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

Action number: CA20129 Multichem

Grantee name: Jaroslav Kočišek

Details of the STSM

Title: **Fragmentation of iron pentacarbonyl clusters by ions in nuclear-stopping regime**

Start and end date: 11/05/2024 to 18/05/2024

Description of the work carried out during the STSM

Within the STSM we aimed to measure fragmentation patterns for the decomposition of iron pentacarbonyl clusters by heavy ions. Iron pentacarbonyl is a model molecular precursor for the focused ion beam-induced deposition technique (FIBID). We performed pilot experiments in 2021 where we observed interesting behavior pointing to the exclusively high efficiency of Ne^+ projectile in the fragmentation. However, during that experimental campaign, the Ne^+ projectile was also the projectile with highest ratio of nuclear to electronic stopping in iron pentacarbonyl aggregates. Therefore, we were not able to disentangle if the effect is related to stopping power regime or to the projectile. The goal of the present STSM was to answer this question. Particularly, we planned measurements with projectiles having high nuclear-stopping component.

The experiments were performed at the COLIMACON end station at the ARIBE facility of GANIL. The clusters were prepared using the slow aggregation technique in a liquid nitrogen-cooled He flow channel. The temperature of the source was kept at -185C, He flows at 150l/min through a 0.5 mm aperture at the end of the aggregation channel. The iron pentacarbonyl sample was kept in a glass cylinder at 295~K and added into the He flow using a needle valve. The formed beam of $[Fe(CO)_5]_n$ clusters was crossed by the ion beam. The used projectiles were Ne^+ at 6keV, Ar^{8+} at 64keV and Ar^{2+} at 12keV. The measurements this time were influenced by two general electricity shutdowns at the GANIL facility on Monday and Wednesday. Particularly the Wednesday shutdown complicated the measurements a lot as it was during the full load inlet of the iron pentacarbonyl sample that resulted in metal deposits over several components of the system, including the heating elements required for temperature control inside the aggregation source. This required a breakdown of vacuum and cleaning, which significantly shortened our total beamtime and reduced the number of used projectiles with respect to the planned spectrum. Despite these complications, we were able to reproduce the previous data for Ne^+ and Ar^{8+}

[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.

projectiles that are necessary for extrapolation of the previous data of the new projectile as well as measured a new data set for the Ar^{2+} projectile with the nuclear stopping component at the same level as for Ne^{+}. This measurement allows us to make the resolution aimed in the STSM as described in the next part of the report.

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

The ultimate goal of the measurement was to confirm the unique characteristics of neon projectiles in the fragmentation of iron pentacarbonyl clusters. We estimate the effectivity of the ligand removal in the cluster environment as a ratio of the fragment cluster to the non-fragmented parent cluster in the obtained mass spectra. For that, our previously obtained value for Ne^{+} at 6keV is 1.5 while that for He^{2+} at 16keV is only 0.8. For the Ar^{2+} projectile measured during the STSM, having the same nuclear-to-electronic stopping ratio as a previously studied Ne^{+} at 6keV, the ratio is 1.2. This way we are able to confirm that the intense fragmentation by Ne is really an unique characteristics of the projectile.

Several more interesting results were obtained, which are presented graphically in Fig. 1 and 2. Figure 1 shows the comparison of the fragmentation spectra of $[Fe(CO)_5]_n$ clusters in the monomer spectral region for previously measured He^{2+} at 16keV and for the Ar^{2+} projectile measured during the STSM. We can see that the high electronic excitation induced by He results only in very low fragmentation and primarily by losing the CO ligands in the form of CO^{+} molecular cations. In the case of Ar^{2+} the fragmentation is much more intense showing a strong atomic ion signal for oxygen or iron.

Another interesting observation is in Figure 2, where *m/z* 50 to 90 spectral region is shown with ions such as Fe^{+} or $FeCO^{+}$. There, the presently measured Ar^{2+} projectile data are compared to that of highly charged Ar^{8+}. The distorted peak shapes for the multiply charged projectile are due to the high kinetic energy of the fragments caused by the Coulombic explosion of the multiply charged cluster ions. Apparently, the collision with low charge state Ar^{2+} does not lead to this process and rather slow fragment ions are observed.

