



Experiment title:

RIXS, XES and HERFD-studies on the d-electron structure and ligand bonding of transition metal carbonyl clusters as model systems for heterogeneous and homogeneous catalysts

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Report:

Despite their tremendous importance in catalysis, the electronic structure of transition metal (TM) carbonyls is mostly unknown. A better knowledge of the metal d-shell electronic structure, i.e. oxidation and spin state, effects of ligands and local symmetry on orbital hybridization, will help to understand and improve the working principle of catalysts. It was thus proposed to employ RIXS, XES and HERFD-XAS spectroscopy to study element-selectively the metal valence shell in a systematic study of well characterized homogeneous model systems of iron with catalytically relevant ligands. About 40 samples of references, iron-carbonyls and derivatives were measured by $K\beta$ -detected HERFD-XAS, $K\beta$ -XES, valence-to-core XES and valence-to-core RIXS. Data analysis including theoretical calculations using ORCA are currently carried out. As an example, the results for simple iron carbonyl clusters and some derivatives are presented in figure 1, where the HERFD-XANES spectra are compared to transmission XANES experiments.

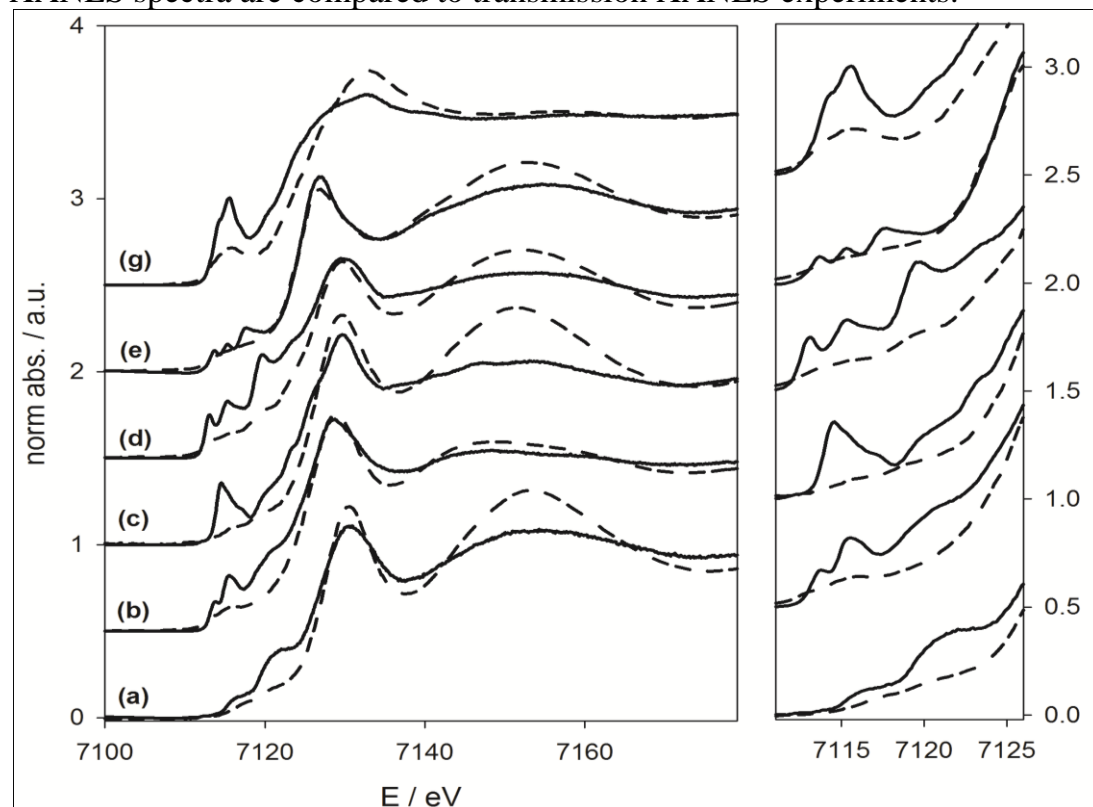


Fig. 1: HERFD-XANES (solid line) spectra in comparison to transmission XANES (dashed line) experiments (left):
 (a) $Fe(CO)_5$,
 (b) $Fe(CO)_3$ (octatetraene),
 (c) $Fe_2(CO)_9$,
 (d) $Fe_3(CO)_{12}$,
 (e) $Fe(CO)_3(NO)$,
 (f) $Fe_2(CO)_4Cp_2$.
 The prepeak area is shown enlarged on the right.

In figure 2, the corresponding valence-to-core RIXS spectra are shown, where the influence of the additional ligands octatetraene, cyclopentadienyl (Cp) and NO in $\text{Fe}(\text{CO})_3(\text{octatetraene})$, $\text{Fe}_2(\text{CO})_4\text{Cp}_2$ and $\text{Fe}(\text{CO})_3(\text{NO})$ are obvious. These signals are now attributed by DFT calculations, but it is clear that such effects can be used for in-situ studies of carbonyl compounds and ligand exchange reactions.

