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

Action number: CA20129

Grantee name: Laura Carlini

Details of the STSM

Title: Mass spectrometry characterization of triazole molecular targets via laser-induced ionization

Start and end date: 01/07/2024 to 13/07/2024

Description of the work carried out during the STSM

The main goals of this STSM were

i) To contribute to the implementation/optimization of the new experimental set-up under construction by Dr. Dariusz Piekarski at IPC PAS in Warsaw to perform mass spectrometry characterization via laser-induced ionization on 1,2,3-triazole and its derivatives;

ii) To discuss the experimental results obtained in our laboratory (CNR-ISM, Montelibretti) and to compare them with the quantum chemistry calculations implemented by Dr. Dariusz Piekarski.

During the first week of this STSM, I contributed to the implementation of the experimental set-up by assembling the TOF-MS chamber and the gas-line and performing preliminary tests for the high-harmonic generation. In Figure 1 is reported a picture of the laser room equipped with a Jasper 20 laser (Fluence.technology) and an experimental chamber for TOF-MS measurements. The laser parameters are:

- average power: 0.5-20 W
- output wavelength: 1030±5 nm
- pulse energy: 0.01-160 mJ
- repetition rate: 0.1-28 MHz
- pulse duration:<300 fs

[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.

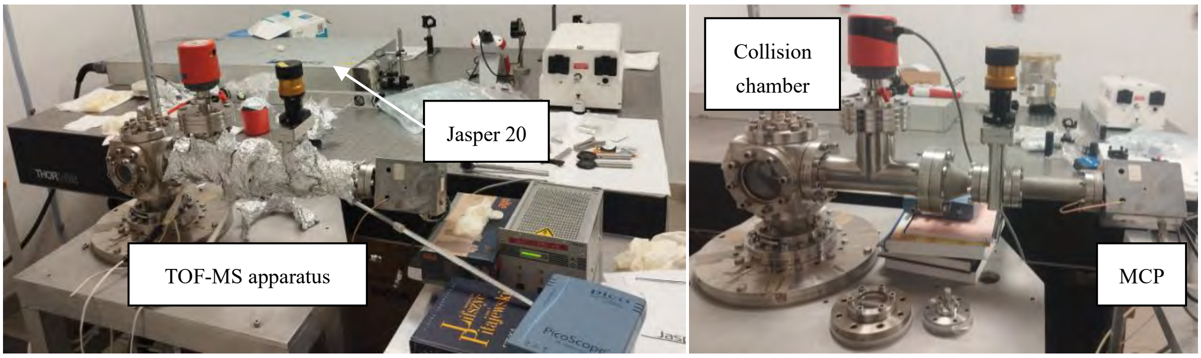


Figure 1. *The new experimental set-up under construction in the Institute of Physical Chemistry of Polish Academy of Sciences (Warsaw).*

For the preliminary tests, the collision chamber (Figure 2) has been equipped with a gas-line to evaporate samples in liquid form. A new oven to sublimate solid samples is under construction in the CIMAP laboratories (GANIL facility, Normandy) and will be soon integrated in the collision chamber. The schematic picture of this source is shown in Figure 3.