We can see that iron pentacarbonyl provides an interesting system for benchmarking calculations. Particularly the Coulombic explosion is interesting for dynamical calculations. The STSM therefore primarily contributed to the tasks Task 1.3 and 1.5 of the action. We are now trying to establish contacts with computational chemistry groups within the action to help us to gain better insight into the fundamental physical mechanisms behind the unique characteristics of Ne projectile in the decomposition of iron pentacarbonyl clusters and possibly also FIBID in general. In parallel, we are drafting the publication from the results that will contribute to further dissemination of the results and presentation of the action to a broader scientific community within the Task 4.2

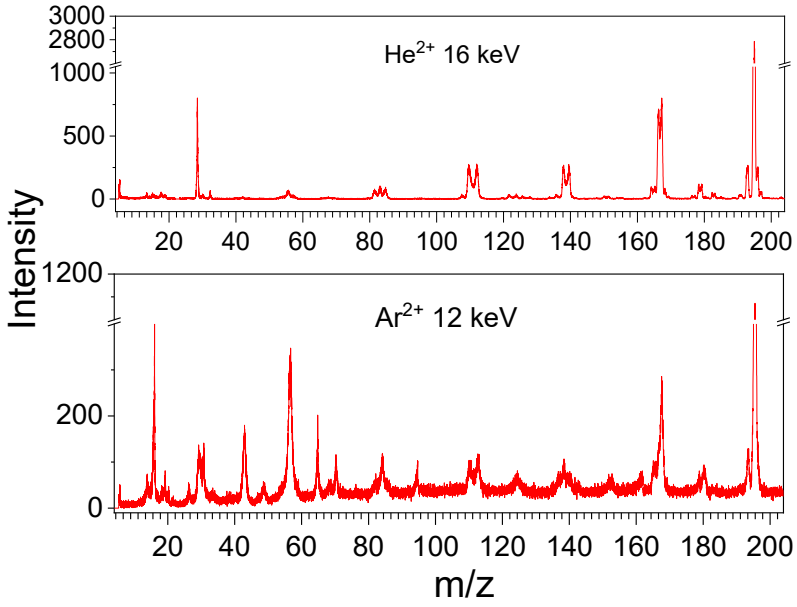

Figure 1 Part of the mass spectra for fragmentation of iron pentacarbonyl clusters in collisions with Ar^{2+} and He^{2+} projectiles, demonstrating stronger fragmentation and a much higher number of single atom fragments for Ar^{2+} interacting in nuclear-stopping regime in comparison to He^{2+} dominated by electronic excitation.

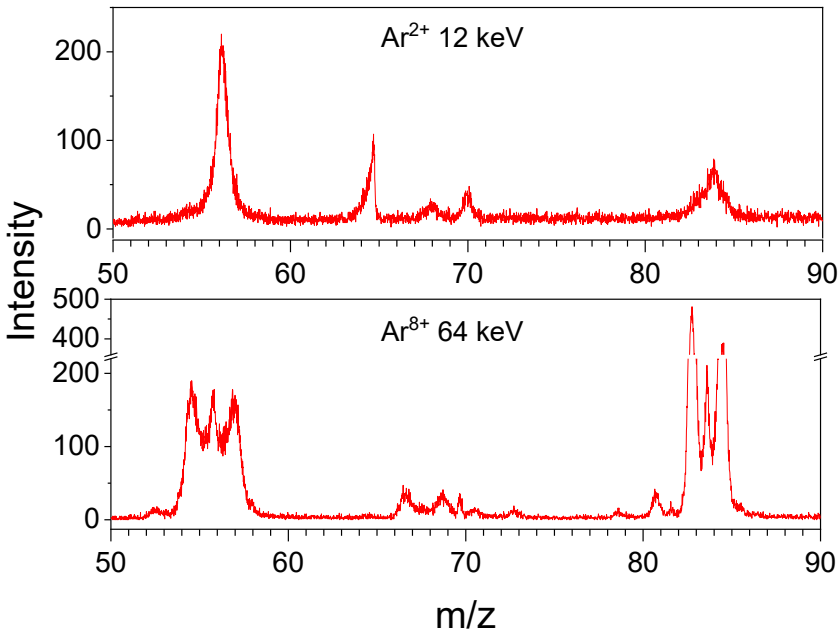

Figure 2 Part of the mass spectra for fragmentation of iron pentacarbonyl clusters in collisions with Ar^{2+} and Ar^{8+} projectiles, demonstrating significant differences in ion kinetic energies. Apparently, the Coulomb explosion process contributes to the Ar^{8+} spectra producing fast ions appearing as side bands of the central peaks of the Fe^{+} or $FeCO^{+}$ fragment ions.