

# Probing the Electronic Structure of Substituted Ferrocenes with High-Resolution XANES Spectroscopy

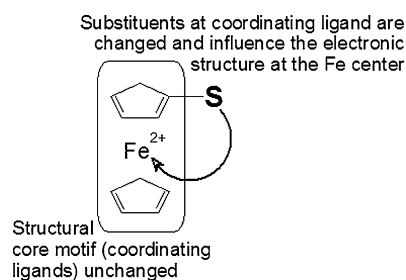
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In situ studies by X-ray spectroscopic methods, especially by X-ray absorption spectroscopy (XAS), have contributed important insights into catalytic reactions and the underlying molecular mechanisms.<sup>[1]</sup> While the extended X-ray absorption fine structure (EXAFS) region can provide information on the geometric structure around a metal center,<sup>[2]</sup> the XANES (X-ray absorption near edge structure) region of XAS spectra contains information on the electronic structure. In K-edge XAS experiments, the first unoccupied states reached by the 1s electron after excitation are metal d-states. However, as such a 1s → nd transition is dipole forbidden, the resulting so-called pre-edge signals (prepeaks) are of weak intensity.<sup>[1a]</sup> If molecular complexes and catalysts are considered, these prepeaks contain detailed information about the lowest unoccupied molecular orbitals (LUMO). So far, the lifetime broadening of conventional K-edge XAS experiments limits their applicability for probing the LUMO states. On the other hand, in L-edge XAS<sup>[3]</sup> a more intense 2p → nd transition can be used,<sup>[4]</sup> but because of the use of low-energy radiation, in situ studies of catalytic reactions are not possible with this technique. Therefore, a hard X-ray technique with a better resolution of the final d-states than in conventional XAS is required to probe the electronic structure of catalysts in situ.

High-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS)<sup>[5]</sup> is capable of reducing the life-time broadening. In this technique, the XAS spectra are recorded by monitoring a selected fluorescence channel with an energy resolution smaller than the life time broadening of the core hole.<sup>[6]</sup> With this, the net signal broadening in the XANES region of XAS spectra can be

significantly reduced, which sharpens the very weak signals of dipole-forbidden transitions.

It is therefore surprising that HERFD-XAS measurements have not been applied to overcome the limitations of conventional XAS with respect to processes involving molecular complexes, like in homogeneous catalysis. So far, HERFD-XAS, and also X-ray emission studies, have been mainly applied to heterogeneous catalytic processes<sup>[7]</sup> and enzymatic systems.<sup>[8]</sup> Also HERFD-XAS has been used to elucidate the structure of protein models with iron centers.<sup>[9]</sup> However, these complexes show structural differences already in the first coordination shell. Nothing is known about the power of HERFD-XAS to resolve structural differences beyond the nearest neighbor coordinating atoms and their influence on the electronic structure at the central metal atom. Herein, we want to bridge this gap by pioneering HERFD-XAS studies on transition-metal complexes, which show that this technique is even sensitive for substitution effects at the ligands coordinated to a metal center, that is, effects which are not “visible” to conventional EXAFS analysis. As a first target, we investigate changes in the electronic structure of ferrocene compounds induced by substituents at the cyclopentadienyl (Cp) rings. As indicated in Scheme 1,



Scheme 1. Illustration of the approach to demonstrate the resolving power of HERFD-XAS with respect to changes beyond the first ligand sphere.

the ferrocene structural motif remains unchanged throughout the study. Only the substituents are changed, which affects the electronic structure at the iron center.

Herein, we demonstrate that these subtle changes can be probed by HERFD-XANES and explained with TD-DFT calculations. Such substituted ferrocenes play an important role in (bimetallic) catalysis,<sup>[10]</sup> the preparation of switchable self-assembling monolayers (SAMs)<sup>[11]</sup> and electronic com-

