

Mapping chemical bonding of reaction intermediates with femtosecond X-ray laser spectroscopy

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Abstract. We determine the pathways in the photo-dissociation reactions of Fe(CO)₅ both in the gas phase and in solution by mapping the valence electronic structure of the reaction intermediates with femtosecond X-ray laser spectroscopy.

1 Introduction

Molecular structure and bonding determine the dynamic pathways of molecules in their multidimensional landscapes and thus define the outcome of chemical reactions. Characterizing chemical bonding in short-lived reaction intermediates is hence the key to understanding chemical selectivity.

Here we present our time-resolved X-ray view of a molecular dissociation reaction. We address photo-dissociation of the prototypical transition-metal carbonyl molecule Fe(CO)₅ both in the gas phase and in solution (Figure 1) [1]. How chemical bonding evolves during these reactions is largely unknown and the reaction pathway is debated in solution [2-4]. We use X-ray laser spectroscopy to map the electronic structure during dissociation with femtosecond time resolution [5]. This gives direct access to chemical bonding, spin and oxidation state of the metal center in the reaction intermediates and complements structural probes [6]. As we probe the same observables in gas phase and in solution our data enable a critical assessment of the role of the solvent in Fe(CO)₅ photo-dissociation.

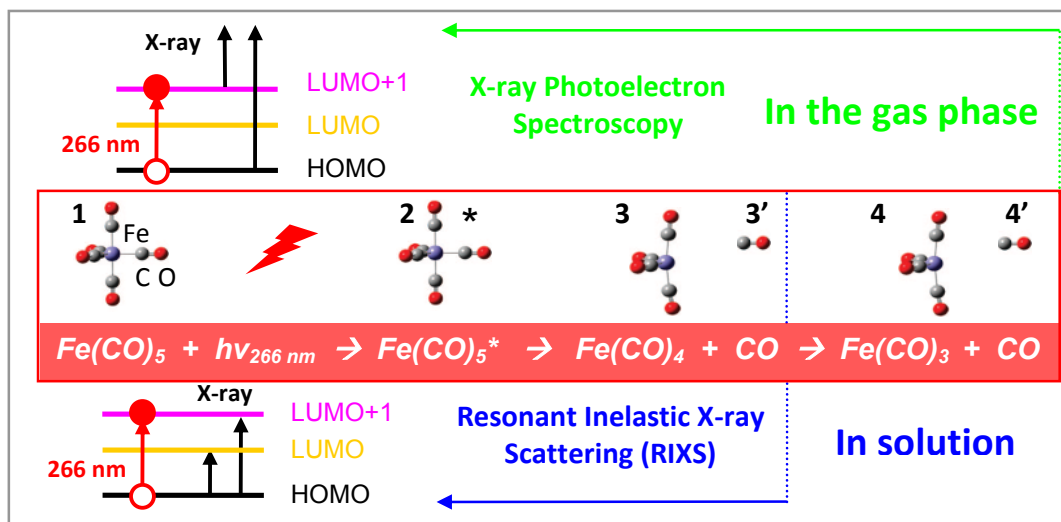


Fig. 1. Simplified scheme for the photo-dissociation reaction of $\text{Fe}(\text{CO})_5$ in the gas phase and in solution upon pumping at 266 nm (middle) [1] with labels 1-4': 1 ground state $\text{Fe}(\text{CO})_5$, 2 photo-excited $\text{Fe}(\text{CO})_5$, 3 $\text{Fe}(\text{CO})_4$, 3' photo-dissociated CO, 4 $\text{Fe}(\text{CO})_3$ and 4' thermally ejected CO. In solution, the reaction stops at 3/3'. We probe the evolution of occupied levels with time-resolved X-ray photoelectron spectroscopy in the gas-phase (top) and of valence excitations by measuring photon energy losses with time-resolved inelastic X-ray scattering (RIXS) in solution (bottom).

2 Experimental

$\text{Fe}(\text{CO})_5$ molecules were pumped at 266 nm and probed at defined time delays with X-ray pulses from the X-ray free electron laser sources FLASH in Hamburg, Germany, for the gas-phase reaction and from the Linac Coherent Light Source (LCLS) in Stanford, USA, for the solution reaction (concentration 1 mol/l in ethanol). In the gas phase, valence band (Figure 2, left), core 3p and resonant core-to-valence 3p \rightarrow 3d photoelectron spectra (not shown) were measured. In solution, RIXS at the Fe L-edge was used as a probe of the valence electronic structure (Figure 2, right). The temporal resolution in both experiments amounted to ~ 300 fs given by the jitter between optical and X-ray lasers. Multi-configurational ab initio calculations of the X-ray spectra were performed to identify and characterize in detail the reaction intermediates.

