

# Photochemical Formation and Electronic Structure of an Alkane $\sigma$ -Complex from Time-Resolved Optical and X-ray Absorption Spectroscopy

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**ABSTRACT:** C-H bond activation reactions with transition metals typically proceed via the formation of alkane  $\sigma$ -complexes, where an alkane C-H  $\sigma$ -bond binds to the metal. Due to the weak nature of metal-alkane bonds,  $\sigma$ -complexes are challenging to characterize experimentally. Here, we photochemically prepare the model  $\sigma$ -complex Cr(CO)<sub>5</sub>-alkane from Cr(CO)<sub>6</sub> in octane solution and characterize the nature of its metal-ligand bonding interactions. Using femtosecond optical absorption spectroscopy, we find photo-induced CO dissociation from Cr(CO)<sub>6</sub> to occur within the 100 fs time-resolution of the experiment. Rapid geminate recombination by a fraction of molecules is found to occur with a time constant of 150 fs. The formation of bare Cr(CO)<sub>5</sub> in its singlet ground state is followed by complexation of an octane molecule from solution with a time constant of 8.2 ps. Picosecond X-ray absorption spectroscopy at the Cr L-edge and O K-edge provides unique information on the electronic structure of the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex both from the metal and ligand perspectives. We find substantial destabilization of the lowest unoccupied molecular orbital upon coordination of the C-H bond to the undercoordinated Cr center in the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex, accompanied with rehybridization between metal and ligand orbitals. Our study demonstrates the value of combining optical and X-ray spectroscopic methods as complementary tools to study the properties of alkane  $\sigma$ -complexes as the decisive intermediates in C-H bond activation reactions.

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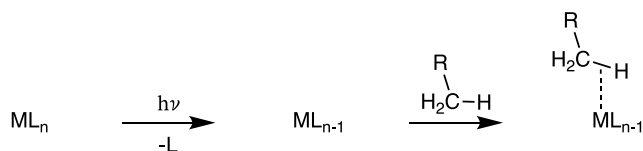
## INTRODUCTION

Alkane  $\sigma$ -complexes play a critical role in C-H bond activation reactions with transition metal complexes. They constitute the decisive intermediates in which an alkane C-H bond directly coordinates and interacts with the transition metal<sup>1-3</sup>. Due to their low polarizability, however, alkanes are generally poor electron donors and acceptors. The bond strength between the metal and the alkane C-H bond in  $\sigma$ -complexes is therefore typically very weak. Still, the subtle degree of polarization induced in the C-H bond through binding to the metal site in  $\sigma$ -complex intermediates critically determines the reactivity towards bond cleavage in C-H activation reactions<sup>4</sup>. In pursuit of understanding this unusual bonding configuration, a rich literature of complexes, in which alkane C-H bonds act as ligands bound to a metal center, has emerged over the decades<sup>3,5-7</sup>.

Various routes exist towards preparation of alkane  $\sigma$ -complexes. Direct preparation in the solid state has been achieved by hydrogenation of metal-bound alkenes<sup>8,9</sup> as well as in solution via protonation of a metal-bound alkyl group at very low temperature<sup>10</sup>. The most common routes to preparing alkane  $\sigma$ -complexes, however, are photochemical ones<sup>3</sup> (see Scheme 1). The photo-induced elimination of a ligand from certain transition metal complexes leads to the creation of an

undercoordinated and highly reactive species capable of binding an alkane from solution. This type of photochemical preparation has been the basis for a wide range of spectroscopic investigations of alkane  $\sigma$ -complexes. Early flash photolysis experiments in low-temperature matrices as well as solution unambiguously established that alkanes can indeed act as ligands in a metal complex<sup>11-14</sup>. Later, nuclear magnetic resonance (NMR) and time-resolved infrared (IR) spectroscopy, in particular, were instrumental in characterizing the structure of alkane  $\sigma$ -complexes as well as their mechanistic role in C-H activation reactions<sup>15-22</sup>.

As the precursor to Cr(CO)<sub>5</sub>-alkane, one of the first ever observed alkane  $\sigma$ -complexes<sup>11,13,14</sup>, chromium hexacarbonyl (Cr(CO)<sub>6</sub>) has long served as a model systems for both, developing a general mechanistic understanding of photo-induced ligand exchange as well as gaining specific insight into the nature and properties of alkane  $\sigma$ -complexes<sup>6</sup>. However, while constituting a thoroughly studied model system, experimentally resolving the ultrafast timescales of the formation of Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complexes has proven difficult. NMR spectroscopy is intrinsically slow compared to ligand-exchange dynamics, and can only probe species, which are meta-stable on nano- to



**Scheme 1.** Reaction scheme of photochemical alkane  $\sigma$ -complex formation.

millisecond timescales. Time-resolved IR spectroscopy accesses the timescales necessary to detect  $\sigma$ -complexes but has limited sensitivity to their electronic structure and to the sub-picosecond regime of excited-state and dissociation dynamics due to the broad and overlapping IR absorption bands of vibrationally hot species on these timescales.

Here, we combine femtosecond optical absorption and picosecond X-ray absorption spectroscopy<sup>23,24</sup> to determine, based on the complementary time scales and properties these methods access, the photochemical pathway of formation and the bonding characteristics of  $\sigma$ -complexes with  $Cr(CO)_6$  in alkane solution. Femtosecond optical absorption spectroscopy has been used before to follow the initial steps in the ligand-exchange dynamics of  $Cr(CO)_6$  and other transition metal complexes in various solvents including alkanes<sup>25–32</sup>. Due to insufficient time-resolution and detection sensitivity, however, these investigations were unable to robustly resolve and assign the intermediates along the alkane  $\sigma$ -complex formation from  $Cr(CO)_6$  observed on the femtosecond timescale<sup>25,30</sup>. For instance, it has remained unclear what the timescale of CO dissociation in solution is, whether CO dissociation produces a bare  $Cr(CO)_5$  fragment in solution before binding to an alkane and, if so, whether  $Cr(CO)_5$  is present in its ground or an excited state. Answering these questions is critical for developing a fundamental mechanistic understanding of ligand-exchange reactions as the basis for alkane  $\sigma$ -complex formation in photochemical C-H activation reactions with transition metals.

Time-resolved X-ray absorption spectroscopy has previously been shown to provide information highly complementary to the information provided by time-resolved optical and infrared absorption spectroscopy. Measuring the extended absorption fine structure (EXAFS) at the tungsten L-edge has recently allowed Bartlett et al. to determine metal-alkane bond lengths in  $W(CO)_5$ -alkane  $\sigma$ -complexes<sup>33</sup>. By evaluating the character of main-edge transitions in the rhodium L-edge absorption spectrum, the metal-alkane orbital interactions upon formation of rhodium-alkane  $\sigma$ -complexes as well as the ensuing C-H bond cleavage via oxidative addition have recently been observed<sup>34</sup>. The direct access of X-ray absorption spectroscopy to the relevant metal d-derived orbitals by the  $2p \rightarrow nd$  transitions underlying transition-metal L-edges allows to evaluate the degree to which metal d-orbitals hybridize with incoming alkane C-H bonds. Such properties of alkane  $\sigma$ -complexes, which have thus far mostly been studied using theory<sup>35–38</sup>, can now be validated experimentally<sup>34</sup>. Here, we use the respective capabilities of femtosecond optical absorption and picosecond X-ray absorption spectroscopy to establish the photochemical pathways of  $Cr(CO)_6$  dissociation in octane solution and to characterize the electronic structure of the resulting  $Cr(CO)_5$ -alkane  $\sigma$ -complex.