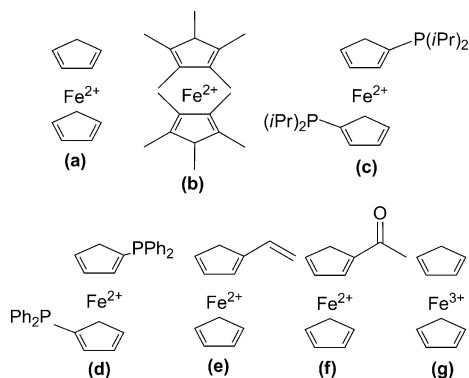
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pounds.<sup>[12]</sup> The influence of substituting groups at the Cp ring on the electronic structure has been studied both experimentally and theoretically.<sup>[13]</sup> However these experimental studies are limited to soft X-ray absorption spectroscopy,<sup>[4,14]</sup> which cannot be used for in situ studies due to the low radiation energy, and photoelectron spectroscopy<sup>[13c]</sup> or X-ray emission experiments<sup>[8e]</sup> that only provide information about occupied orbitals. Here, we demonstrate how the complementary information on unoccupied orbitals can be probed with hard X-ray.

As examples, we considered the mono- and disubstituted ferrocene complexes (a)–(g) shown in Scheme 2. A compari-



Scheme 2. Ferrocene-derived compounds (a)–(g) subjected to HERFD-XANES measurements and TD-DFT calculations.

son of conventional transmission mode XANES with the corresponding HERFD-XANES spectra recorded at the  $K\beta_{1,3}$  main line of ferrocene (a),  $\text{Fe}(\text{CpPPh}_2)_2$  (d), and  $\text{Fe}(\text{Cp})(\text{CpAc})$  (f) are shown in Figure 1. Although significant differences in the electronic structure are expected due

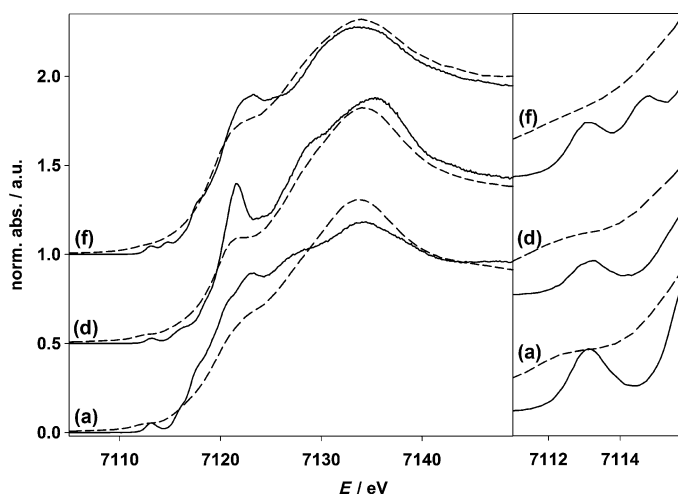


Figure 1. Comparison of conventional (dashed line) and HERFD-XANES (solid line) spectra for complexes (a), (d), and (f). The enlarged prepeak region is shown on the right; the spectra have been shifted for clarity.

to the acetyl or the two diphenylphosphino substituents, hardly any effects are observed in the conventional transmission XANES spectra. In the HERFD-XANES spectra, the net signal broadening is reduced from about 5 eV to 1.5 eV. This reveals significant differences in the 1s→3d prepeak region around 7113 eV as well as for the region around 7121 eV, which can now be used for detailed comparison with calculations.

As a starting point for the discussion of the electronic structure of the considered substituted ferrocene complexes, a molecular orbital diagram for the most relevant orbitals in ferrocene obtained from density-functional theory (DFT) calculations is shown in Figure 2. The LUMO is the doubly

