Improving the sensitivity of QEXAFS using modulation excitation spectroscopy

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Abstract. Modulation excitation spectroscopy (MES) is a promising tool to analyze time-resolved EXAFS data during reproducible catalytic processes and was applied in two different experiments to evaluate the benefits compared to conventional analysis strategies. Thereby, phase sensitive detection (PSD) was applied directly to the x-ray absorption spectra as well as to the Fourier transformed extracted EXAFS. In both cases the results were discussed with respect to the achievable level of noise reduction as well as the possibilities to better understand the underlying mechanisms of the reactions, more precisely the dynamics and possible intermediate species. The results clearly demonstrate serious limitations for the application of MES in time-resolved EXAFS studies as soon as more sophisticated steps than averaging over several modulation cycles are performed

1. Introduction
In catalysis and materials science often only small but rapid structural changes occur under varying reaction conditions. In this case modulation excitation spectroscopy (MES) has received much attention which makes use of monitoring the structural changes by periodically changing the conditions [1,2]. In case of reversible structural changes the alternating part of the signal, which is the frequency response of the active species to the applied excitation, can be separated from the often dominant non-varying part. Furthermore, by considering only frequencies that can be assigned to the excitation, it is possible to efficiently suppress random noise. For catalytic applications, the technique has been widely used in infrared spectroscopy [2]. In addition, it has been found useful when studying materials by Raman spectroscopy and XRD [3].

In a first step we straightforwardly improved the signal-to-noise ratio by averaging over all cycles [4] which is possible due to the exactly known cycle duration T and the fact that T is an integer multiple of the measurement time for one spectrum. With this approach the original time resolution of the experiment is maintained while photon statistics are significantly improved. Afterwards, the more advanced phase sensitive detection (PSD) approach can be applied, where the spectra of the cycle are studied with the modulation frequencies only and the measured response is resolved dependent on the phase shift to the applied modulation [5]. An alternative way to increase sensitivity is low pass filtering followed by conventional XAS data analysis. Presently, it is strongly discussed which of these approaches is more useful or how they complement each other. Hence, we present here a comparison of the two approaches by analysing QEXAFS data in two model reactions [6].
2. Results
A Pt-Rh/Al₂O₃ catalyst was investigated during catalytic partial oxidation of methane in 6%CH₄/3%O₂/He and in 5%H₂/He by periodically switching the gas atmospheres every 60 s and collecting two absorption spectra each second during three full cycles with T = 120 s. Reproducing the collected absorption data with Fourier series (FS) or applying phase-sensitive detection (PSD), both with the first order frequency \( \omega = \frac{2\pi}{T} \) only, yield the same results either as function of time or phase as shown in Figure 1b. The non-varying part of the signal, which is the spectrum resulting from averaging over all spectra, can be added to proceed with standard XAFS analysis tools. Alternatively the results can be compared directly to difference spectra of reference compounds. A strong smoothing effect can be observed by comparing the results to the difference spectra of the raw data shown in Figure 1a. However, here evidently the significant changes in the spectra occur around 90 s (switch to methane), as clearly recognizable with the minimum whiteline feature at about 11570 eV in Figure 1a. With first order FS/PSD all changes are forced to follow a sinusoidal function with \( \omega = \frac{2\pi}{T} \). Thus there is a symmetry leading to an artificial maximum in whiteline intensity at 30 s. Applying low pass filtering with a cut-off slightly above \( \omega \) yields the difference spectra in Figure 1c. The quality of noise suppression is similar to the one achieved with the FS/PSD approach, but it is still possible to localize the major changes in the spectra at 90 s. Considering these results low pass filtering seems to be the preferred choice and it cannot be confirmed that FS/PSD is an outstanding tool to for example increase surface sensitivity in catalytic experiments.

As a second example a Cu/Al₂O₃ catalyst at 322 °C was investigated during periodic reduction and reoxidation induced by switching between 21%O₂/He and 5%H₂/He gas streams every 60 s (see also [7]). A combination of XANES linear combination analysis (LCA) and EXAFS fitting was applied to the low pass filtered 1200 spectra of one cycle. The results are shown in Figure 2. An intermediate Cu(I) state is visible during both transitions and detailed information about the sample composition during the entire experiment is available. It was already shown that the application of low pass filtering on absorption spectra is superior to FS/PSD approaches. Thus, in Figure 3 results are presented where first order PSD was applied to the Fourier transformed EXAFS data. The application of PSD is more promising compared to the absorption spectra because distinct shells as function of the atomic distance are obtained. Due to the high level of smoothing it is possible to immediately recognize the typical patterns of oxidized and reduced copper for different phases. However, it is

Figure 1. Pt-Rh catalyst measured at Pt L₃-edge: (a) difference spectra, (b) application of FS/PSD, (c) application of low pass filtering. The phases in the legend are valid for (b) only, where also the vertically scaled and shifted non-varying part is displayed.
much more difficult to find evidences for the intermediate Cu(I) state via the PSD approach in this case as the first shells of CuO and Cu$_2$O show strong overlapping. Moreover, following the intensity of the Cu-O and Cu-Cu peaks shown in the inset of Figure 3 once more demonstrates the problem to correctly reproduce the dynamics of the reaction with this first order approach, especially compared to the LCA results in Figure 2, where it is clear that the Cu(0) contribution is not well represented by a sinusoidal function.

![Figure 2](image2)

In addition to the shown investigations an approach was developed using the calculated phases in R-space to more directly access the phase information as function of the local distance R [6]. Theoretically it should be possible to obtain three different phases here according to the three different shell configurations of the contributing species. However, due to the close relationship of CuO and Cu$_2$O (overlapping peaks in radial distribution function) in this example as well as the typically high disorder contributions in catalysis in general (small particles, high temperatures), the usefulness of this approach still has to be evaluated in more detail with more experimental data.

![Figure 3](image3)

**3. Discussion and conclusion**

The results show that modulation excitation spectroscopy in combination with PSD can be used to significantly reduce noise in X-ray absorption spectra. Thereby, a low pass character is achieved which can be controlled by the number of contributing orders, while the dynamics of the resulting
spectra as function of time only consist of frequencies directly linked to the modulation. However, low pass filtering with similar cut-off frequencies yields spectra with about the same signal-to-noise ratios while no artefacts are introduced as it is coercively the case for low order PSD. In contrast to other techniques like infrared spectroscopy, where PSD is successfully applied, the EXAFS spectra do not provide well separated features, also not in R-space.

We can conclude that modulation excitation spectroscopy combined with low pass filtering and linear combination analysis is therefore a much better tool to improve data quality in time resolved X-ray absorption spectroscopy than PSD which deteriorates time resolution and only results in difference spectra. The presented results further suggest that averaging over several modulation cycles and applying controlled filtering (enhanced sensitivity) followed by conventional XANES/EXAFS data analysis are the best approaches to analyze time-resolved XAS data (see also ref. [6]).

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