distorted geometries account for all experimental features. Fig. 2b shows the spectra and electronic configurations, which correspond to excited singlet-state $\text{Fe}(\text{CO})_4$ ($d_\pi^7 d_\sigma^{*1}$, 1B_2), triplet-state $\text{Fe}(\text{CO})_4$ ($d_\pi^7 d_\sigma^{*1}$, 3B_2), singlet-state $\text{Fe}(\text{CO})_4$ ($d_\pi^8 d_\sigma^{*0}$, 1A_1), “hot” singlet $\text{Fe}(\text{CO})_5$ ($d_\pi^8 d_\sigma^{*0}$, 1A_1), as represented by structures with distorted geometries compared to the optimized one) and singlet complexes with the solvent $\text{Fe}(\text{CO})_4\text{-EtOH}$ ($d_\pi^8 d_\sigma^{*0}$, $^1A'$).

The most informative spectral regions in our data, labeled **1-4** in Fig. 2a, maximally overlap with the calculated spectral features best able to identify and distinguish the respective intermediate species. The intensities at negative transfers in region **1** result from outgoing x-rays with higher energy than the incoming x-rays and can only result when the x-rays inelastically scatter off $\text{Fe}(\text{CO})_4$ fragments in d_π and d_σ^* electronic excited states (representing the first report of RIXS from excited states, to the best of our knowledge). Region **2** is dominated by contributions of excited and triplet $\text{Fe}(\text{CO})_4$. We emphasize that RIXS gives unique chemical resolution, as integrating over the energy transfer and only measuring time-dependent changes in x-ray absorption would prevent us from distinguishing the dynamics of the species assigned to regions **1** and **2**. Region **3** identifies the dynamics of ligated $\text{Fe}(\text{CO})_4$ species, i.e. $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{-EtOH}$. Region **4** corresponds to the $2p \rightarrow 2\pi^*$ x-ray resonances with $d_\pi \rightarrow 2\pi^*$ RIXS transitions in most of the calculated species, and seems dominated by the depletion of $\text{Fe}(\text{CO})_5$.

The temporal evolution of the Fe L₃-RIXS intensities measured in regions **1-4** is plotted in Fig. 2c, together with the result of a kinetic model that simultaneously fits the sum of the calculated excited-state singlet, triplet and ligated Fe(CO)₄ spectra in each region to the measured data [see the Supplementary Information section 3. for details of the kinetic model and the contribution of singlet Fe(CO)₄]. This fitting procedure indicates the appearance of the excited singlet state of Fe(CO)₄ (¹B₂) within the time resolution of our experiment [which is insufficient to resolve the initial, UV-generated excited state of Fe(CO)₅]. This allows us to unambiguously assign, within the single-electron orbital picture, the related RIXS intensities at negative energy transfers to 2p→d_π excitations in excited Fe(CO)₄ (d_π⁷d_σ^{*1}, ¹B₂) with predominant inelastic scattering to states with d_π⁸d_σ^{*0} configuration. As is apparent from the molecular orbital diagram of excited Fe(CO)₄ in Fig. 2b, these transitions entail negative energy transfer because the incident photon energy is smaller than the scattered photon energy. Note that the detection and characterization of electronic excited states free from background by non-excited states, enabled by RIXS at negative energy transfers, provides a powerful approach to studying the electronic excited states of chemically active molecules.

