

Report on the outcomes of a Virtual Mobility¹

Action number: CA20129

Grantee name: Juraj Fedor

Virtual Mobility Details

Title: Chemistry induced by photoelectrons at the liquid-air interface vs. electron impact on liquid microjets

Start and end date: 01/05/2024 to 30/06/2024

Description of the work carried out during the VM

Description of the virtual collaboration and activities carried out during the VM, with focus on the work carried out by the grantee. Any deviations from the initial working plan shall also be described in this section.

The virtual collaboration proceeded via online meetings. We had regular meetings every Friday at 13:00 CEST. Apart from these regular meetings, there were three ad-hoc calls to discuss urgent problems in the laboratory. Typically present at the meetings were J. Fedor and D. Habiger, J. Verlet and F. Pritchard joined two times.

The work carried out during the VM followed the working plan in the application almost exactly. In summary, the student from Prague, D. Habiger, successfully built a new experimental setup in Durham for probing chemical changes at the air-liquid interface. The individual steps were:

- We decided to use Hafnium as a photocathode material. Hafnium has a low work function (3.9 eV) and sufficient chemical stability. The 257 nm pulsed laser (4.82 eV photon energy) was used to produce photoelectrons.
- The photoelectron current was measured using an integrating picoamperemeter. Unfortunately, due to low signal levels, it was not possible to record the photocurrent as a function of time with an oscilloscope.
- The volt-ampere characteristics of the solutions with different conductivity (varying concentration of NaCl) has been measured. From these measurements it was concluded that a significant part of the recorded current is ion current, created due to sputtering of the photocathode.
- The test experiments with offline analysis of chemical changes in the solution were performed. We have decided to use terephthalic acid which is often used as a chemical dosimeter – upon reaction with OH radicals it produces hydroxyterephthalic acid which can be detected using fluorescence spectroscopy (Horiba Fluorolog QM spectrometer has been used for this purpose).

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.

In the project proposal we expected to use coumarin-3- carboxylic acid (3-CCA), however, the experiments performed in Prague in the meantime showed that 3-CCA has a lower sensitivity due to a fluorescence of the primary compound. The test experiments with the offline analysis showed a clear production of OH radicals. Their concentration was increasing with the exposure time quadratically, which suggests a second-order kinetics.

- Finally, the setup was modified for the in-situ detection of OH radicals. For this purpose, an excitation beam of 310 nm has been added, and the resulting fluorescence light of the hydroxyterephthalic acid has been collected by a pair of parabolic mirrors and analysed using a portable spectrometer.

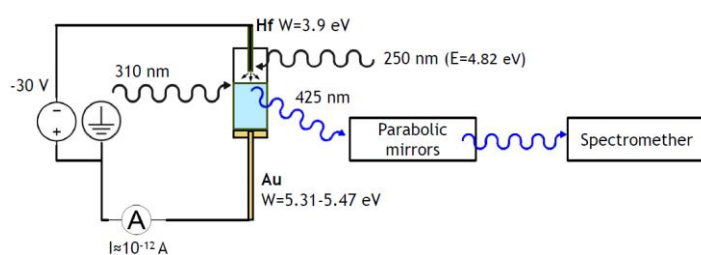


Figure 1 Scheme of the setup constructed at Uni Durham during the VM period.

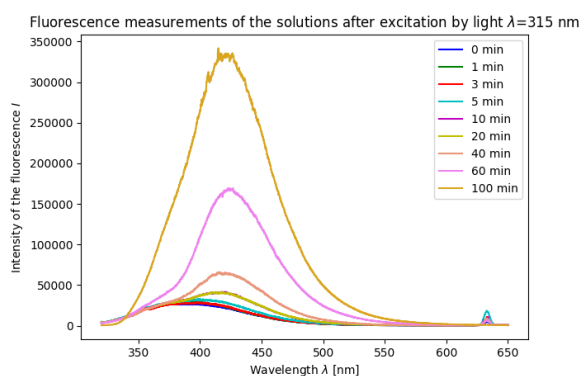


Figure 2 Emission spectra from the solution of terephthalic acid after the excitation at 315 nm. Different samples were irradiated for different time in the reactor depicted in Figure 2.

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

Description and assessment of whether the VM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the VM. Agreed plans for future follow-up collaborations shall also be described in this section.

The main output of the VM is a working setup at Uni Durham which utilizes the photoelectrons emitted from the Hafnium photocathode to induce production of OH radicals and their in-situ detection by fluorescence spectroscopy. The proof-of-principle spectra have been recorded during the VM. It turns out, some of the OH radicals are induced electrochemically, by the reactions initiated by Hafnium ions sputtered from the photocathode.

The Durham group will work on developing this setup further. The following steps are foreseen:

- Enabling the vertical scan of the in-situ OH detection from the surface towards the anode to monitor the special distribution of the radicals.

- Using a surfactant (e.g. perfluorooctanesulfonic acid, PFOS) to selectively probe the processes at the interface.
- Possibly implementing time-resolved transient absorption spectroscopy in this setup.

All these steps will be done in close collaboration with the Prague group. We are planning a common publication summarizing the experiments on terephthalic acid described here and those performed on our liquid-jet setup in Prague.

An important outcome of the VM will be also the diploma thesis of D. Habiger, containing these results. He is currently writing the thesis and plans to defend it at the University of Chemistry and Technology in Prague in autumn.

By setting up two complementary apparatuses for probing the irradiation-driven chemistry (IDC) in liquid solutions we have advanced the experimental capacities available within the MultiChem Action. This contributes to the Action capacity-building objective and to the research co-ordination objective. As to the WG1 tasks, the VM has addressed T1.2 (Exploration of ion irradiation induced chemistry of complex biomolecular systems). In spite of aiming for purely photoelectron-induced chemistry, we found out that ion-induced production of OH radicals certainly occurs in the system. One of the future activities will be to disentangle the effect of electrons and ions. In the near future (autumn 2024) we also plan to address the task T1.5 (Investigation of radiation-induced metal-based nanoparticles) in both setups, in close collaboration with C. Sicard-Roselli from Paris-Saclay.