## METHODS

**Materials.**  $Cr(CO)_6$  was prepared in n-octane (purchased from Sigma-Aldrich) at concentrations of 7 mM for the time-resolved transient optical and 20 mM for the X-ray absorption

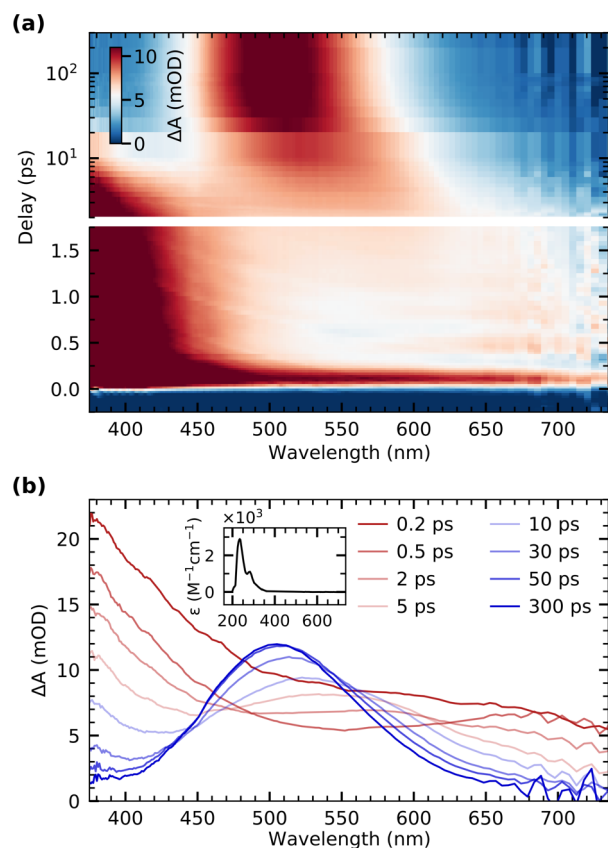
measurements. To achieve the concentration of the X-ray absorption measurements, the sample was stirred and put into a sonication bath for up to  $\sim 1$  h.

**Transient UV-visible absorption spectroscopy.** Time-resolved UV-visible measurements were conducted using a 3 kHz Ti:sapphire amplified laser system (Spectra Physics Spitfire Ace, 90 fs, 800 nm). The sample was prepared as a free-flowing 300  $\mu m$  thick wire-guided liquid sheet. The sample was optically excited by the third harmonic of the fundamental laser wavelength with a fluence of 4.6 mJ/cm<sup>2</sup>. A super-continuum pulse (generated in a 1-mm calcium fluoride plate) was used to probe the absorbance change in transmission using a prism-based imaging spectrograph and a CCD detector, while a second super-continuum pulse served as a reference. The data was chirp-corrected by using the delay at half rise of the signal onset for every wavelength. The time resolution as determined by the rise time of the transient absorption signals was  $\sim 100$  fs. Pump-probe measurements of the pure octane solvent under the same experimental conditions showed a negligible contribution of a coherent artifact to the pump-induced signal around zero delay.

**Time-resolved X-ray absorption spectroscopy.** The time-resolved X-ray absorption measurements were performed at the UE52-SGM beamline<sup>39</sup> of the BESSY II synchrotron. The X-ray absorption data were acquired in transmission geometry using a flatjet sample delivery system<sup>40,41</sup>. The liquid sample was transported into the experimental vacuum chamber via two colliding jets, thereby forming a thin liquid sheet. To form a stable octane sheet, flow rates were kept between 4.5 and 5 ml/min using a pair of nozzles with a diameter of  $\sim 50$   $\mu m$ . The thickness of the liquid sheet was between 4.3  $\mu m$  and 4.6  $\mu m$  throughout all measurements as estimated from the comparison of the transmissions at 528 eV (O K-edge) and 573 eV (Cr L-edge) to tabulated values<sup>42</sup>. The bandwidth of the incidence X-rays was  $\sim 200$  meV at the O K-edge and  $\sim 250$  meV at the Cr L-edge. The sample was optically excited by the fourth harmonic of a fiber laser (Amplitude Tangerine, 1030 nm, 350 fs) at 258 nm wavelength. The repetition rate of the laser was set to 208 kHz for all measurements. The laser pulse energy was  $\sim 5$   $\mu J$  at a spot size of  $\sim 60 \times 100$   $\mu m^2$  at the sample amounting to an overall laser fluence of  $\sim 100$  mJ/cm<sup>2</sup>. The time resolution as derived from the rise time of the transient X-ray signals was  $\sim 45$  ps (determined by the X-ray pulse duration).

**Computational details.** Geometry optimizations were performed with the Gaussian 16 quantum chemistry suite<sup>43</sup> on the level of density functional theory (DFT) theory using the TPSSh functional<sup>44,45</sup> and the def2-TZVP<sup>46,47</sup> basis set.  $Cr(CO)_6$  was optimized in  $O_h$  symmetry,  $Cr(CO)_5$  in both,  $C_{4v}$  as well as in  $C_{2v}$  symmetry and  $Cr(CO)_5$ -butane in  $C_1$  symmetry. The butane-based  $\sigma$ -complex was used instead of the octane-based  $\sigma$ -complex to reduce the computational cost. Solvent effects were incorporated in the geometry optimizations by implicit solvation given by the conductor-like polarizable continuum (CPCM) model<sup>48,49</sup> using a dielectric constant corresponding to octane ( $\epsilon = 1.9406$ ). Based on these structures, the Cr L-edge spectra were simulated using the restricted active space self-consistent field<sup>50</sup> (RASSCF) wavefunction while the optical and O K-edge spectra were simulated using time-dependent density functional theory (TD-DFT). The details of each method are described below.

The RASSCF Cr L-edge absorption spectra were simulated in OpenMolcas<sup>51</sup>. For all spectra, the active space was constructed by rotating the Cr 2p orbitals (frozen at the Hartree-Fock level)



**Figure 1** (a) Overview of the transient optical absorption data of  $\text{Cr}(\text{CO})_6$  in octane solution following photoexcitation with a 266 nm laser pulse. (b) Transient absorption spectra for selected pump-probe delays displaying an initial broad absorption feature throughout the observed spectral range followed by formation of a transient absorption band centered at around 500 nm. The steady-state absorption spectrum of  $\text{Cr}(\text{CO})_6$  is shown in the inset.

into the RAS1 subspace and allowing at most 1 hole in the RAS1 subspace, rotating occupied valence orbitals in RAS2 and low-lying virtual orbitals in RAS3, allowing for at most 2 electrons in the RAS3 subspace. Starting with  $\text{Cr}(\text{CO})_6$ , 16 electrons are distributed in 19 orbitals corresponding to the  $1t_{1u}$  ( $2p$  core-orbitals),  $5e_g$  ( $\sigma$   $\text{CO-d}_{x^2-y^2}$  and  $\sigma$   $\text{CO-d}_{z^2}$ ) and  $2t_{2g}$  ( $d$ - $\pi$   $\text{CO}^*$ ) occupied orbitals as well as the  $9t_{1u}$  ( $\pi$   $\text{CO}^*$ ),  $2t_{2u}$  ( $\pi$   $\text{CO}^*$ ),  $3t_{2g}$  ( $\pi$   $\text{CO}^*$ - $d$ ) and  $6e_g$  ( $d_{x^2-y^2}$ - $\sigma$   $\text{CO}$  and  $d_{z^2}$ - $\sigma$   $\text{CO}$ ) unoccupied orbitals resulting in a wavefunction denoted RAS(16,1,2;3,5,11). For the RASSCF L-edge spectra, zeroth-order relativistic effects were incorporated by the Douglas-Kroll-Hess Hamiltonian<sup>52</sup> for the ANO-RCC-VTZP basis set<sup>53,54</sup> used for all atoms. 80 singlet and 80 triplet valence states were independently solved for by a state-averaged RASSCF wavefunction. 320 singlet and 480 triplet core-excited states were independently solved for by a state-averaged RASSCF wavefunction by using the HEXS keyword in the RASSCF module in OpenMolcas. The subsequent spin-orbit coupled L-edge spectra were obtained by the RASSI module<sup>55</sup>. All other complexes ( $\text{Cr}(\text{CO})_5$  ( $C_{4v}$ ),  $\text{Cr}(\text{CO})_5$  ( $C_{2v}$ ) and  $\text{Cr}(\text{CO})_5$ -butane) employed the same active space allowing for changes in orbital character. All spectrum calculations were performed in  $C_1$  symmetry.