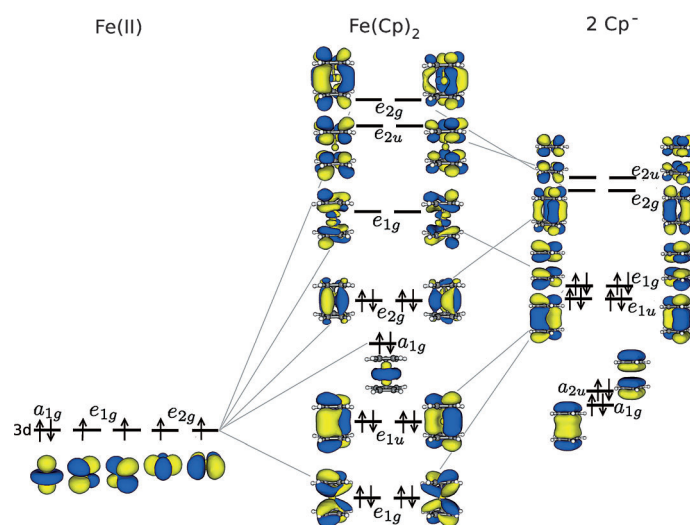


Figure 2. Schematic molecular orbital diagram for ferrocene. The ordering of the orbitals corresponds to a DFT calculation (BP86/TZP) and iso-surface plots of the most important DFT orbitals are also included.

degenerate  $e_{1g}$  orbital,<sup>[15]</sup> which is the antibonding combination of the Fe  $d_{xz}$  and  $d_{yz}$  orbitals with the  $\pi$ -orbitals of the Cp ligands. The prepeak at 7113.2 eV in the XANES spectrum of ferrocene can be assigned to the dipole-forbidden transition from the Fe 1s orbital to these  $e_{1g}$  orbitals. Changes in these lowest unoccupied orbitals are induced by different substituents on the Cp ligands, which can be identified by comparing the HERFD-XANES prepeaks. Only the high resolution of these spectra allows for a deconvolution, and the isolated prepeaks of (a)–(g) are depicted in Figure 3. The positions and relative intensities of the isolated prepeaks are summarized in Table S11 of the Supporting Information.

To complement the experimental results and to allow for an assignment of the observed prepeaks to unoccupied molecular orbitals, we have performed time-dependent DFT (TD-DFT) calculations,<sup>[8b,c,16]</sup> using both the non-hybrid BP86 exchange-correlation functional<sup>[17]</sup> and the B3LYP hybrid functional.<sup>[18]</sup> The calculated spectra are included in Figure 3, and the unoccupied orbitals corresponding to these prepeak transitions are depicted in Figure 4.

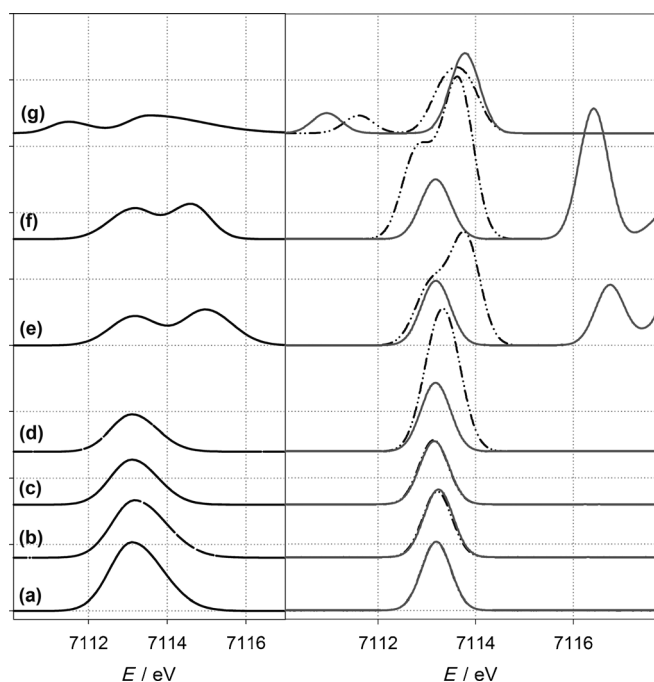


Figure 3. Left: normalized, isolated prepeaks from the experimental HERFD-XANES spectra of the complexes (a)–(g). Right: prepeaks from TD-DFT calculations with BP86/def2-QZVPP (black dash-dotted line) and B3LYP/def2-QZVPP (grey solid line).

