Report on the outcomes of a Short-Term Scientific Mission[[1]](#footnote-1)

Action number: CA18212

Grantee name: Vera Brieskorn

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| **Details of the STSM**  Title: Simulating the excited-state dynamics of a Ru organometallic complex using stochastic-selection ab initio multiple spawning  Start and end date: 31/08/2023 to 21/09/2023 |
| **Description of the work carried out during the STSM**  Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section. |
| *(max. 500 words)*  During the first days of my STSM I got a first impression of the dynamics code implemented by the group of Prof. Curchod alongside getting to know the group members while also accomplishing the more practical task of setting up my workstation. As a next step, I carried out a Wigner sampling on the [RuCp(C6H6)]+ S0 ground state structure which I had already optimized during my electronic structure benchmark calculations in Vienna. From the 1000 initial conditions yielded by the sampling, I chose one structure to perform initial AIMS, SSAIMS, and AIMSWISS simulations on, based on the comparison of the TDDFT spectrum for the 1000 samples to the experimental UVVis spectrum of [RuCp(C6H6)]+. This workflow allowed me to not only get a first idea on the practical aspects of the AIMS approach and its modifications but also made me realize that determining the hapticity and monitoring its change over time in [RuCp(C6H6)]+ is not as straight forward as initially assumed. This circumstance motivated me to spend more time than initially planned on developing geometrical parameters able to monitor changes in the three-dimensional structure of the Ru complex. The parameters I developed relate the hapticity change of the Bz ring in [RuCp(C6H6)]+ to changes of distances and angles in the molecule, properties that can be determined experimentally. Alongside the development of geometrical parameters, I also deepened my understanding of the AIMS approach and the further developments SSAIMS and AIMSWISS by discussing the theoretical foundations with members of the group.  After performing AIMS, SSAIMS, and AIMSWISS simulations for a small molecule (ethylene) I am now able to apply these methods to my metal complexes. I obtained a deeper understanding of how the modifications to the standard AIMS approach affect the computational feasibility of a calculation and ran a few trajectories for the ruthenium complex to decide on reasonable and practical input parameters. The task of analyzing these simulations will still accompany me in Vienna as the aforementioned development of geometrical parameters describing the time-dependent hapticity change took longer than first anticipated. In addition, I encountered a second complication when realizing that the analysis of data from a simulation including the coupling between population on different electronic states is far more complex than for a classical simulation not taking the interaction of separate states into account. Due to these complications, I will still devote time to analyzing the data I obtained during this STSM when I am back in Vienna. Considering this task, the tools for analysis of geometric changes will certainly be further developed and shared with the members of the group of Prof. González who will surely benefit from the ideas I gathered and will verify their applicability to other metal complex systems. I will also be able to apply the tools monitoring hapticity change over time on the TSH dynamics that I carried out in the group of Prof. González, which will make the comparison between the TSH and the AIMS results even more insightful. |
| **Description of the STSM main achievements and planned follow-up activities**  Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.  *(max. 500 words)*  During my STSM I got to know the tools and approaches necessary for carrying out ultrafast excited state simulations on metallorganic systems in gas phase which will allow me to independently perform such calculations in the future. By carrying out a series of runs on [RuCp(C6H6)]+ using the AIMSWISS approach developed in the group of Prof. Curchod, I was able to generate data that will provide deeper insight into the evolution of a metallorganic complex after photoexcitation and possible bond breaking pathways, an outcome contributing to the WG2 of the CA18212. In addition to the simulations showing the interesting behavior of [RuCp(C6H6)]+ after photoexcitation obtained during my stay with Prof. Curchod, the analytical tools I developed for describing the hapticity change will not only be of use for me personally but might also provide a useful approach for investigating geometry changes in various types of metallorganic systems. This is because the tools account for the metal-ligand orientation, and not only distances between atoms, which is crucial for studying the hapticity change over time.  Furthermore, the analysis of the excited state dynamics will provide insight into the likeliness of a new ligand coordinating to [RuCp(C6H6)]+ by correctly describing and analyzing the photoinduced geometry changes competing with radiative relaxation pathways. Investigating this question is well in line with the interests of CA18212 WG2 and WG3 targeting the distribution between radiative relaxation and non-radiative relaxation via geometrical changes and the search for model systems to study interesting reactions in gas phase. An accurate description of the competing radiative and non-radiative relaxation pathways in [RuCp(C6H6)]+ is now possible due to the ability to carry out AIMSWISS simulations more accurately describing relaxation mechanisms than TSH and an insightful analysis can now be performed employing the tools developed during my STSM.  From a more personal point of view, I will continuously benefit from my STSM as firstly, the skill to carry out non-standard AIMS simulations will prove to be crucial for my future work. Secondly, the possibility of seeing the way people in another group work together has generally provided me with more insight into how scientific collaboration can be managed. To specify this, I was able to see how the task of writing a piece of software in a team was handled by a different group.  More generally speaking, the experiences I made when applying the approaches used by the group of Prof. Curchod to a metallorganic complex will contribute to making these approaches more feasible for such systems, a circumstance the field of photoexcitation on metallorganic complexes can generally benefit from. On another note, the deepening of connections between the group of Prof. González in Vienna and Prof. Curchod in Bristol will surely facilitate any future collaboration allowing for a more fruitful exchange of knowledge and skills between the two groups. |



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. [↑](#footnote-ref-1)