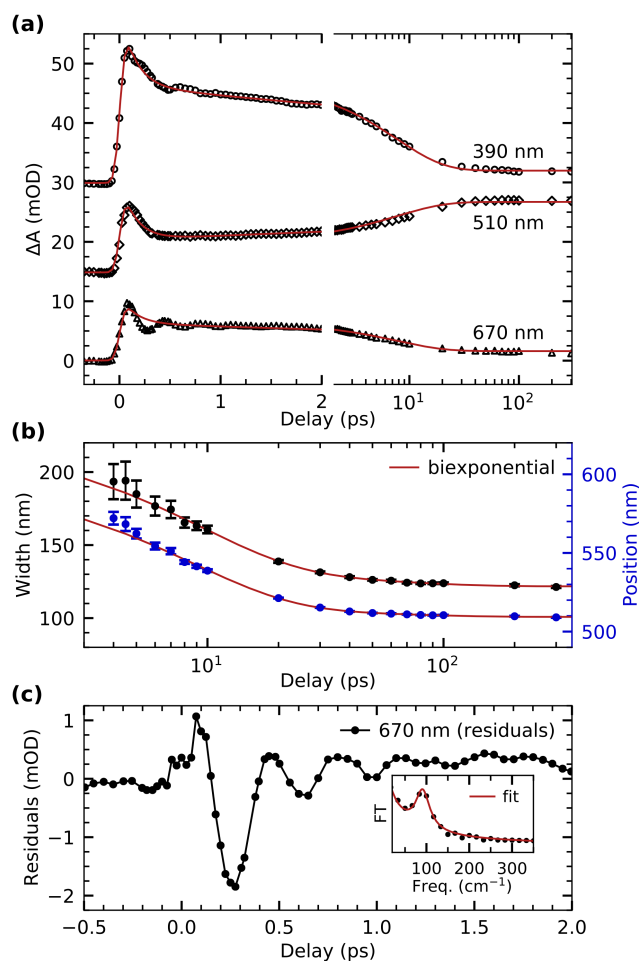
TD-DFT calculations of the optical and O K-edge absorption spectra were performed using the ORCA quantum chemistry

package<sup>56,57</sup> at the B3LYP level of theory<sup>58,59</sup> with the def2-TZVP basis set<sup>46,47</sup>. For computational efficiency, the RIJCOSX approximation<sup>60</sup> was used. For the optical absorption spectra, 30 roots were calculated. For the O K-edge absorption spectra, the Pipek-Mezey orbital localization scheme<sup>61</sup> was used and the excitation window was restricted to only include the O 1s orbitals. The number of calculated roots was set to 30 roots per O atom for the different species.

The simulated optical absorption spectra were generated by convolving the calculated transitions with a Gaussian function with a width of 0.3 eV full width at half max (FWHM) to account for the experimental and inhomogeneous broadening. The simulated X-ray absorption spectra were generated by convolving the calculated transitions with a Pseudo-Voigt function. The Lorentz contribution to the Voigt function accounts for the tabulated lifetime broadening<sup>62</sup> of 0.32 eV FWHM at the Cr  $L_3$ -edge, 0.76 eV at the Cr  $L_2$ -edge and 0.18 eV at the O K-edge. The Gaussian contribution of 0.4 eV FWHM throughout the Cr L-edge and 0.8 eV at the O K-edge accounts for the experimental and inhomogeneous broadening. To align the calculated spectra with the experimental spectra, a uniform shift of -6.47 eV was applied at the Cr L-edge, whereas a shift of +13.7 eV was applied at the O K-edge. This is done to compensate for errors accumulated from the approximations used in simulating the X-ray absorption spectra. The relative shifts between each species are therefore preserved within each method used.

## RESULTS AND DISCUSSION

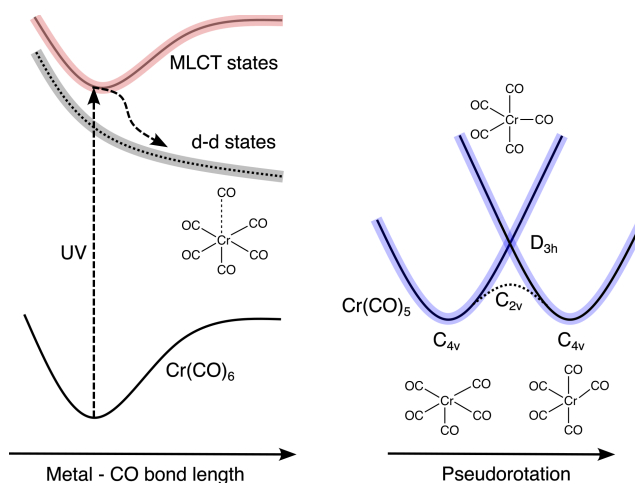
**Transient UV-visible absorption spectroscopy.** Fig. 1a shows an overview of the transient optical absorption data of  $\text{Cr}(\text{CO})_6$  in octane solution covering pump-probe delays up to 300 ps. Representative cuts along the spectral range are displayed in Fig. 1b for selected pump-probe delays. The inset in Fig. 1b shows negligible steady-state absorption of  $\text{Cr}(\text{CO})_6$  in the spectral range probed in the transient absorption measurements. The time-resolved data qualitatively reproduce earlier transient absorption data of  $\text{Cr}(\text{CO})_6$  and other metal hexacarbonyl complexes in various solvents including alkanes<sup>25,29,30</sup>. With improved detection sensitivity and temporal resolution, our measurements now reveal new information. Within the time-resolution of the experiment, a broad absorption appears, which stretches across the observed spectral range at the earliest measured time delays and which decreases in spectral bandwidth within the first few hundred femtoseconds. At the same time, a strong absorption band can be observed for wavelengths shorter than 450 nm (Fig. 1a). Additionally, oscillatory signals are apparent at delay times below 2 ps in the spectral range between 600 nm and 720 nm (oscillatory signals are faintly visible below 450 nm as well, as detailed below). Within a few picoseconds, we see a broad transient absorption band emerging in the red part of the spectrum and gradually moving to shorter wavelengths concomitant with the decay of the absorption below 450 nm (Fig. 1a). An additional blue-shift as well as a narrowing of the absorption band around 500 nm takes place on the timescale of tens to hundreds of picoseconds (Fig. 1b). This prominent absorption band was previously observed and identified as a transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the solvent-complexed  $\text{Cr}(\text{CO})_5$  fragment in its electronic ground state<sup>13</sup>. Notably, the energy of this transition was shown to scale with the bond strength towards the associated molecule<sup>11,14</sup> and we will use this property later in our analysis.



**Figure 2** (a) Delay traces extracted at three different wavelengths and modelled with a global fit based on a biexponential model. (b) Width and position of the transient absorption band arising after photoexcitation in the range of 480 nm to 640 nm as a function of pump-probe delay. The evolution of both, width and position, are modelled by a biexponential function. (c) Residuals of the global fit of the delay trace at 670 nm from panel (a) with a Fourier transfer (FT) analysis of the residuals depicted in the inset. The fit is the sum of a Lorentzian line shape and, to account for the background, the inverse frequency  $\nu$ ,  $a/\nu$ , where  $a$  is a fit parameter.