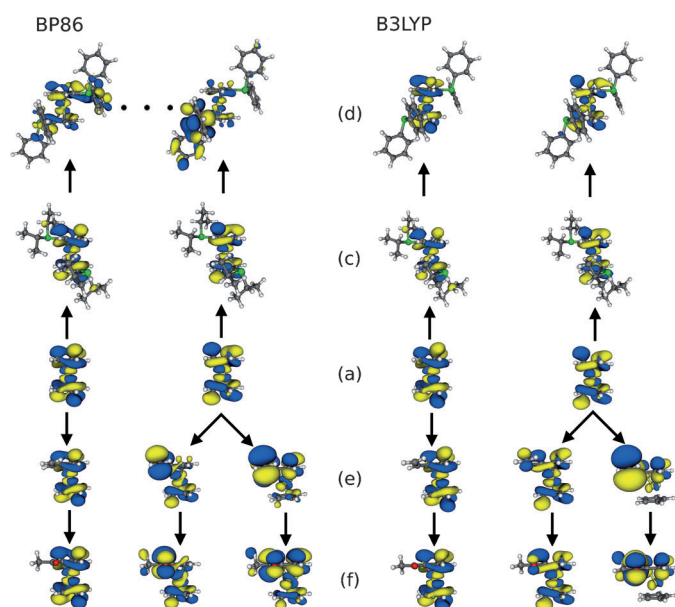


Figure 4. Isosurface plots of the unoccupied molecular orbitals probed by the prepeak transitions as obtained from TD-DFT calculations with BP86/def2-QZVPP (left) and with B3LYP/def2-QZVPP (right). In cases where more than one orbital transition contributes to one excitation, the corresponding linear combination of unoccupied orbitals is shown (see the Supporting Information). In the BP86 calculations for  $\text{Fe}(\text{CpPPH}_2)_2$  (d) ten individual excitations to different unoccupied orbitals contribute to the prepeak, of which only two are shown here.

For ferrocene (a), the LUMO is degenerate and there is only a single prepeak with a weak quadrupole intensity caused by the  $1s \rightarrow e_{1g}$  transition (see Figure 4). We note that the TD-DFT calculations provide identical results for the eclipsed and the staggered conformation. For  $\text{Fe}(\text{Cp}^*)_2$  (b) the LUMO is unchanged since the methyl substituents have very little effect on the intensity and energy of the calculated prepeak, which agrees with the experimental spectra. For the phosphine-substituted ferrocenes,  $\text{Fe}(\text{CpP}i\text{Pr}_2)_2$  (c) and  $\text{Fe}(\text{CpPPh}_2)_2$  (d), the position of the experimentally observed prepeak agrees with the one in ferrocene, but its intensity decreases. Although great care was taken to avoid particles size and self-absorption effects, they cannot be fully excluded since no angle dependent measurements were carried out. The effect of different isomers can be excluded as they do not affect the energy levels. For  $\text{Fe}(\text{CpP}i\text{Pr}_2)_2$ , the calculations show that the degeneracy of the LUMO is only slightly lifted. The substituents cause a small distortion of the two LUMO orbitals (see Figure 4), which leads to a splitting of ca. 0.1 eV. However, this does not affect the calculated prepeak intensity. For  $\text{Fe}(\text{CpP}i\text{Pr}_2)_2$ , both BP86 and B3LYP provide almost identical results. On the other hand, for  $\text{Fe}(\text{CpPPh}_2)_2$  the  $\pi$ -orbitals of the phenyl rings mix with those of the Cp rings in the BP86 calculations, resulting in very delocalized orbitals. Altogether, there are ten unoccupied orbitals that contribute to the calculated prepeak (two examples are included in Figure 4). This mixing lifts the symmetry of the LUMO orbitals and introduces large electric dipole contributions. Thus, a significant increase of the calculated prepeak intensity is found in the BP86 calculation. However, this increase does not agree with the experimental observation. On the other hand, with the hybrid B3LYP functional the corresponding orbitals are localized either on the Cp rings or on the phenyl rings. In this case, only two orbitals that resemble the LUMO in ferrocene contribute to the prepeak, and the calculated intensity is similar to the one in  $\text{Fe}(\text{CpP}i\text{Pr}_2)_2$ . By combining the experimental and computational results, we can conclude that in  $\text{Fe}(\text{CpPPh}_2)_2$  the phenyl rings do not contribute to the LUMO.