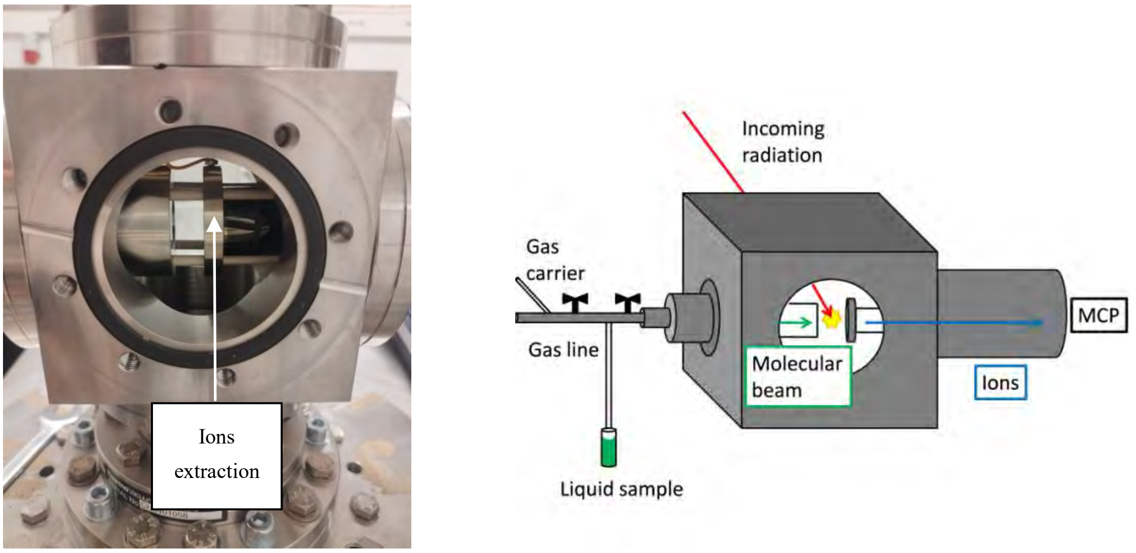


Figure 2. *Left panel: the collision chamber for experiments. Right panel: schematic of the experimental set-up for liquid samples.*

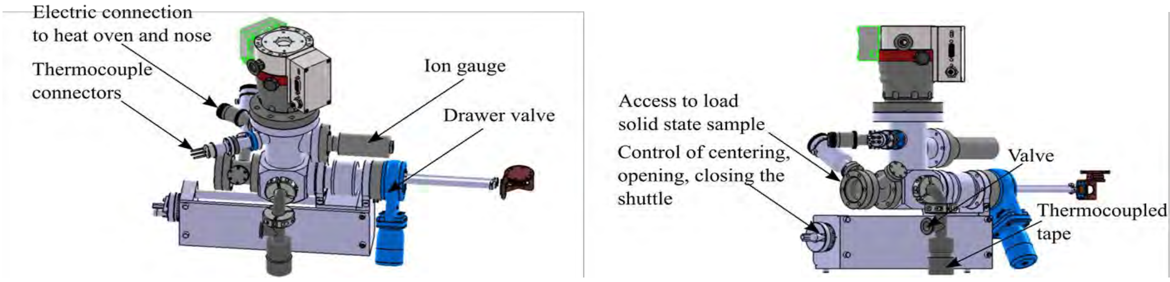


Figure 3. *Schematic of the molecular beam source under construction in the CIMAP laboratories (GANIL facility, Normandy).*

The vacuum pressure after cleaning and baking-out the chamber was of about $1 \cdot 10^{-7}$ mbar. Few bars of gas carrier will be needed to bring the sample in the interaction region, so the starting vacuum pressure in chamber should be at least of the order of high 10^{-8} mbar. For this reason, it has been decided to equip the set-up with a new turbomolecular pump with higher pumping speed.

Due to a delay in the shipment of the appropriate BBO crystal and optics for high-harmonic generation, a first attempt to generate higher harmonics has been made by using a set-up customized for a 1050 nm laser to produce green light (2nd harmonic generator from Light Conversion UAB, Lithuania). A figure of the high-harmonic generation set-up is reported in Figure 4. As expected, the presence of many parameters to be optimized, such as the correct alignment and focusing, the setting of the laser power and the thickness and orientation of the crystal made the task too time-consuming to be completed during this STSM.