Cuts along the pump-probe delay axis for selected wavelengths are displayed in Fig. 2a for closer inspection. The three delay traces are modelled by a global fit based on a biexponential model, yielding a fast time constant of  $150 \pm 10$  fs and a slower time constant of  $7.7 \pm 0.3$  ps. The first time constant of 150 fs, which describes the initial decrease of the broad absorption across the observed spectral range, quantitatively reproduces dynamics reported in earlier femtosecond IR measurements<sup>63</sup>, where the recovery of the bleach signal on the same timescale was assigned to geminate recombination of dissociated CO with the  $\text{Cr}(\text{CO})_5$  fragment. The second time constant of 7.7 ps we instead assign to the association of an octane molecule from solution in agreement with previous femtosecond studies on  $\text{Cr}(\text{CO})_6$  as well as other metal carbonyls<sup>29,30,32,34</sup>.

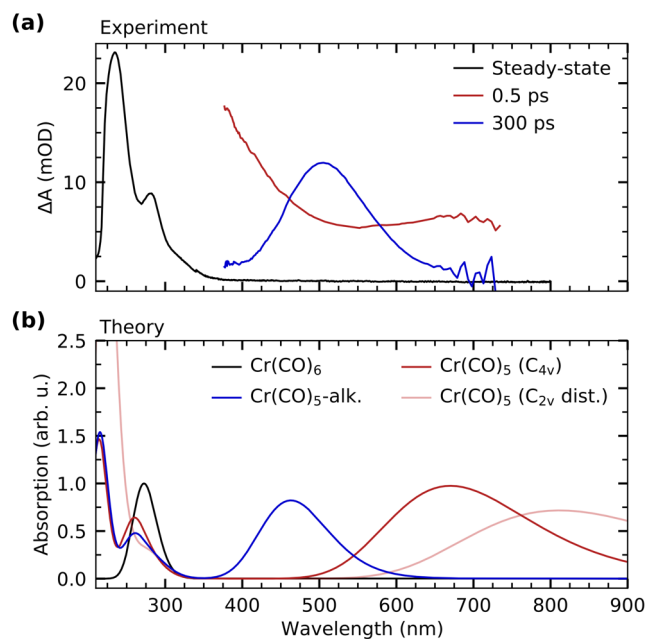
The results of the analysis of the width and position of this HOMO  $\rightarrow$  LUMO absorption band are shown in Fig. 2b (see Supporting Information for details of the analysis). The evolution of both, width and position, are well described by a biexponential temporal behavior, where the fast component of  $8.6 \pm$



**Scheme 2.** Schematic depiction of the potential energy surfaces along photo-induced CO dissociation from  $\text{Cr}(\text{CO})_6$  and subsequent formation of the  $\text{Cr}(\text{CO})_5$  fragment (adapted from Ref. 68).

0.6 ps is in good agreement with the timescale of  $7.7 \pm 0.3$  ps determined from the global fit of the delay traces in Fig. 2a and assigned to  $\sigma$ -complex formation. Given that the two values stem from independent observables, we define the mean of  $8.2 \pm 0.4$  ps as the time constant for  $\sigma$ -complex formation. The slower time constant of  $53 \pm 12$  ps of the biexponential fit is assigned to thermalization of the  $\sigma$ -complex with the solvent environment, in agreement with previous measurements of other metal carbonyls in solution<sup>29,30,64</sup>. We find the final peak position of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex after  $\sim 100$  ps to be at 510 nm. This wavelength is in excellent agreement with the band position of  $\text{Cr}(\text{CO})_5$  bound to an alkane in solution and in noble gas matrices as derived from flash photolysis measurements<sup>12–14</sup>.

The oscillatory signal observed right after the UV excitation in the red part of the overview map in Fig. 1a can be isolated by evaluating the residuals from the fit of the delay trace at 670 nm displayed in Fig. 2c. A Fourier-analysis of these data (shown in the inset) reveals a single frequency of  $91 \pm 1 \text{ cm}^{-1}$ . This is in good agreement with the coherent oscillations observed in the photochemistry of gas-phase  $\text{Cr}(\text{CO})_6$ <sup>65–67</sup>. In the gas-phase, these oscillations have been assigned to equatorial Cr-CO bending modes in the  $S_0$  ground state of  $\text{Cr}(\text{CO})_5$  with  $C_{4v}$  symmetry. These modes are thought to be populated following the passing of the  $S_1$  excited state of  $\text{Cr}(\text{CO})_5$ , which exhibits  $D_{3h}$  symmetry<sup>65–68</sup> (see Scheme 2). We measure a dephasing time of  $830 \pm 50$  fs for the coherent oscillations observed here, in excellent agreement with the value of  $815 \pm 20$  fs measured in the gas-phase<sup>65</sup>. The matching oscillation frequencies and dephasing times clearly indicate that the same equatorial Cr-CO bending modes of  $\text{Cr}(\text{CO})_5$  are populated in solution and in the gas-phase. In solution, and in cases where  $\text{Cr}(\text{CO})_5$  does not undergo geminate recombination, our findings thus suggest that the octane solvent has no measurable influence on the nature of the initial wavepacket dynamics along the dissociation pathway, nor does the solvent seem to influence the dephasing time of the oscillations. As in the gas-phase, we think, the excess vibrational energy is first dissipated via intramolecular vibrational energy redistribution (IVR) to lower-energy modes of the solute. However, the solvent must already provide a bath for energy dissipation within the first picoseconds because, unlike in the gas-phase<sup>65,67</sup>, additional ligand dissociation is not

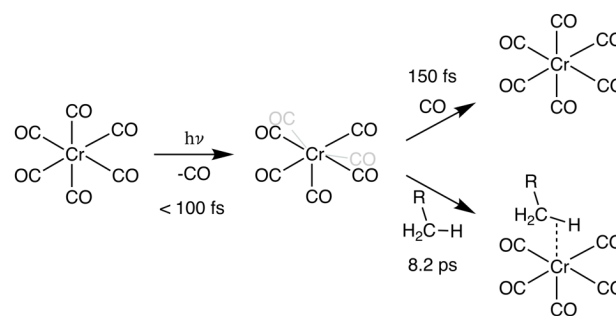


**Figure 3** (a) Steady-state optical absorption spectrum of  $\text{Cr}(\text{CO})_6$  compared with transient optical absorption spectra at 0.5 ps and 300 ps pump-probe delay. For comparison, the steady-state spectrum is scaled. (b) Calculated absorption spectra of  $\text{Cr}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_5$  in  $C_{4v}$  and a  $C_{2v}$  distorted symmetry as well as the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex at the TD-DFT level of theory. The calculated spectrum of  $\text{Cr}(\text{CO})_6$  is scaled so that the transition at  $\sim 290$  nm is 1. All other species are scaled accordingly.

observed in solution. It is thus conceivable that the time constant of 8.2 ps, which we assign to the formation of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex, includes a component, which corresponds to a further thermalization of the bare  $\text{Cr}(\text{CO})_5$  with the solvent environment, and that thermalization and alkane association are concerted processes.

It is noteworthy that the coherent oscillations we observe appear in the far-red part of the transient absorption spectrum. Previous flash photolysis experiments of  $\text{Cr}(\text{CO})_5$  in a neon matrix<sup>13</sup> as well as in perfluorocyclohexane solution<sup>14</sup> observed the fingerprint HOMO  $\rightarrow$  LUMO absorption band in the range of 620 to 630 nm. Because neon and perfluorocyclohexane have been considered to be non-interacting moieties, this has been interpreted to be the signature of bare  $\text{Cr}(\text{CO})_5$ . The absorption spectrum at 0.5 ps in Fig 1b exhibits an absorption band at even higher wavelengths at around 670 nm, which indicates that even neon and perfluorocyclohexane weakly bind the undercoordinated metal center and shift the HOMO  $\rightarrow$  LUMO absorption band to higher energy with respect to the band position measured here. Besides this sensitivity to the nature of the moiety bound to the metal center, it has further previously been shown that the energy of the HOMO  $\rightarrow$  LUMO absorption band also depends on structural distortions and the specific symmetry of the  $\text{Cr}(\text{CO})_5$  fragment<sup>13,69,70</sup>. Both, our observations of a transient absorption band in the far-red absorption range as well as the modulation of the band by the same characteristic oscillations as in the gas-phase therefore strongly point to the formation of bare  $\text{Cr}(\text{CO})_5$  in solution.