For  $\text{Fe}(\text{Cp})(\text{CpVinyl})$  (e) and  $\text{Fe}(\text{Cp})(\text{CpAc})$  (f) two prepeaks, which are split by 1.48 eV and 1.82 eV, respectively, are observed in the experimental spectra with an intensity ratio of 1:1.16 and 1:1.22 respectively. From these values as well as Figure 1, it is evident that the resolution of these two transitions is only possible by HERFD-XAS. A similar splitting has been observed previously in L-edge spectra of  $\text{Fe}(\text{CpAc})_2$ , where a value of 1.12 eV is found.<sup>[4]</sup> This splitting can be understood with the help of our TD-DFT calculations. The  $\pi$ -orbitals of the acetyl and vinyl substituents interact with one of the LUMO orbitals, resulting in the two orbitals shown in Figure 4. As these are not symmetric anymore, the intensity of the transitions to these orbitals increases and is now dominated by the electric dipole contribution. On the other hand, the other orbital (see Figure 4) is perpendicular to the substituent  $\pi$ -orbitals and remains unchanged. The transition to this orbital only has a small quad-

rupole intensity. Even though BP86 and B3LYP provide a very similar orbital picture, the splitting between the two prepeaks is too small with BP86, whereas it is overestimated with the B3LYP hybrid functional.

Finally, in ferrocenium (**g**) there is a vacancy in the  $e_{2g}$  orbital, which is occupied in ferrocene. Therefore, in the HERFD-XANES spectra the first prepeak appears 1.6 eV lower in energy than in ferrocene. The second prepeak, which is due to the transition to the unoccupied  $e_{1g}$  orbital, is shifted by ca. 0.4 eV to higher energies. This is qualitatively reproduced by the TD-DFT calculations, but these underestimate the intensity of the first prepeak and predict a too large intensity for the second prepeak. However, the treatment of excitations in open-shell molecules within (TD-DFT) is problematic and cannot account for multiplet effects,<sup>[19]</sup> which might be important for ferrocenium.<sup>[14]</sup>

In conclusion, we could show how high-energy resolution fluorescence detection X-ray absorption spectroscopy is able to reveal electronic transitions in the prepeak region of K-edge XAS spectra, which are sensitive to substituents at the cyclopentadienyl ligand of ferrocene compounds. Application of the HERFD technique thus makes K-edge spectroscopy as sensitive to electronic changes as L-edge XAS, but using hard X-rays. The in situ and in operando investigation of ligand effects, especially with respect to bimetallic ferrocene-based materials under almost any experimental condition becomes possible for the first time. The HERFD-XANES prepeaks can be assigned with the help of TD-DFT calculations. Even though these calculations do not provide quantitative agreement with experiment, they still allow for a reliable assignment of the observed prepeaks and make it possible to identify the unoccupied molecular orbitals probed by these transitions. With the presented combination, HERFD-XANES spectroscopy can be considered as a tool of very high potential for the element specific in situ investigation of substituent effects at coordinating ligands on the electronic structure of transition-metal complexes. It is thus a unique technique, capable of explaining catalytic activity on an electronic level.

## Experimental Section

High-energy resolution X-ray absorption experiments were performed at beamline ID26 at the European Synchrotron Radiation Facility<sup>[20]</sup> using the <311> reflection from a double Si crystal monochromator. HERFD spectra were measured with an X-ray emission spectrometer in horizontal plane.<sup>[6b,21]</sup> Sample, analyzer crystal and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry.<sup>[5a]</sup> Details of the HERFD experiments can be found in the supplementary information.

Quantum chemical calculations were performed with the ADF 2010.01<sup>[22]</sup> and ORCA 2.8.0<sup>[23]</sup> program packages. Molecular structures were optimized with DFT (BP86/TZP) with ADF. For all complexes, calculations were performed for the different possible conformers. XAS spectra were calculated using TD-DFT and Ahlrichs' def2-QZVPP basis set<sup>[24]</sup> following the methodology of Neese and co-workers.<sup>[8b,c,16]</sup> The energy scale is shifted by 181.97 eV and 151.08 eV in the BP86 and B3LYP calculations, respectively. Additional computational details are given in the Supporting Information.

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