Motivation Letter

Dear Prof. Császár

in this letter I will describe my motivation to apply for a Short Term Scientific Mission (STSM) grant for the topic "Automatic Exploration of Excited-State Reactive Events" in the frame of the COST action CM1405 "Molecules in Motion" (MOLIM).

Currently, I am a second-year PhD student in the group of Prof. Leticia González at the University of Vienna (Austria). My topic of my PhD studies is the investigation of ultrafast intersystem crossing in organic molecules. In particular, I am interested in the photophysical and photochemical properties of nitro aromatic compounds, e.g., nitrated polycyclic aromatic hydrocarbons (NPAHs). NPAHs constitute widespread environmental pollutants that display photoinduced cyto- and genotoxicity, e.g., promoting the formation of skin cancer. A key point to understanding their mode of action is the elucidation of the processes taking place in their excited states.

In the investigation of reactions taking place in the excited states of molecules, there are two major issues to consider: the time scale of the reactions and the presence of multiple competing pathways. When the reactions take place on a slow time scale, they may not be studied directly by excited-state dynamics simulations as the combination of the long simulation times and the typically high computational costs of excited-state calculations preclude this approach. Furthermore, when there are multiple reactive pathways present, obtaining a clear overall picture of all reactions requires a large number of trajectories to explore all possible reaction pathways. Both problems are encountered in the investigation of the reactive processes taking place after photoexcitation in nitrobenzene (NB). NB is a model system for NPAHs and, although being small, exhibits a large variety of reactive photoinduced processes as well as intersystem crossing, both taking place on a similar picosecond time scale. A few theoretical studies that investigate individual processes of the photoinduced reactions of NB have been published. However, to obtain a more complete picture it is necessary to account for all possible reaction pathways at the same time.

Instead of investigating excited-state reactions by dynamics simulations, a different approach is to explore the excited-state potential energy surfaces (PES) and locate the most important regions which include the reactants and all possible products and transition states. For the exploration of the ground-state PES, an automated method to locate the regions, called transition state search using chemical dynamics simulations (TSSCDS), has recently been developed by Prof. Emilio Martínez-Núñez at the University of Santiago de Compostela (Spain). For this STSM, it is planned to extend the TSSCDS method to allow also the exploration of excited-state PES. For this, an interface of the TSSCDS code to the TERACHEM program package will be enabled. TERACHEM is able to run time-dependent density functional theory (TDDFT) calculations on GPUs, which allow for much faster calculations compared to the traditionally used CPUs. After the interface has been enabled, first, test calculations on simple model systems will be run, before the new method will be employed to study the reactive processes after photoexcitation in NB. Thus, the following tasks should be accomplished during this STSM (4 weeks):

1. Interfacing TSSCDS to run with TERACHEM (2 weeks)
2. Test calculation and analysis for simple test systems (1 week)

3. Start of the study of excited-state reactive paths of nitrobenzene (1 week)

For a successful realization of the planned tasks (described above), a close colloboration with Prof. Martínez-Núñez is necessary. This is best achieved, when I visit the group of Prof. Martínez-Núñez and will be able to learn directly from his expertise and work under his supervision. The results obtained during this STSM will not only be greatly beneficial for my current studies but the implementation of the excited-state TSSCDS method surely is of great interest other theoretical chemists working in the field of photochemistry. Thus, I apply for a STSM grant to visit the group of Prof. Martínez-Núñez.

Yours sincerely,
J. Patrick Zobel