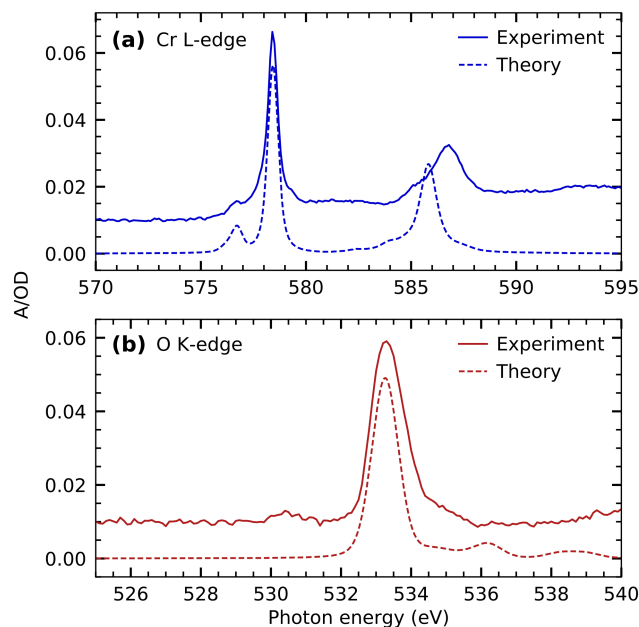
As we show in the following, the purely experimental assignments of the transient optical absorption bands to specific species are confirmed by calculated spectra. Fig. 3a contains the experimental steady-state absorption spectrum of  $\text{Cr}(\text{CO})_6$  as



**Scheme 3.** Determined photochemical pathway and associated timescales of alkane  $\sigma$ -complex formation following CO dissociation from  $\text{Cr}(\text{CO})_6$  in octane solution.

well as transient absorption spectra of bare  $\text{Cr}(\text{CO})_5$  (delay of 0.5 ps) and the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex (delay of 300 ps). Our simulated spectra of  $\text{Cr}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_5$  and the  $\text{Cr}(\text{CO})_5$ -octane  $\sigma$ -complex calculated at the TD-DFT level of theory are shown in Fig. 3b. Confirming our experimental assignments, the long-lived transient band at 510 nm can be identified with theory as the fingerprint of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex. Bare  $\text{Cr}(\text{CO})_5$  in its  $C_{4v}$  ground state geometry instead exhibits an absorption band centered at  $\sim 670$  nm. Our calculations also indicate a strong sensitivity of the position of the  $\text{Cr}(\text{CO})_5$  HOMO  $\rightarrow$  LUMO absorption band to structural distortions. A shift from 670 nm to 800 nm is calculated when going from the  $C_{4v}$  ground state geometry of  $\text{Cr}(\text{CO})_5$  to a  $C_{2v}$  distorted structure. This distorted structure can be thought to represent a prevalent structure of vibrationally excited  $\text{Cr}(\text{CO})_5$  where Cr-CO bonds are bent towards the  $C_{2v}$  geometry of the transition state along the pseudo-rotation coordinate<sup>68</sup> (compare Scheme 2). In our calculations, the structure was generated by a restricted optimization of  $\text{Cr}(\text{CO})_5$  in  $C_{2v}$  symmetry, where two opposing equatorial CO groups are bent out of plane by a fixed angle of  $15^\circ$ . An oscillatory motion in  $\text{Cr}(\text{CO})_5$  between  $C_{4v}$  and  $C_{2v}$  symmetry along the bending mode of the equatorial CO ligands would thus modulate the intensity in the optical absorption spectrum around 670 nm as observed experimentally. This explains the coherent oscillations on sub-picosecond timescales in this spectral region (see Fig. 1a).

We note that the strong absorption band observed during the first picoseconds below 450 nm (see Fig. 1a) is not reproduced by theory for any of the calculated species. Still, since the band decays with a time constant of 8.2 ps as the final  $\text{Cr}(\text{CO})_5$ -alkane product rises, we can tentatively attribute the absorption band below 450 nm to a transition of bare  $\text{Cr}(\text{CO})_5$ . During the first picoseconds, bare  $\text{Cr}(\text{CO})_5$  can be expected to be structurally far from thermal equilibrium. The associated vibrational excitations may then allow the nominally symmetry-forbidden absorption below 450 nm to adopt its substantial oscillator strength. This effect, however, is not reproduced by our level of theory, which is based on vibrational and electronic ground states. Our assignment of the absorption band below 450 nm to bare  $\text{Cr}(\text{CO})_5$  is corroborated in addition by assessing the residuals of the delay trace at 390 nm (see Fig. S1 in the Supporting Information). The delay trace at that wavelength exhibits the same, albeit less pronounced, characteristic oscillations within the first picosecond as the trace at 670 nm, which we identified as one of the fingerprints of the bare  $\text{Cr}(\text{CO})_5$  intermediate. This assignment of the band below 450 nm is also consistent with its initial intensity decrease with a time constant of 150 fs. The magnitude of the decrease is  $\sim 30\%$ , which is in good agreement



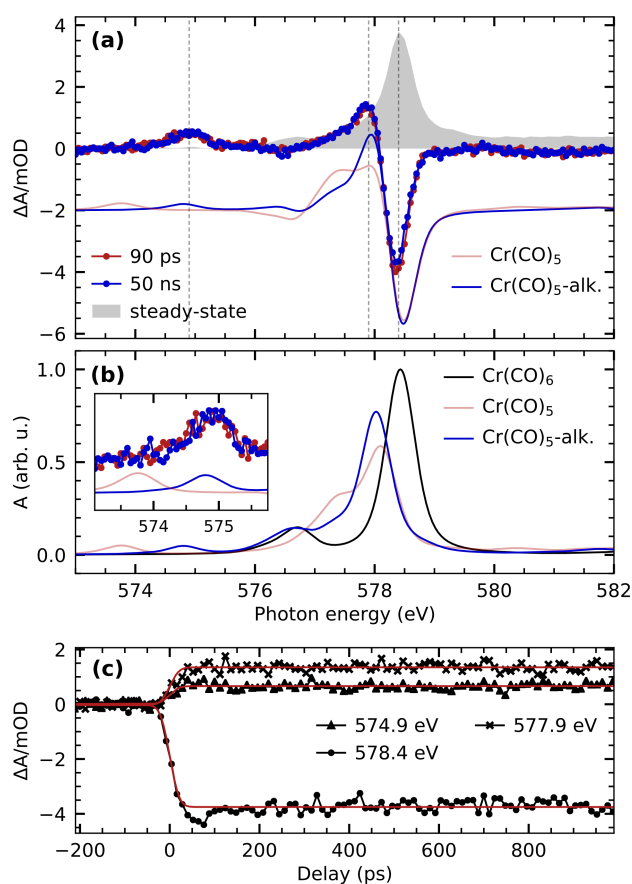
**Figure 4** Steady-state X-ray absorption spectra of  $\text{Cr}(\text{CO})_6$  in octane solution measured at the (a) Cr L-edge and (b) O K-edge compared with calculated spectra at the RASSCF and TD-DFT level of theory, respectively.

with the previously determined yield for geminate recombination of 34% for  $\text{Cr}(\text{CO})_5$  in alkane solution<sup>71</sup>.