The decay of excited singlet-state Fe(CO)₄ (¹B₂) coincides with the rise of the triplet Fe(CO)₄ ground state in solution (³B₂), for which our model gives a time constant of 300±100 fs. Within the experimental uncertainty, our data indicate the simultaneous rise of coordinatively saturated “hot” Fe(CO)₅ arising from geminate recombination with CO and of Fe(CO)₄-EtOH arising from complexation with solvent molecules (fitted time constant 200±100 fs). The failure of kinetic models without triplet Fe(CO)₄ (³B₂) (dashed curve in Fig. 2c, region 2) or without ligated Fe(CO)₄ (dashed curve in Fig. 2c, region 3) justifies the use of three distinct photoproducts in the kinetic modeling and underlines the robustness of our detection of triplet Fe(CO)₄ (³B₂) in parallel with “hot” Fe(CO)₅ and Fe(CO)₄-EtOH. Because we cannot spectroscopically distinguish geminately recombined “hot” Fe(CO)₅ from solvent-

complexed $\text{Fe}(\text{CO})_4\text{-EtOH}$, their ratio in the kinetic model is fixed to one to four based on the measured quantum yield of 0.8 for solvent-separated $\text{Fe}(\text{CO})_4$ and CO^{21} .

Figure 3 sketches the reaction pathways established in this study, with detection of the excited singlet-state $\text{Fe}(\text{CO})_4$ ($^1\text{B}_2$) confirming the suggestion¹⁶ that the primary reaction steps in solution also involve the singlet pathway as seen in the gas phase^{17, 18}. The proposed relaxation of excited singlet $\text{Fe}(\text{CO})_4$ ($^1\text{B}_2$) to singlet $\text{Fe}(\text{CO})_4$ ($^1\text{A}_1$) via internal conversion¹⁷ is consistent with our data (see the Supplementary Information section 3.d.), but we also observe triplet $\text{Fe}(\text{CO})_4$ ($^3\text{B}_2$) that was previously seen in solution^{19, 4} and in rare-gas matrix¹⁶ experiments. This triplet arises from a singlet state with a time constant of 300 fs, consolidating the notion⁶ that sub-ps intersystem crossing appears to be common in the excited-state dynamics of transition-metal complexes^{7, 22-24}. The persistence of the triplet $\text{Fe}(\text{CO})_4$ ($^3\text{B}_2$) up to our maximum time delay of 3 ps is consistent with it undergoing a slow, spin-forbidden reaction with intersystem crossing to a solvent-complexed singlet state on the 50-100 ps time scale^{4, 5, 25}. However, the observed branching on a sub-ps time scale into the competing and simultaneous reaction channels of spin crossover and ligation to form coordinatively saturated species introduces an efficient pathway circumventing this spin barrier. It also supports the idea that the high density of electronic excited states and the relatively large amount of excess energy available in the system determine the course of the excited-state dynamics, rather than spin selection rules alone^{5, 6}. Fast ligation could be facilitated along the singlet pathway, confirming the general notion that solvent-stabilized metal centers form fast^{3, 4, 11} and consistent with the observation of unsaturated carbonyl $\text{Cr}(\text{CO})_5$ forming a solvent complex in alcohol solution within 1.6 ps²⁶. An alternative proposal²⁰ for $\text{Fe}(\text{CO})_5$ involves concerted exchange of CO and EtOH on the time scale of ligand dissociation of 100-150 fs. This would also proceed along a singlet pathway and in agreement with our results, as the temporal resolution of our measurements is not sufficient to distinguish between this concerted and the alternative sequential process. Revealing in detail

the influence of solvent-solute interactions will have to be the subject of future studies, which could also explore whether the structure of the solute prior to dissociation²⁰ influences the excited-state branching ratio between the different pathways.

We find that the ligation capability of $\text{Fe}(\text{CO})_4$ is mostly determined by its d_σ^* LUMO, which receives σ donation from occupied CO or ethanol ligand orbitals. Population of the antibonding d_σ^* orbital in excited singlet ($^1\text{B}_2$) and triplet ($^3\text{B}_2$) $\text{Fe}(\text{CO})_4$ impedes σ donation from ligands (see sketches in Figure 3), explaining the inertness of these species against ligation; this problem is absent in the ligation channel that produces coordinately saturated species. Establishing this correlation of orbital symmetry with spin multiplicity and reactivity²⁷ is enabled by the atom specificity with which x-ray laser based femtosecond-resolution spectroscopy can explore frontier-orbital interactions. This ability gives unique access to the reaction mechanisms of metal complexes, in a way that extends and complements methods that probe structural dynamics in ultrafast chemical processes in solution²⁸⁻³⁰.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Figure legends

