	Experiment title: Implementation and demonstration of modulation excitation spectroscopy for sensitivity enhancement and dynamic behaviour analysis	**Experiment number**: CH 2809
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Shifts:	**Local contact(s)**: Wouter van Beek	*Received at ESRF:*

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Report:

The aim of this project was to carry out preliminary modulation exciataion (enhanced) spectroscopy (MES) and diffraction experiments at the Swiss-Norwegian Beam Line (SNBL) in collaboration with the beamline scientists to judge if the modulation enhanced (ME) approach can bring new possibilities and opportunities to to the tools already available at the ESRF.

One of the main advantages of the ME technique is the great enhancement of sensitivity, thus time-resolution, which allows investigating fast chemical and physical transitions and their kinetics and thus broadens the range of measurement possibilities.

As a test case, we studied the transient behaviour of a catalytic reaction, NO_x storage-reduction (NSR) where surface and bulk compositions of the catalyst dynamically change within some seconds, using concentration stimulation (3000 ppm NO/NO_2 + 3 % O_2 in He vs. 3 % H_2 in He) at 573 K in a flow-through capillary reactor.

Fig. 1 shows the experimental setup developed in this study. The critical component is the gas-switching which is triggered externally by a hardware clock. The states of catalyst located in a capillary reactor were monitored by XRD and Raman simultaneoulsy. The effluent gas components were measured by mass spectrometry (MS). The data acquisition of Raman spectrometer and periodic gas-switching were synchronized to facilitate the data analysis. The XRD measurements were not synchronized, but the acquired data with a number of modulated cycles were averaged into one cycle period in a quasi-synchronized manner by data-point extrapolation to average at the same time point of the period.
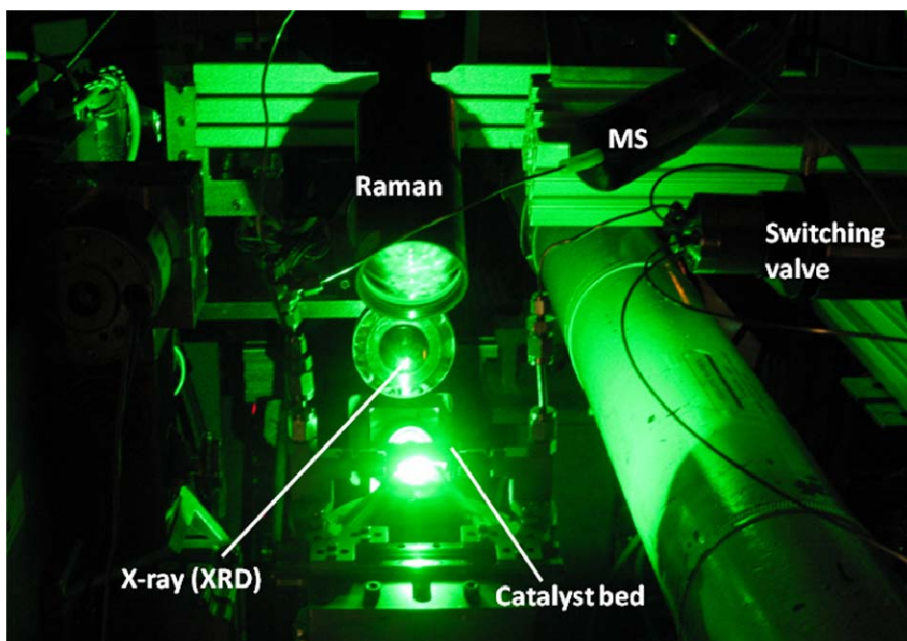
Fig. 1: ME Raman-XRD setup

Fig. 2 shows one of the advantages of the ME appraoch after averaging in time-domain. In this experiment, we have measured ca. 30 NSR cycles where the data quality of one cycle is not good enough to evaluate the spectral features. However, after proper averaing the data quality is grately increased as shown in Fig. 2 (right) and small details of the band evolution and features can be discussed.