Our experimental data therefore allow to robustly establish the ultrafast pathway leading to the formation of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex in octane solution (see Scheme 3): As in the gas-phase, CO dissociation and formation of  $\text{Cr}(\text{CO})_5$  occurs on a timescale below 100 fs<sup>65–67</sup> and thus within the time-resolution of the experiment here. With a time constant of 150 fs, a fraction of bare  $\text{Cr}(\text{CO})_5$  molecules undergoes geminate recombination with CO groups, which have not escaped the first solvation shell following dissociation. Those  $\text{Cr}(\text{CO})_5$  molecules that do not geminately recombine clearly occur in their electronic ground state in  $C_{4v}$  symmetry with characteristic equatorial Cr-CO bending modes, which dephase with a time constant of 830 fs. The  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex then forms with a time constant of 8.2 ps via a ground state reaction, in which an octane molecule binds to the bare  $\text{Cr}(\text{CO})_5$ . With a time constant of 53 ps, the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex vibrationally cools and persists thereafter.

**Time-resolved X-ray absorption spectroscopy.** Fig. 4a and 4b show the steady-state X-ray absorption spectra of  $\text{Cr}(\text{CO})_6$  in octane solution measured at the Cr L-edge and O K-edge, respectively. The shapes of both spectra are in good agreement with previous soft X-ray absorption measurements on  $\text{Cr}(\text{CO})_6$  in 1-pentanol solution<sup>72</sup>. Below the measurements, spectra calculated at the RASSCF level of theory are shown for the Cr L-edge as well as the TD-DFT level of theory for the O K-edge. The calculations are in good agreement with experiment and can hence be used to assign the observed spectral features.

The L-edge absorption spectrum of  $\text{Cr}(\text{CO})_6$  in Fig. 4a is split into the  $L_3$  and  $L_2$ -edges due to spin-orbit coupling in the core-excited state final states. The  $L_3$ -edge is characterized by two absorption resonances. Based on our calculations, the less intense pre-edge resonance at 576.5 eV can be assigned to excitations of Cr 2p electrons into unoccupied CO  $\pi^*$  orbitals of  $t_{2g}$



**Figure 5** (a) Experimental and calculated transient Cr  $L_3$ -edge absorption difference spectra of  $\text{Cr}(\text{CO})_6$  in octane solution. Calculations are performed at the RASSCF level of theory. Difference spectra of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex and the  $\text{Cr}(\text{CO})_5$  fragment are generated with respect to  $\text{Cr}(\text{CO})_6$  (spectrum of the respective species minus spectrum of  $\text{Cr}(\text{CO})_6$ ). For better comparison, the depletion of the calculated  $\text{Cr}(\text{CO})_5$ -alkane difference spectra is scaled to match the depletion of the experimental spectrum and the  $\text{Cr}(\text{CO})_5$  difference spectrum is scaled accordingly. The experimental steady-state spectrum is additionally shown for comparison and scaled to match the amplitude of the depletion of the transient difference spectra. (b) Calculated  $L_3$ -edge absorption spectrum of  $\text{Cr}(\text{CO})_6$ , the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex as well as the  $\text{Cr}(\text{CO})_5$  fragment. The maximum of the  $\text{Cr}(\text{CO})_6$  spectrum is scaled to 1 and the other spectra are scaled accordingly. The inset shows a closeup of the transient pre-edge region between 573.1 eV and 575.75 eV (c) Pump-probe delay traces measured at the energies indicated in (a). The delay traces are modelled with a step-function broadened by a Gaussian function.

symmetry. The transitions underlying this resonance carry oscillator strength due to  $\pi$ -backdonation and the associated hybridization of the CO  $\pi^*(t_{2g})$  orbitals with the occupied d-derived orbitals of the same symmetry. The stronger main resonance at 578.5 eV is instead due to excitations of Cr 2p electrons into unoccupied 3d-derived orbitals of  $e_g$  symmetry. Notably, this ordering of resonances at the metal L-edge is different than in other metal carbonyls of lower symmetry<sup>34,73,74</sup> as well as the isoelectronic ferrous hexacyanide<sup>75,76</sup>. In these complexes, excitations into the unoccupied d levels are at lower energy than excitations into ligand  $\pi^*$  orbitals. This different ordering reflects the higher coordination number in  $\text{Cr}(\text{CO})_6$  compared to other metal carbonyls as well as, compared to ferrous

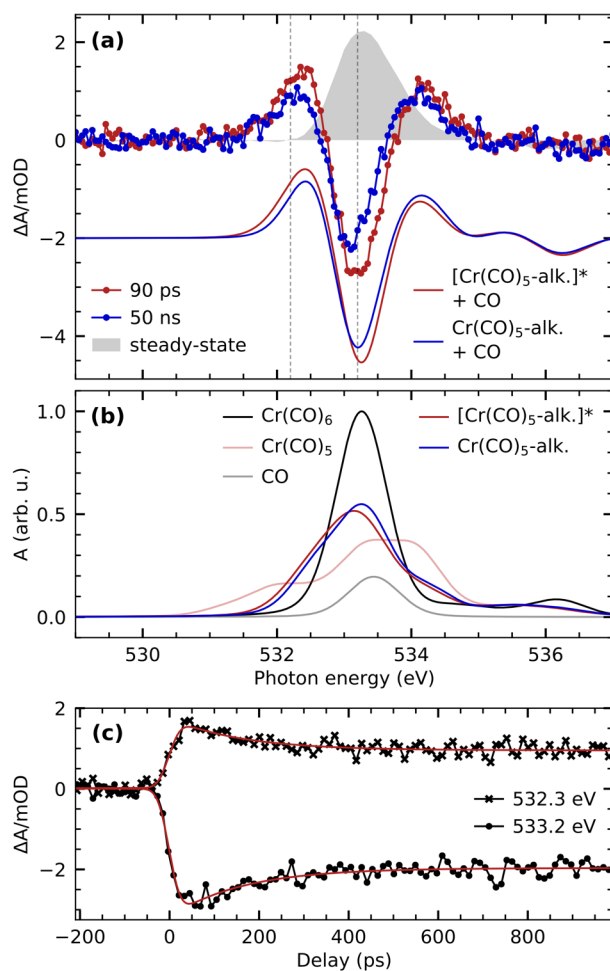
hexacyanide, the carbonyl group being a stronger  $\pi$  acceptor than the negatively charged cyanide group. Overall, this causes a higher ligand field in  $\text{Cr}(\text{CO})_6$  and a destabilization of the unoccupied metal d orbitals to higher energies than the ligand  $\pi^*$  orbitals.

The O K-edge spectrum shown in Fig. 4b is dominated by a strong absorption resonance at 533.3 eV. Based on our TD-DFT calculations, this resonance can be assigned to excitations of O 1s electrons into the unoccupied CO  $\pi^*$  manifold involving specifically orbitals of  $t_{1u}$  and  $t_{2u}$  symmetry in agreement with previous studies on solution and gas-phase  $\text{Cr}(\text{CO})_6$ <sup>72,77,78</sup>. The low-intensity pre-peak at a photon energy of 530.5 eV is instead tentatively assigned to impurities stemming from the sample preparation. Specifically, based on comparison to previous gas-phase electron energy loss spectroscopy measurements<sup>77,79,80</sup>, the pre-peak is most likely due to molecular oxygen dissolved in the octane solution, which was accumulating during the sample preparation (see experimental section).

Fig. 5a shows the transient Cr L<sub>3</sub>-edge absorption spectra of  $\text{Cr}(\text{CO})_6$  in octane solution compared with calculated transient spectra as well as with the  $\text{Cr}(\text{CO})_6$  steady-state spectrum (for comparison, the absolute calculated spectra from which the differences in Fig. 5a are generated are shown in Fig. 5b). The two experimental difference spectra in Fig. 5a were recorded at 90 ps and 50 ns after UV excitation and are identical in shape and intensity. Both spectra exhibit substantial depletion at the energy of the main resonance at 578.4 eV as well as positive transient intensities at 577.9 eV and 574.9 eV. The delay traces taken at these energies, shown in Fig. 5c, are well-described by a step function convolved with a Gaussian function with  $\sim 45$  ps FWHM representing the temporal resolution in the X-ray experiments. This is consistent with our transient optical absorption measurements in that the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex is expected to form within the time resolution of the X-ray absorption measurements. Both transient X-ray absorption difference spectra thus constitute the electronic-structure fingerprint of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex.