Figure 1: Scheme and results of the experiment. **a** Scheme with optical-laser pump and soft x-ray probe after the pump-probe time delay Δt . The intensity of resonant inelastic x-ray scattering (RIXS) is measured at the Fe L_3 -absorption edge with a dispersive grating spectrometer. **b** Electron configuration of ground-state $\text{Fe}(\text{CO})_5$ with single-electron transitions of x-ray probe and laser-pump processes (orbital assignments according to Fe 2p and 3d or ligand 2π character and according to symmetry along the Fe-CO bonds, * marks antibonding orbitals). RIXS at the Fe L_3 -absorption edge with scattering to final $d_\pi^7 d_\sigma^*^1$ ligand-field excited states. Optical $d_\pi \rightarrow 2\pi^*$ excitation triggers dissociation. **c** Measured Fe L_3 -RIXS intensities (encoded in color) versus energy transfer and incident photon energy. **Top:** Ground-state $\text{Fe}(\text{CO})_5$ (negative delays, probe before pump). **Middle** and **bottom:** Difference intensities for delay intervals of 0-700 fs and 0.7-3.5 ps, respectively, isolating transients by subtracting scaled intensities of un-pumped $\text{Fe}(\text{CO})_5$ from the measured intensities (scaling factor 0.9). For details of the experiment and a deduction of the scaling factor see the Supplementary Information section 1.

Figure 2: Fe-specific changes in the electronic structure of $\text{Fe}(\text{CO})_4$ upon femtosecond spin crossover and ligation. **a** Measured Fe L_3 -RIXS of $\text{Fe}(\text{CO})_5$ (top, same as Fig. 1c) and measured difference intensities (bottom, integrated intensities of all positive pump-probe delays minus integrated intensities of all negative delays). Boxes **1-4** mark energy-transfer/incident-photon energy regions for which the temporal evolutions of intensities are

plotted in **c**. **b** Calculated Fe L₃-RIXS intensities and electronic configurations of the given species ($2p \rightarrow \text{LUMO}$ and $d_\pi \rightarrow d_\sigma^*$ transitions marked by arrows, note that the LUMO can be d_σ^* or d_π depending on the electron configuration). **c 1-4** Measured intensities in regions **1-4** versus pump-probe delay (circles with error bars reflecting twice the standard deviation) with the best global fit of a kinetic model (solid lines) with extracted populations of excited (E), triplet (T) and ligated (L) Fe(CO)₄ [L is a sum of “hot” Fe(CO)₅ and Fe(CO)₄-EtOH]. The dashed lines in **2 (3)** represent alternative models without triplet (ligated) Fe(CO)₄. The measured signals stayed constant up to 3 ps. For details of the calculations, structures and energies of the species and how ligation in Fe(CO)₄-EtOH can occur be via the alkyl or hydroxyl group see the Supplementary Information section 2.

Figure 3: Schematic reaction pathways of Fe(CO)₄ in ethanol. Parallel evolution from excited singlet-state Fe(CO)₄ to triplet-state Fe(CO)₄ via spin crossover (rise of triplet with time constant 300±100 fs) and to coordinatively saturated “hot” singlet Fe(CO)₅ via geminate recombination and Fe(CO)₄-EtOH via solvent-complex formation [rise of ligated Fe(CO)₄ with time constant 200±100 fs]. A triplet pathway to Fe(CO)₄-EtOH complex formation within 50-100 ps is indicated in grey. Interaction of the d_σ^* LUMO of Fe(CO)₄ with a ligand σ orbital (different phases are shown in black and white) is shown in the sketches with ligand-to-Fe σ donation in the coordinatively saturated species.

a **b** **c**

Non-interacting

Complex formation

Interacting