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

Action number: CA20129

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Details of the STSM

Title: Solvation effects on molecular excitation and decay dynamic

Start and end date: 27/11/2024 to 04/12/2024

Description of the work carried out during the STSM

The aim of the scientific project between the Uppsala University and the University of Chemistry and Technology Prague is to investigate X-ray induced processes in organic molecules with biological importance in aqueous environment both experimentally and theoretically. The first step in this project was the STSM to DESY, Hamburg to perform the experiments at P04 beamline.

When a high-energy photon is absorbed, it primarily causes ionization of the biomolecule's core levels, rapidly followed by Auger-Meitner cascades. In the biological environment, these dynamics are affected by the presence of water. Water opens up additional non-local relaxation processes such as Intermolecular Coulombic Decay (ICD) and Electron Transfer Mediated Decay (ETMD). During this STSM we explored how solvation affects X-ray-induced processes by conducting high-resolution photoelectron spectroscopy experiments on a set of organic molecules in both the gas phase and aqueous medium. The chosen samples were all liquids (acetonitrile, propylamine, pyridine, pyrimidine, and pyrrole) with high vapour pressure and good solubility in water allowing us to conveniently perform the experiments in the gas and liquid phases. The measurements went according to the initial plan. The first day involved conducting essential safety training, ensuring all participants were briefed on proper beamline and laboratory protocols. This was followed by the alignment of the experimental setup, which included the calibration of the equipment and fine-tuning to optimize conditions for the measurements. First, we started with the gas phase measurements. The liquid samples were introduced into the setup via a gas line. The sample container was kept in the chiller at fixed temperature slightly below the room temperature. Next, we continued with liquid jet measurements. The primary objective was to record Auger spectra at various photon energies (Auger 2D maps), focusing on the C1s and N1s thresholds. After completing the measurements for all the samples (except for the pyrrole in the liquid phase as the sample has not arrived in time), the final day of the STSM involved cleaning the setup and the chemistry lab and ensuring all data was secured and stored for further analysis.

[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.

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

The main achievement of this STSM is the successful completion of the planned experiments at P04 beamline of PETRA III synchrotron facility, with nearly all objectives met. The electron spectroscopy measurements as a function of photon energy on a set of organic molecules in both the gas and liquid phases provided a comprehensive dataset, which will now be analyzed to explore electron dynamics and non-local decay processes.

The follow-up activities include Zoom meetings with the collaborators regarding the data analysis and calculations. So far, we have held one post beamtime meeting and formulated the main directions in the data analysis to present the calibrated data in a way needed for the comparison with the theory. We have divided the experimental data for the analysis between the beamtime participants. Currently dr. Eva Muchova (host contact for this STSM) is working on modelling the resonant Auger maps via the Feschbach-Fano formalism combined with the EOM-CCSD framework. The resonant part of the spectrum requires accurate modelling of the initial core-excited states at the fc-CVS-EOM-EE-CCSD level while the final states are typically described at the EOM-IP-CCSD level with inclusion of triple excitations to correctly account for the spectator channels. The non-resonant part of the spectrum is modelled at the fc-CVS-EOM-IP-CCSD level to describe the initial core-ionized states and at the EOM-DIP-CCSD level to account for the final doubly ionized states. The partial decay widths are calculated using the respective one- and two-body Dyson functions and continuum part is described as a plane wave. The most challenging part of the Auger 2D maps is the onset of ionization or possible charge-transfer states which would require time-dependent approaches that are currently not applicable for the core-excited/ionized fastly decaying states. Comparing theory to the experimental Auger maps measured in the gas phase and in aqueous medium, we will be able to see the differences.

After the data analysis and calculations are done, we start writing a manuscript describing the findings. The work conducted during the STSM and after that will contribute to advancing understanding in the field of biomolecules' molecular electron dynamics in solvated environments. Finally, we plan to publish the findings from our experiments and calculations as a research paper in an open-access journal.