This is again consistent with our calculated Cr L<sub>3</sub>-edge difference spectra of bare  $\text{Cr}(\text{CO})_5$  and the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex spectra in Fig. 5a. While both calculated difference spectra reproduce the experimentally observed depletion at 578.4 eV and the positive intensity around 577.9 eV, only one of the calculated spectra reproduces the energy of the transient pre-edge peak seen in experiment at 574.9 eV (see inset in Fig. 5b). The peak at 574.9 eV is well reproduced by the calculated spectrum of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex whereas the bare  $\text{Cr}(\text{CO})_5$  fragment has a peak at  $\sim 1$  eV lower incidence photon energy. The calculated spectrum of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex additionally shows better agreement in terms of spectral shape around 577.5 eV.

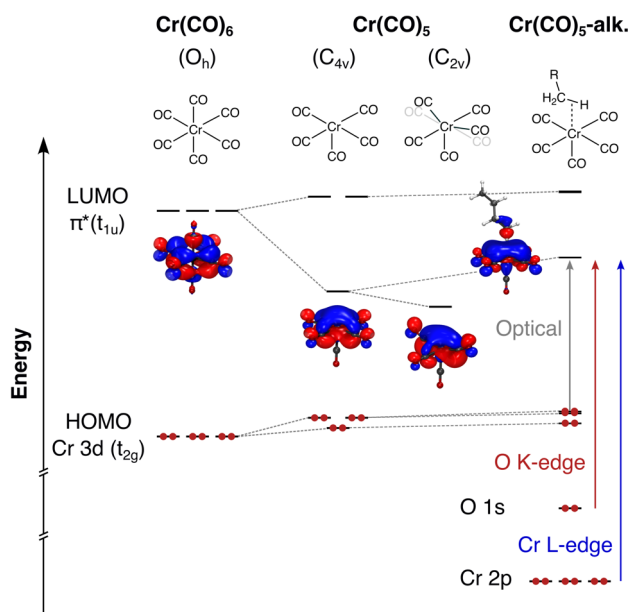
Measured O K-edge steady-state and transient difference spectra of  $\text{Cr}(\text{CO})_6$  in octane solution are compared with calculated difference spectra in Fig. 6a (absolute calculated spectra are shown in Fig. 6b). The two experimental difference spectra (recorded at the same pump-probe delays as at the Cr L<sub>3</sub>-edge) exhibit substantial depletion of the main steady-state absorption resonance at 533.2 eV as well as induced absorption in the pre- and post-edge region at 532.3 eV and 534.2 eV. In contrast to the Cr L<sub>3</sub>-edge difference spectra, however, the amplitudes of the transient difference spectra change as a function of pump-probe delay. The delay traces measured at the transient pre-edge at 532.2 eV as well as at the depletion at 533.2 eV are displayed in



**Figure 6** (a) Transient O K-edge absorption difference spectra of  $\text{Cr}(\text{CO})_6$  in octane solution compared with calculated difference spectra of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex and the free CO as well as the  $\text{Cr}(\text{CO})_5$  fragment and the free CO with respect to the  $\text{Cr}(\text{CO})_6$  species. The depletion of the calculated difference spectrum, which represents the sum of the  $\text{Cr}(\text{CO})_5$ -alkane  $\sigma$ -complex and the free CO, is scaled to match the depletion of the experimental spectrum at 50 ns. The calculated difference spectrum of the “hot”  $[\text{Cr}(\text{CO})_5\text{-alkane}]^*$   $\sigma$ -complex plus the free CO is scaled accordingly. The generation of the “hot”  $[\text{Cr}(\text{CO})_5\text{-alkane}]^*$   $\sigma$ -complex spectrum is discussed in the main text. The experimental steady-state spectrum is additionally shown for comparison and scaled to match the amplitude of the depletion of the transient difference spectrum at 50 ns. (b) Calculated O K-edge absorption spectra of all species considered in generating the difference spectra displayed in (a). The maximum of the  $\text{Cr}(\text{CO})_6$  spectrum is scaled to 1. All other spectra are scaled accordingly. (c) Pump-probe delay traces measured at the energies indicated in (a). The delay traces are modelled with a single-exponential decay of a primary species to a stable product.

Fig. 6c. Their temporal evolutions are well-described by single-exponential decays with a common time constant of  $160 \pm 20$  ps of a primary species to a secondary meta-stable species.

The observed signatures are similar to transient O K-edge signatures measured for the photochemistry of  $\text{Cr}(\text{CO})_6$  in 1-pentanol solution. There, the observed absorption differences were assigned to the migration dynamics of C-H to O-H coordination towards the  $\text{Cr}(\text{CO})_5$  species<sup>72</sup>. In the absence of any functional groups besides C-H bonds in the alkane solution, the here



**Scheme 4.** Orbital correlation diagram along CO dissociation from  $\text{Cr(CO)}_6$  to  $\text{Cr(CO)}_5$  and  $\sigma$ -complex formation to  $\text{Cr(CO)}_5\text{-alkane}$  with main optical (grey), O K-edge (red), and Cr L-edge absorption transitions (blue).

observed signal changes are instead assigned to the decay of high-frequency CO stretching modes of the  $\sigma$ -complex. These modes have previously been shown to be excited following ligand-exchange in  $\text{Cr(CO)}_6$  in alkane solutions<sup>25,64,81</sup>. The vibrational excitations have been reported to only weakly couple to lower-energy vibrations and to relax on a timescale of 160 ps, in excellent agreement with our measurements.

The comparison of the experimental and theoretical difference spectra in Fig. 6a explains how these vibrational excitations are reflected in the O K-edge absorption spectra. The spectrum at 50 ns corresponds to the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex plus the dissociated CO ligand. At this delay time, the complex can be safely assumed to be vibrationally cold. At 90 ps instead, the agreement of the calculated spectrum of a “hot”  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex with experiment at the pre-edge at 532.3 eV as well as at the main-edge at 533.2 eV suggests that the  $\sigma$ -complex is still vibrationally excited. To reflect vibrational excitations in the calculated spectrum, we empirically added a red shift of 0.1 eV to the incident photon energy of the cold  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex spectrum. The rationale is that excitation of the CO stretching mode leads to a higher average CO bond length, which stabilizes the CO  $\pi^*$  orbitals and shifts O  $1s \rightarrow \text{CO } \pi^*$  resonances to lower energies. We also added an additional 0.1 eV Gaussian broadening to the “hot”  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex spectrum (in addition to the broadening applied to the spectra of vibrationally cold species, see Computational details) to reflect the higher degree of conformational motion as a result of the vibrational excitation<sup>82</sup>.

**Probing the orbital correlation diagram.** The combination of time-resolved optical and X-ray absorption spectroscopy at the Cr L-edge and O K-edge allows to follow the evolution of unoccupied valence orbitals upon CO dissociation and alkane  $\sigma$ -complex formation from three different perspectives. A schematic summary of the evolution of the energies of the decisive valence orbitals and how they are accessed by the three different

absorption spectroscopy methods is shown in Scheme 4 (a comprehensive orbital correlation diagram of all valence orbitals included in the active space of the RASSCF calculations is shown in Fig. S2 in the Supporting Information).