3 Results

A selection of our femtosecond time-resolved X-ray laser spectroscopy results is shown in Figure 2. The differential gas-phase valence-band photoelectron spectra (Figure 2A) display positive intensities arising from the appearances of CO and photoproducts and negative intensities due to the depletion of $\text{Fe}(\text{CO})_5$. By accounting for $\text{Fe}(\text{CO})_5$ depletion we deduce the valence-band photoelectron spectrum of $\text{Fe}(\text{CO})_4$ at a delay of 1 ps. This shows how, compared to $\text{Fe}(\text{CO})_5$, the Fe 3d levels are shifted and the shape of the CO molecular bands are modified by the loss of one CO ligand. This information on chemical bonding complements structural information from electron diffraction [6]. The CO peak (Figure 2B) at short delays rises in a step-like fashion due to CO dissociation from $\text{Fe}(\text{CO})_5$ (3' in Figure 2B) and it increases exponentially for later delays (4' in Figure 2B) due to thermal CO desorption from vibrationally hot $\text{Fe}(\text{CO})_4$. This is direct evidence for the sequential CO loss postulated in [2]. With our RIXS approach we probe for the first time a chemical reaction in solution with femtosecond RIXS. The data shown in Figure 2C display the valence excitations probed locally and in an element- and site-selective way at the Fe center of

$\text{Fe}(\text{CO})_4$. Comparison to theory (not shown) shows that $\text{Fe}(\text{CO})_4$ is in a singlet state in contrast to [3] and in agreement with [4]. According to our data (Figure 2D and calculations) $\text{Fe}(\text{CO})_5$ is excited to a 1MLCT state ($1 \rightarrow 2$) and relaxes within our time resolution to a 1LF state ($2 \rightarrow 3$) with subsequent dissociation to singlet $\text{Fe}(\text{CO})_4$. In contrast to the gas phase the excess energy in $\text{Fe}(\text{CO})_4$ is dissipated to the solvent and no further CO is lost. Details on chemical bonding, spin and oxidation state as inferred from a comparison to our calculations will be presented in addition.

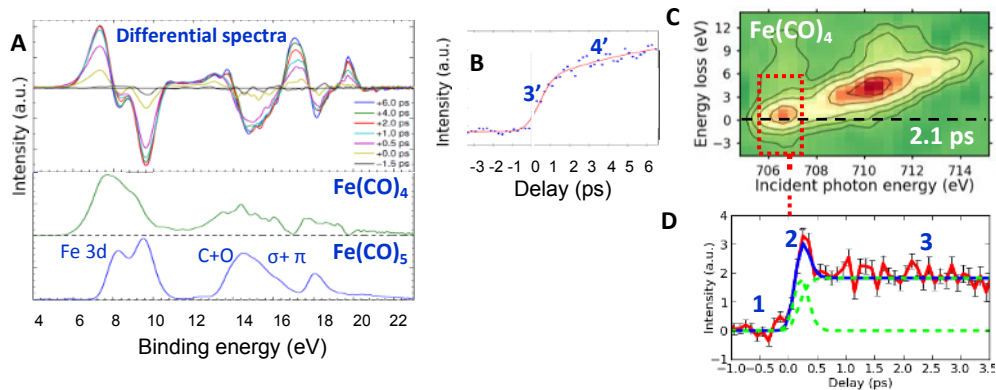


Fig. 2. Femtosecond time-resolved X-ray laser spectra mapping $\text{Fe}(\text{CO})_5$ dissociation in the gas-phase (A, B) and in solution (C-D). A: Gas-phase valence-band photoelectron spectra of, from top to bottom, CO, $\text{Fe}(\text{CO})_5$ for various pump-probe delays (differential spectra), $\text{Fe}(\text{CO})_4$ (calculated from the differential spectrum at 1 ps), $\text{Fe}(\text{CO})_5$ with the Fe 3d and the C and O σ and π molecular orbitals. B: Intensity of the CO peaks vs. delay (circles) with a fit curve (line, step function plus exponential increase). C: RIXS spectra (energy loss vs. incident photon energy tuned to the Fe L-absorption edge) of solvated $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$ (taken at 2.1 ps), respectively. D: Intensity of the marked region vs. delay (red) and a fit curve (blue, Gaussian plus step function).

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References

1. M. Poliakoff and J. J. Turner, *Angew. Chem. Int. Ed.* **40**, 2809 (2001).
2. S. A. Trushin, W. Fuss, K. L. Kompa and W. E. Schmid, *J. Phys. Chem. A* **104**, 1997 (2000).
3. P. T. Snee, Ch. K. Payne, S. D. Mebane, K. T. Kotz and C. B. Harris, *J. Am. Chem. Soc.* **123**, 6909 (2001).
4. B. Ahr, M. Chollet, B. Adams, E. M. Lunny, Ch. M. Laperle and Ch. Rose-Petruck, *Phys. Chem. Chem. Phys.* **13**, 5590 (2011).
5. Ph. Wernet, *Phys. Chem. Chem. Phys.* **13**, 16941 (2011).
6. H. Ihee, J. Cao, A. H. Zewail, *Angew. Chem. Int. Ed.* **40**, 1532 (2001).