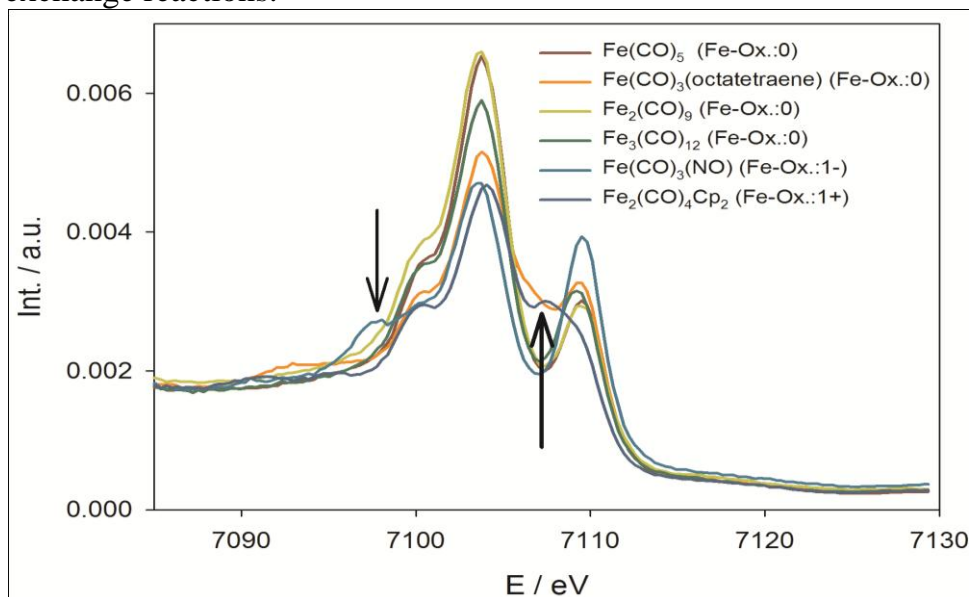


Fig. 2: Valence-to-core X-ray emission spectra of (a) $\text{Fe}(\text{CO})_5$, (b) $\text{Fe}(\text{CO})_3(\text{octatetraene})$, (c) $\text{Fe}_2(\text{CO})_9$, (d) $\text{Fe}_3(\text{CO})_{12}$, (e) $\text{Fe}(\text{CO})_3(\text{NO})$, (f) $\text{Fe}_2(\text{CO})_4\text{Cp}_2$. The influence of the additional ligand in comparison to the pure carbonyl ligands are highlighted by arrows.

Finally, valence-to-core RIXS spectra are shown in figure 3. Currently concerted efforts are taken in cooperation with Kirstina Kvashnina (ESRF) and the theory-group of Christoph Jacob (Karlsruhe) to calculate those spectra, which is challenging due to the highly covalent character of the investigated compounds. Nevertheless, it is expected that understanding the data will further enlight the catalytic role that carbonyl compounds play as active compounds or intermediates. The present study serves as basis for more sophisticated in-situ measurements of catalytic and photocatalytic reactions planned for the near future.

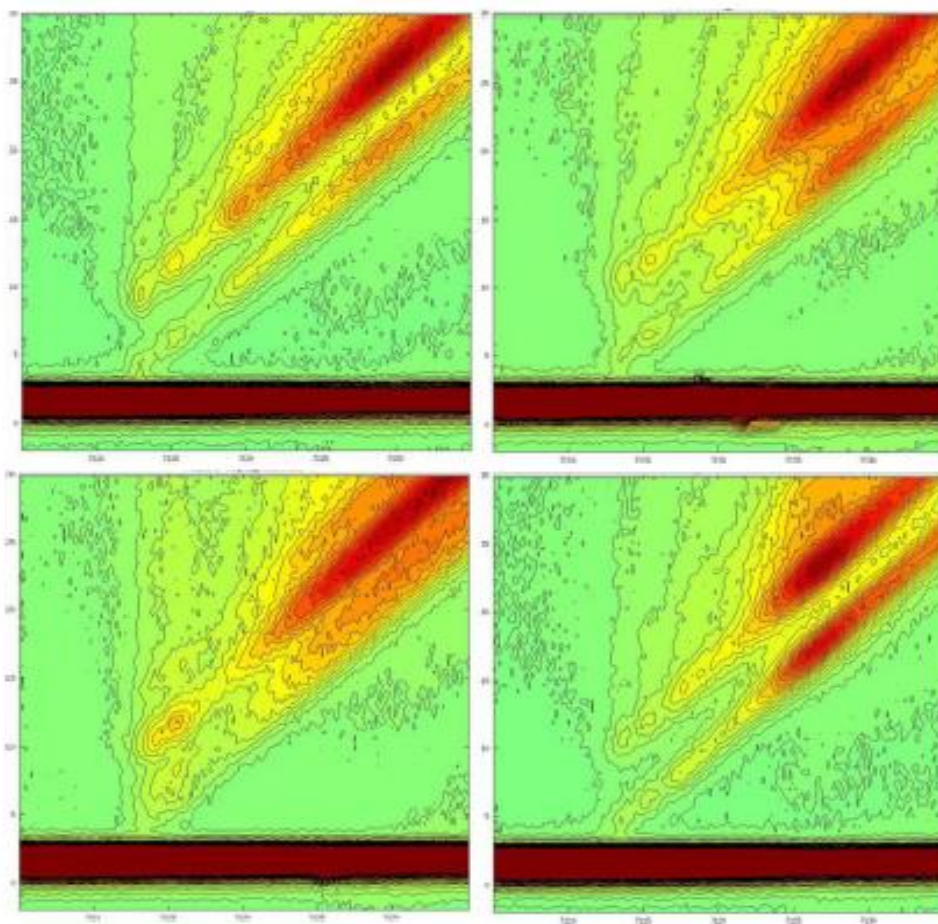


Fig. 3: valence-to-core RIXS planes of $\text{Fe}_3(\text{CO})_{12}$ (top left), $\text{Fe}(\text{CO})_3(\text{octatetraene})$ (top right), $\text{Fe}_2(\text{CO})_4\text{Cp}_2$ (bottom left), $\text{Fe}(\text{CO})_3(\text{NO})$ (bottom right). The energy transfer is plotted against the incident energy in all figures.