CO dissociation from  $\text{Cr(CO)}_6$  is initially triggered by a HOMO  $\rightarrow$  LUMO metal-to-ligand charge transfer (MLCT) excitation involving Cr  $3d (t_{2g}) \rightarrow \text{CO } \pi^* (t_{1u})$  transitions with an absorption band centered at around 290 nm (see Fig. 3). CO dissociation breaks the  $O_h$  symmetry and is predominantly reflected in a major decrease of energy of one of the former CO  $\pi^* (t_{1u})$  orbitals in the  $\text{Cr(CO)}_5$  fragment (see Scheme 4). Since the HOMOs remain relatively stable, the LUMO energy drop can be experimentally observed in the time-resolved optical absorption data (see Fig. 3). The structural changes associated with the coherent oscillation of the Cr-CO bending mode further decrease the energy of the LUMO as our calculations suggest and in agreement with experiment (see Scheme 4). Distortion from  $C_{4v}$  to  $C_{2v}$  moves two equatorial CO groups out of plane, which reduces hybridization of the nominal CO  $\pi^*$  orbital with the Cr  $d_{z^2}$  orbital (see orbital plots in Scheme 4)<sup>68</sup>. This change in orbital overlap stabilizes the LUMO and causes the observed red-shift of the HOMO  $\rightarrow$  LUMO absorption band in  $C_{2v}$  distorted structures (Fig. 3). In the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex, the bonding interactions between the Cr and the C-H bond increase the LUMO energy as observed in the blue-shift of the HOMO  $\rightarrow$  LUMO absorption band back to higher energies in the optical absorption spectrum (see Scheme 4 and Fig. 3).

This evolution of orbital energies is mirrored in the time-resolved X-ray absorption spectra. Following CO dissociation and alkane association, the LUMO remains an orbital of predominantly CO  $\pi^*$  character. It does, however, also adopt some degree of Cr  $d_{z^2}$  character due to the discussed changes in Cr-CO hybridization. This emergence of Cr  $d_{z^2}$  character is seen in the increase of orbital amplitude of the LUMO at the Cr center when going from  $\text{Cr(CO)}_6$  to the two  $\text{Cr(CO)}_5$  geometries and the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex (Scheme 4). By  $d_{z^2}$  admixture, the LUMO becomes accessible in Cr L-edge absorption via dipole-allowed  $2p \rightarrow 3d$  transitions, which can be experimentally observed via the pre-edge peak at 574.9 eV in the transient  $L_3$ -edge spectrum of the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex (Fig. 5a). Notably, while the transient  $\text{Cr(CO)}_5$  fragment cannot be observed with picosecond X-ray absorption spectroscopy, the calculated shift of the Cr L-edge pre-edge peak of  $\sim 1$  eV in the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex to higher energy with respect to bare  $\text{Cr(CO)}_5$  mirrors the behavior of the optical absorption.

In a complementary way, the predominant ligand character of the LUMO can be accessed with O K-edge absorption spectroscopy. In contrast to the Cr  $L_3$ -edge, the O K-edge probes the LUMO through dipole-allowed transitions of O  $1s$  electrons into the CO  $\pi^*$  orbitals, which have substantial O  $2p$  character. The LUMO of the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex is observed as a transient pre-edge transition at 532.3 eV (Fig. 6a). As in the Cr  $L_3$ -edge, a shift of the pre-edge between the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex and the bare  $\text{Cr(CO)}_5$  fragment can be seen (Fig. 6b), again reflecting the relative shift in LUMO energy as a result of alkane binding in the  $\text{Cr(CO)}_5\text{-alkane } \sigma$ -complex (Scheme 4).

Besides providing complementary insights into the evolution of the LUMO along the photochemical pathway, the time-resolved X-ray absorption data at the Cr  $L_3$ -edge and O K-edge further inform on the evolution of the full manifold of unoccupied Cr  $3d$  and ligand CO  $\pi^*$  orbitals, respectively (see Supporting Information for full orbital correlation diagram). The absence of



depletion at 576.7 eV in the measured Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex spectrum, a region of 2p  $\rightarrow$  CO  $\pi^*(t_{2g})$  transitions (Fig. 5a), points to the low impact the ligand-exchange has on the  $t_{2g}$  manifold. Both, the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex as well as Cr(CO)<sub>6</sub>, exhibit a similarly intense resonance at the same energy (see Fig. 5b), reflecting the unchanged energies of the CO  $\pi^*(t_{2g})$  orbitals as well as their unchanged hybridization with Cr 3d orbitals in both species. The Cr L<sub>3</sub>-edge spectrum of the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex further reflects the splitting of the 3d( $e_g$ ) orbitals as a result of the breaking of O<sub>h</sub> symmetry upon ligand-exchange. This can be seen by the splitting of the main-edge resonance in the calculated Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex spectrum, which, in addition to the main maximum at 578 eV, exhibits an shoulder at 577.2 eV (see Fig. 5b). In experiment, this splitting is visible by the extension of the positive transient intensity in Figure 5a around 577.3 eV in addition to the peak centered at 577.8 eV. Intensity in this range is attributed to excitations of Cr 2p electrons into predominantly the  $d_{z^2}$  orbital, whereas the main maximum reflects excitations predominantly into the  $d_{x^2-y^2}$  orbital. Both sets of transitions carry less oscillator strength compared to the main resonance in Cr(CO)<sub>6</sub>. This difference is due to the hybridization of CO  $\pi^*$  orbitals with the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals in the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex, mixing that is allowed in the broken symmetry of Cr(CO)<sub>5</sub>-alkane and forbidden in the O<sub>h</sub> symmetry of Cr(CO)<sub>6</sub>. This effect of symmetry breaking is mirrored in the  $t_{2u}$  manifold of the CO  $\pi^*$  orbitals. Two  $t_{2u}$  orbitals of Cr(CO)<sub>6</sub> are destabilized following ligand-exchange (Scheme 4), explaining the induced absorption at 534.2 eV in the O K-edge spectrum of the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex (Fig. 6a and b).

## CONCLUSION

We have used a combination of femtosecond optical absorption spectroscopy and picosecond X-ray absorption spectroscopy at the metal L-edge and ligand K-edge to probe the photochemistry and electronic structure evolution of Cr(CO)<sub>6</sub> in octane solution. The femtosecond optical absorption data allowed to robustly establish the photochemical pathway of alkane  $\sigma$ -complex formation from Cr(CO)<sub>6</sub>. Bare Cr(CO)<sub>5</sub> was found to form within the time-resolution of the experiment followed either by geminate recombination with a time constant of 150 fs or octane association to form the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex with a time constant of 8.2 ps. Preceding  $\sigma$ -complex formation, the Cr(CO)<sub>5</sub> fragments, which do not recombine, exhibit coherent oscillations in the optical absorption data. Their frequency and dephasing time are characteristic of equatorial Cr-CO bending modes in the ground state of Cr(CO)<sub>5</sub> as shown in comparison to the CO dissociation dynamics of gas-phase Cr(CO)<sub>6</sub>.

With the robustly established photochemical pathways based on the optical absorption data, we then used X-ray absorption spectroscopy to characterize the electronic structure of the Cr(CO)<sub>5</sub>-alkane  $\sigma$ -complex. The ligand-exchange breaks the octahedral symmetry leading to a rehybridization between metal and ligand orbitals. Substantial shifts of the LUMO energy were found to be the dominant consequence of the ligand-exchange and the LUMO energy could be identified as a sensitive electronic structure fingerprint of the impact of CO dissociation and alkane association.

Time-resolved optical and X-ray absorption spectroscopy allowed us to uniquely probe the manifold of unoccupied orbitals along the pathway of alkane  $\sigma$ -complex formation in solution. Our results demonstrate how this combination of methods

grants highly complementary insight into the evolution of the electronic structure of transition metal complexes along photochemical reaction pathways. We anticipate future studies based on this approach for precisely characterizing the electronic structure of alkane  $\sigma$ -complexes and precursors in relation to their reactivity and mechanistic role in C-H activation reactions.

## ASSOCIATED CONTENT

### Supporting Information

Description of the global fit model; Comparison of the residuals of the delay traces at 390 nm and 670 nm; Extended discussion of the origin of the oscillatory signal; Details on the line shape model; DFT orbital energies; Cartesian coordinates of the DFT optimized structures

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