Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20129

Grantee name: Jakub Vokrouhlický

Details of the STSM

Title: Investigating the Fenton reaction in aqueous solution using X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) employing a liquid flat-jet

Start and end date: 10/06/2025 to 13/06/2025

Description of the work carried out during the STSM

In line with the STSM application proposal, we successfully completed all objectives concerning the setup and conduction of the experiment. In detail, we first optimized the experimental conditions, namely we calibrated the beamline, we adjusted the sample concentration and performed the signal characterization. Thus, we also achieved the first primary goal by mounting our home-built flat-jet setup onto the existing x-y-z manipulator at the GALAXIS beamline at SOLEIL.

Furthermore, we were able to record spectra as a function of the downstream coordinate of the flat-jet leaf. For calibration reasons, we used Cu^{2+} species instead of iron species, which were mentioned in the proposal.

The stability of the liquid flat-jet turned out to be a big problem during the whole beamtime. It required quite high concentrated hydrogen-peroxide (H_2O_2) solutions which in turn created bubbles in the tubes. Thus, we had to purge both pumps and refill the ice batch for every measurement. Nevertheless, the flat-jet became unstable a number of times during the measurement leading to a number of uncompleted data-sets. Due to the properties I have mentioned of H_2O_2 we were not able to measure “live” fenton reaction at the flat jet. One RIXS measurement took approximately 45 to 90 minutes, and we were not able to produces a spectrum without the flat-jet collapsing. We were able to measure “dead” fenton reaction, which means that we premixed the reactants and then we measured the products. The rationale for this strategy was to establish a baseline understanding of the reaction products, which will be invaluable for the successful characterization of a live Fenton reaction in subsequent studies.

Unfortunately, we were not able to measure XAS and RIXS spectra for neither iron nor vanadium species due to the delays caused by the jet instabilities. Moreover, we did not have time to change the MOSARIX alignment. Because the Bragg angle is different for certain elements and the change of the alignment would take whole day of beamtime we have decided to measure only Cu^{2+} species which have not been investigated before while iron species have been measured on MOSARIXS before.

1 This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

We have acquired RIXS spectra of various Cu^{+2} species: $CuCl_2$ (0.25M;1 M; 0.5M) at pH 1, $CuSO_4$ (0.25 M; 0.5M), , $Cu(NO_3)_2$ (0.215M; 0.86M), $CuBr_2$ (0.1 M). The "dead" fenton reaction has been measured at 4 different ratios of chloride to peroxide: $CuCl_2$+H_2O_2 (1:1, 3:1, 1:2, 1:4).The clearest spectra were acquired at the 1:1 ratio(Figure 1).

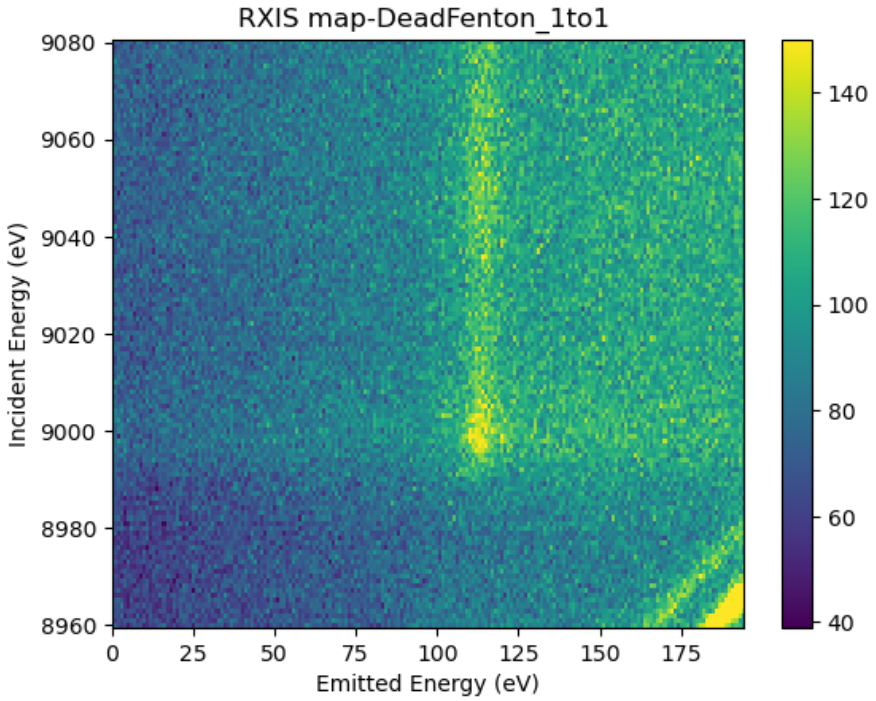

Figure 1: Example of a RIXS spectrum of "dead" fenton reaction ($CuCl_2$+H_2O_2 ratio 1:1).

Description of the STSM main achievements and planned follow-up activities

Even though we were not able to measure "live" fenton reaction we did measure the "dead" fenton reaction, which will also provide us with data that will help us to characterize the electron-transfer mechanism between the transitional metal the ligand in the reaction. The experiment will serve as a first step in characterizing the liquid-liquid interface LLI using hard X-ray RIXS. We will be interpreting the data from the beamtime in the following weeks.

We were able to create a protocol which we use XAS spectra to determine the geometry of the leaf. This enables us to conduct (also future) measurements at MOSARIX faster and more effective. We plan to improve upon our set-up of our flat-jet so we will be able to learn to measure the "live" fenton reaction. As mentioned above, the main problems were the instability of the flat-jet and due to the peroxide solutions – something we aim to improve for future beamtimes.

We aim to apply for future beamtime at GALAXIES as it would allow us to complete our originally envisioned plan. We only achieved parts of our proposed goals in the last session. This includes the planned investigation of the XAS and RIXS spectra of Iron and Vanadium and the study of the "live" Fenton reaction.

Nevertheless, we are planning to provide theoretical (computational) simulations for comparison to the spectra we have measured. As mentioned in the proposal these theoretical methods will allow us to accurately model electronic excitations, spectral properties, and the influence of the environment on irradiated molecules, which is key to understanding the mechanisms of radiation damage.

The short period at SOLEIL proved to be an exceptional opportunity for growth, providing me with a comprehensive understanding of synchrotron experimental methodologies. I am enthusiastic about advancing this knowledge further and I anticipate to gain more experience to contribute more significantly in future beamtime. After this visit, I have now a much better understanding of what I need to simulate in order to model the actual absorption and emission processes of the experiment.

The current results are likely to be part of VIGA project (student scientific project which is a part of Internal Grant Agency) at UCT Prague “Fenton reaction in molecular detail: spectroscopy and computations”.