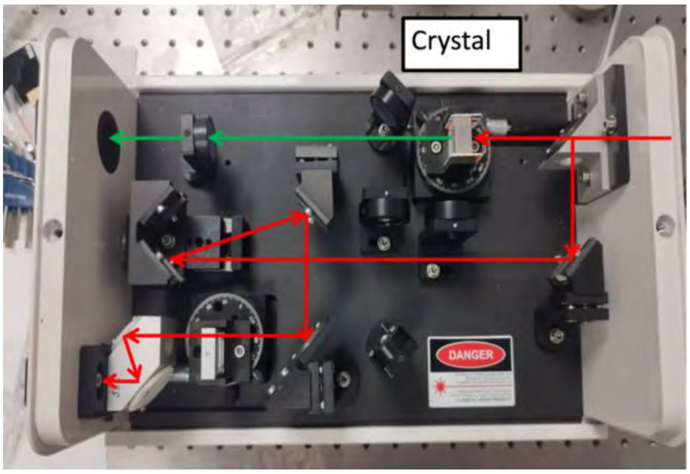
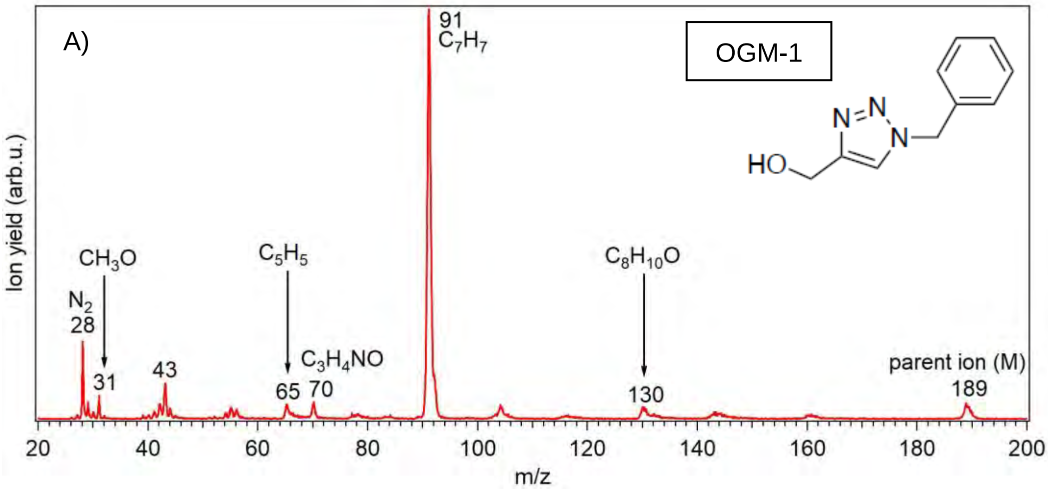


Figure 4. *High-harmonic generator (green arrows) used for the preliminary tests to generate green light. 3rd harmonics is shown with red arrows.*

The second part of the short-term mission has been dedicated to the analysis of the data collected in the CNR-ISM laboratory (Montelibretti, Rome) on the triazole derivative samples OGM-1 and OGM-2 (synthesized by Prof. O. Garcia Mancheno from WWU, Münster) and OGM-3 (commercially available). The experimental data have been compared with the theoretical simulations implemented by the group of Dr. Dariusz Piekarski. Quantum chemical calculations are performed within Density Functional Theory DFT framework as well as at multireference level of theory, i.e. state average four SA4-CASPT2/CASSCF with the active space of 14 electrons in 11 orbitals for 1,2,3-1H-triazole.

The mass spectra of OGM-1 ($C_{10}H_{11}N_3O$), OGM-2 ($C_{10}H_9N_3O_2$) and OGM-3 ($C_6H_5N_3O$) have been reported in Figure 5 (panel A, B and C, respectively) together with the proposed assignment of the main fragments and the molecule structure. The potential energy surface analysis for sample OGM-1 is schematized in Figure 6.