Fig. 3 shows the corresponding phase-domain spectra obtained from the time-domain Raman spectra after the mathematical treatment of the ME technique, namely phase sensitive detection (PSD). The signal-to-noise is further boosted about two order of magnitutde and the in-phase angle analysis revealed the different nature of two major bands observed in Raman, which has not been reported so far.
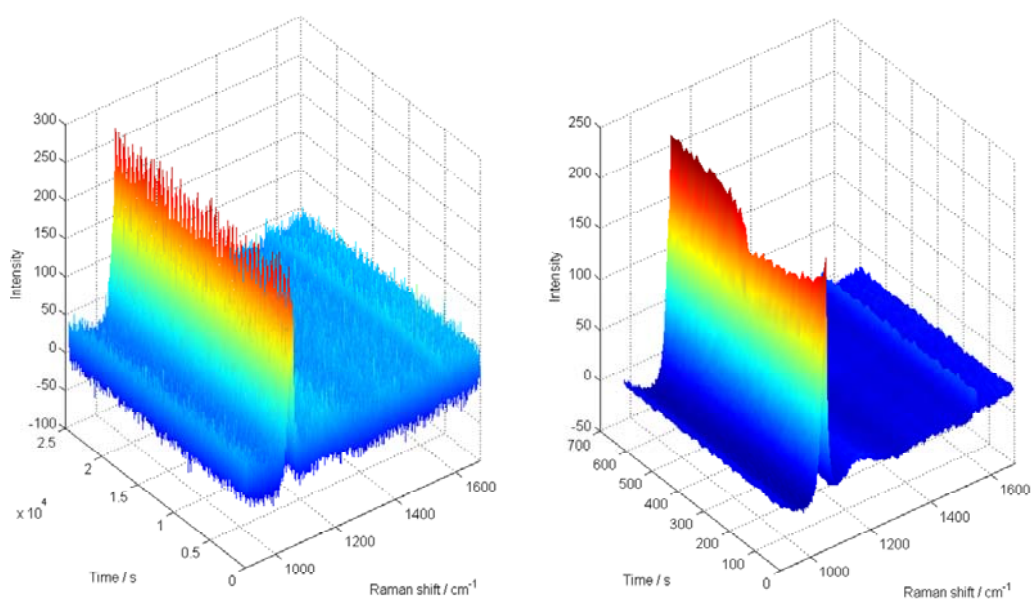

Fig. 2: Signal-to-noise enhancement by averaging in Raman-MES: (left) Raman spectra of ca. 30 NSR cycles, (right) the averaged Raman spectrum

Equivalently, the ME-XRD data showed similar sensitivity enhancement, showing its potential in understand NSR mechanisms and also other challenging chemical problems. However, the behaviour of catalytic reaction in the capillary reactor was strange (probably the capillary diameter was too small) and the results were not satisfactory for proper data-evaluation. Therefore, we further study NSR reactions in our future beamtime with the infrastrucutre develped in this work. In addition we plan to add XAFS into the combined technique to enrich the chemical information.

In summary, we have successfully carried out our first ME experiments to evaluate the power of the technique. The sensitivity enhancement was significant and thus the time-resolution (we went up to less than 10 s in time-resolution, which is not possible without the ME technique with a good data quality). This study made a great step forward in the implementation and demonstration of ME techinque at the ESRF. We will study further the mechanisms of NSR and also other chemical systems in our future work.
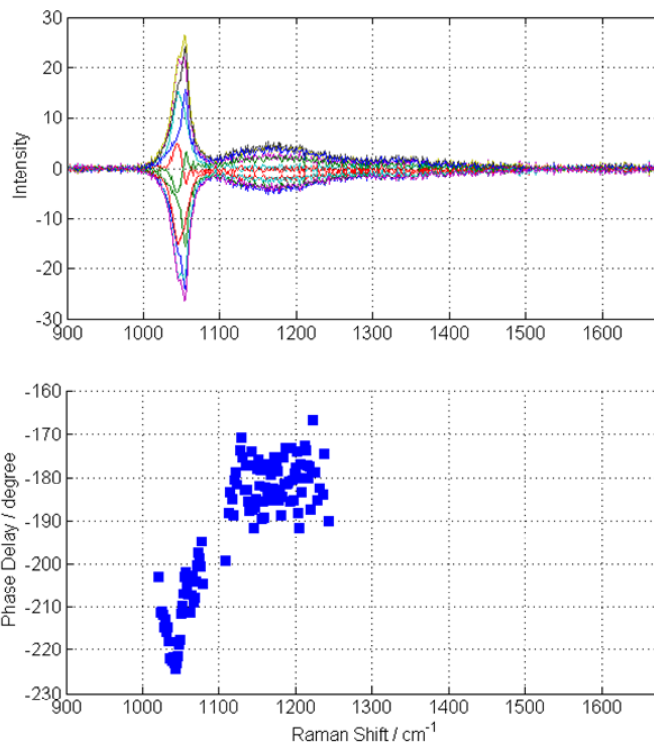

Fig.3: Phase-domain Raman spectra and in-phase angle analysis of the spectra, showing a different nature of the two bands