

Report on the outcomes of a Virtual Mobility¹

Action number: CA20129

Grantee name: Dr. Alexey Verkhovtsev

Virtual Mobility Details

Title: Dissociative ionization of MeCpPtMe₃ studied by means of reactive molecular dynamics

Start and end date: 01/07/2023 to 31/08/2023

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 work carried out during the VM followed the research plan presented in the grant application. The work was performed jointly with Mr. Hlib Lyshchuk and Dr. Juraj Fedor from the J. Heyrovský Institute of Physical Chemistry CAS, Prague, Czech Republic.

(i) A series of DFT calculations were performed to determine the parameters of the reactive rCHARMM force field [1] for reactive MD simulations of MeCpPtMe₃⁺ fragmentation using the MBN Explorer software package [2]. In these calculations, rigid and relaxed potential energy surface scans for different reaction coordinates (particularly different Pt-C bonds between the Pt atom and CH₃ ligands) were explored. The calculations revealed that two methyl groups attached to the Pt atom are bound weaker than the third methyl group, with the corresponding bond dissociation energies equal to ~40 and 70 kcal/mol. A similar analysis was performed for MeCpPtMe₂⁺ and MeCpPtMe⁺ fragments, thus establishing the variation of bond dissociation energies in different molecular fragments.

(ii) The reactive MD simulations of MeCpPtMe₃⁺ fragmentation were carried out using MBN Explorer [2], following the computational approach adopted in earlier studies [3,4]. Two scenarios of energy deposition into the target were considered: (1) The localized energy deposition into a specific covalent bond immediately after the ionization, leading to the cleavage of a specific bond on the femtosecond time scale. (2) Energy transfer into the system's vibrational degrees of freedom via the electron-phonon coupling mechanism. Both processes result in an increase in the cation's internal energy after the energy deposition.

For simulations of the first fragmentation mechanism, the amount of energy remaining in the system after ionization (i.e., excess energy over the first ionization potential) was deposited locally into a specific covalent bond of the target (namely, three different Pt-C bonds, several

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.

different C-H bonds within a methyl group, and a C-C bond between the 5-member Cp ring and a methyl group) and converted into the kinetic energy of the two atoms forming the bond.

The thermal mechanism of fragmentation corresponds to a statistical distribution of the deposited energy over all the degrees of freedom of the target. In this case, equilibrium velocities of atoms corresponding to a given temperature were rescaled depending on the amount of deposited energy.

In both cases, the amount of excess energy deposited into the parent cation varies from 0 to ~15 eV in steps of ~0.4 eV, corresponding to the experimental parameters of the HIPC group.

About 2,000 individual MD trajectories were simulated for each energy deposition mechanism a reliable statistical analysis of the produced molecular fragments. Each simulation was performed for 50 ns, and fragments produced at the end of the simulations were analyzed. The corresponding fragment appearance energies were evaluated from this analysis and compared with experimental data of the dissociative ionization of MeCpPtMe₃ by the team of Dr. Juraj Fedor.

[1] G.B. Sushko, I.A. Solov'yov, A.V. Verkhovtsev, S.N. Volkov, A.V. Solov'yov, *Eur. Phys. J. D* **70**, 12 (2016)

[2] I.A. Solov'yov, A.V. Yakubovich, P.V. Nikolaev, I. Volkovets, A.V. Solov'yov, *J. Comput. Chem.* **33**, 2412 (2012)

[3] P. de Vera, A. Verkhovtsev, G. Sushko, A.V. Solov'yov, *Eur. Phys. J. D* **73**, 215 (2019)

[4] B. Andreides, A.V. Verkhovtsev, J. Fedor, A.V. Solov'yov, *J. Phys. Chem. A* **127**, 3757 (2023)

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.

From the scientific point of view, the performed VM fully achieved its planned goals and expected outcomes. The performed DFT-based relaxed potential energy surface scans revealed that removing one of the weakly bound CH₃ groups leads to the structural reorganization of the MeCpPtMe₂⁺ fragment. This process results in the activation of a new fragmentation channel when a second weakly bound CH₃ group is detached from the parent ion, and an ethane (C₂H₆) molecule is formed. Such a post-irradiation chemical transformation significantly lowers the energy barrier for the release of two CH₃ fragments, in agreement with the experimental observation that the MeCpPtMe⁺ fragment (corresponding to the loss of two methyl groups) has a lower appearance energy than the MeCpPtMe₂⁺ fragment corresponding to the loss of one CH₃ group.

These results provide valuable information about the irradiation-induced chemical transformations in molecular systems relevant to nanofabrication using focused electron beams. The VM, therefore, has contributed to tasks T1.1, T1.3 and T1.5 of WG1 and to the MultiChem research coordination objectives on (i) combining and advancing experimental, theoretical and computational modelling methods for studying, on a molecular level, irradiation-driven chemistry (IDC) processes underlying radiation-induced damage; and (ii) establishing a comprehensive databank of IDC-related quantities.

The outcomes of this study conducted during the VM will form a basis for a joint publication with the HIPC team. It is planned to complete the manuscript and submit it to a peer-reviewed journal by the end of the year.