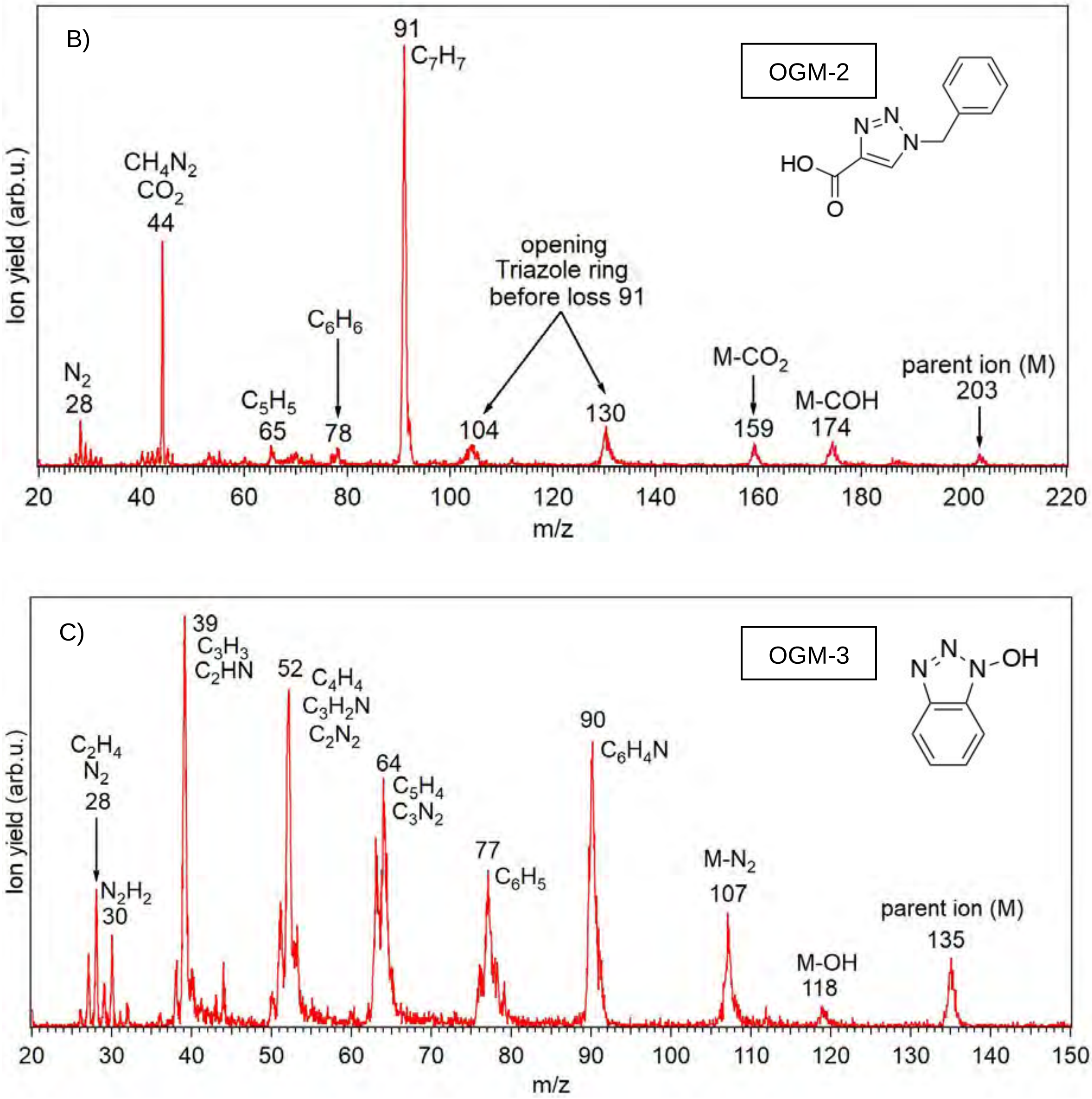


Figure 5. *Mass spectra of OGM-1, OGM-2 and OGM-3 collected in the CNR-ISM laboratories (Montelibretti, Italy) with 21.22 eV incoming radiation are reported in panel A, B and C, respectively. The main fragments, the proposed assignments and the structure of the molecule are reported.*

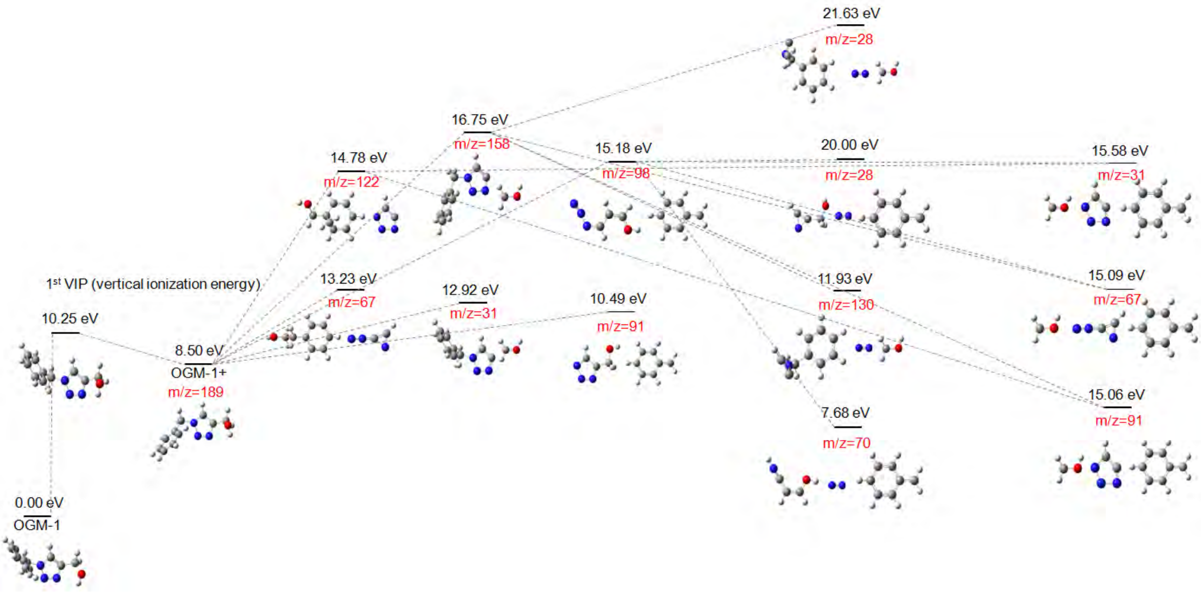


Figure 6. *Potential energy surfaces calculated at the B3LYP/6-311++G(d,p) level of theory for singly charged fragments formed upon ionization of OGM-1. Zero point energy correction is included, relative energies in eV and mass over charge ratio are reported.*

In case of OGM-1 molecule, the fragmentation channel showing the lowest energy (10.49 eV) corresponds to the production of m/z=91 ($C_3H_4NO^+$) directly from the dissociation of the parent ion. This fragment is very stable and dominates the mass spectrum of the molecule (see panel A of Figure 5). It's counterpart, the ion at m/z 98, is not detected in the experiment in good agreement with the theoretical predictions. Indeed, the channel for the production of 98 ion opens above 15 eV and leads to the fragmentation into neutral C_7H_7, neutral N_2 and C_3H_4NO ion (m/z=70) with very low appearance energy (7.68 eV). The intensity of fragment at m/z 67 ($C_2HN_3^+$, according to the theory) is very low in the experimental mass spectrum, on the contrary we detected m/z 65 which may be related to the production of C_5H_5 ion from fragment 91. Among the bigger fragments predicted by the theory, only the ion at m/z 122 ($C_8H_{10}O^+$) has been detected, while we observed other small features around m/z 104, 143 and 160. Finally, the energy and structure corresponding to m/z 43 are not reported as they are difficult to be identified due to the presence of many different fragmentation channels leading to the production of this ion.

The analysis of OGM-2 and OGM-3 is in progress.

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

The aim of this STSM was to continue the collaboration with the group of Dr. Dariusz Piekarski to support the establishment of a new laboratory and its activity. During this period we were able to assemble the TOF-MS chamber and the gas-line for the measurements of liquid samples. We tested the Jasper 20 fs laser with a high-harmonic generation source and we arranged an optical path to test a new customized crystal to produced 2nd harmonic from the 1030 nm laser.

Due to the delay in the delivery of the appropriate BBO crystal and optics for the high-harmonic generation, we could not perform the measurements initially planned for this STSM, i.e. to investigate the chemical reactivity of 1,2,3-triazole and its derivatives by mass spectrometry characterization via laser-induced ionization. Nevertheless, this short-term mission was successful, as we were able to assemble the new experimental set-up which after a proper optimization will be ready for the mass spectrometry measurements.

Moreover, this STSM allowed us to start the data analysis on the samples measured in the CNR-ISM laboratory in Montelibretti (Rome). We compared the experimental data with quantum chemistry calculations, finding a good agreement between experiment and theory for OGM-1 molecule. The data analysis is now in progress on samples OGM-2 ($C_{10}H_9N_3O_2$) and OGM-3 ($C_6H_5N_3O$), and will be combined with the results of the measurements via laser-induced ionization.

Our group will keep in touch with Dr. Dariusz Piekarski for the follow-up activities. The future plans are to

i) mount the gas-line to be able to ionize toluene directly with the 1030 nm laser in order to tune the TOF signal;
ii) test the new crystal for the high-harmonic generation which will be coupled with the TOF-MS chamber for double ionization experiments. The first sample which will be measured is 1,2,3-triazole (liquid sample).
iii) connect the oven under construction in GANIL to the experimental chamber to perform measurements on the derivatives of 1,2,3-triazole (OGM-1, OGM-2 and OGM-3).

Despite we were not able to investigate the chemical reactivity of 1,2,3-triazole and its derivatives as initially planned, this STSM gave me the opportunity to familiarized with the new experimental set-up which will soon allow to perform interesting experiments. I will be involved in the follow-up activities of this laboratory sharing my expertise and advice and, hopefully, I will be able to join again the group of Dr. Dariusz Piekarski to finalize the establishment of the laboratory and its activity.

As the new apparatus will be soon fully assembled and ready to be tested and it will be used to investigate irradiation-driven processes of isolated molecules and molecular clusters, I am sure this STSM contributed positively to the CA20129 Cost Action opening new interesting perspectives for future experiments.

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