ECCL Short Term Scientific Mission Scientific Report

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Host's Name and Institution: Prof. Dr. Štefan Matejčík, Department of Experimental Physics
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Purpose of the visit

Electron beam induced deposition (EBID) allows fabrication of nanometer sized structures on targets of various geometries. Sub nanometer beam diameters can be achieved, but the resulting deposits considerably exceed this resolution. It is suggested that this broadening is caused by the low energy secondary electrons emitted from the substrate. The exact mechanism, however, is not yet fully understood.
Low energy electrons are known to react and fragment molecules via dissociative electron attachment (DEA). Although DEA has been studied extensively for a variety of molecules, little data is available on metal-organic precursors, as typically used in EBID. In return, detailed knowledge of the dissociation processes will enable the design of improved precursors, allowing more accurate deposits of higher purity. The purpose of this STSM was to investigate the precursor molecule cobalt tricarbonyl nitrosyl. From these experiments, we hope to set the ground for a further understanding of electron beam induced deposition, allowing refinement of the process parameters. Furthermore, the visit granted the beneficiary a hands on experience in the field of slow electron attachment with a standard apparatus. The beneficiary is currently working on setting up a crossed beam apparatus that will allow investigations of involatile molecules, namely through laser induced acoustic desorption.

Description of the work carried out

Both electron attachment as well as electron bombardment experiments were carried out. The experiments were performed in a crossed electron/molecular beam setup. The electron beam of defined energy is generated by a trochoidal electron monochromator. The resolution of about 140 meV was established using the well-known electron attachment process SF_6^-/SF_6. The electron beam then crosses perpendicularly with the molecular beam from an effusive beam source. The generated ions are extracted by a weak electric field and accelerated by a series of parallel electrodes onto the aperture of the quadrupole mass analyzer and detected by a single pulse counting technique as a function of incident electron energy. Calibration of the electron energy scale was either carried out with the zero energy electron attachment resonance in SF_6^-/SF_6 for detection of negative ions or Ar^+/Ar for detection of positive ions. Estimations of absolute cross sections were determined relative to the known cross sections of SF_5^-/SF_6 or Ar^+/Ar.

Description of the main results obtained

Dissociative electron attachment to cobalt tricarbonyl nitrosyl $Co(CO)_3NO$

The process of electron attachment to $Co(CO)_3NO$ is a purely dissociative process. No parent anion could be detected. On the other hand, multiple bond breaks can be observed. The negative fragments formed are summarized in table 1. The fragment detected at lowest energy is also the fragment with the highest cross section (figure 1). The resonance can be assigned to $Co(CO)_2NO^-$, which is formed by loss of one CO group. Although a sharp peak is discernible very close to 0 eV, the peak maximum is reached at 0.5 eV. At 1.9 eV, resonances for both $Co(CO)NO^-$ was well as $Co(CO)_3^-$ appear. The later fragment reaches higher peak intensity and exhibits an additional resonance at 6.9 eV. At 2.9 eV, the resonance attributed to $Co(CO)_2^-$ appears with an intensity comparable to that of $Co(CO)NO^-$. Albeit with much lower cross sections, the resonances of $CoNO^-$ and $CoCO^-$ are discernible at 5 eV and 6.6 eV, respectively. Finally, a weak feature around 7.3 eV indicates successful removal of all four ligands to yield Co^- (figure 2).

Table 1: Observed fragments resulting from electron attachment to $Co(CO)_3NO$

$Co(CO)_3NO + e^-$	$\xrightarrow{\text{-CO}} Co(CO)_2NO^-$	145 amu
	$\xrightarrow{\text{-NO}} Co(CO)_3^-$	143 amu
	$\xrightarrow{\text{-2CO}} Co(CO)NO^-$	117 amu
	$\xrightarrow{\text{-CO/NO}} Co(CO)_2^-$	115 amu
	$\xrightarrow{\text{-3CO}} CoNO^-$	89 amu
	$\xrightarrow{\text{-2CO/NO}} CoCO^-$	87 amu
	$\xrightarrow{\text{-3CO/NO}} Co^-$	59 amu

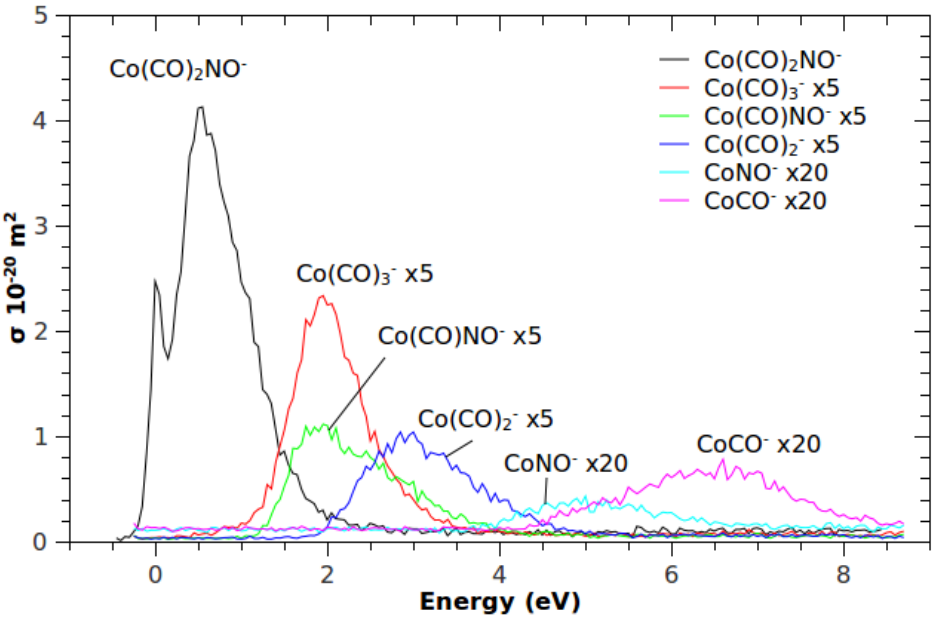

Figure 1: Absolute cross sections for DEA fragments as a function of incident electron energy

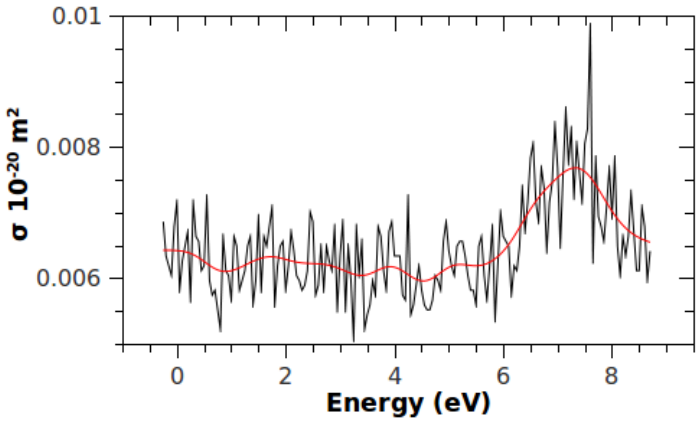

Figure 2: Absolute cross sections for Co^- generation as a function of incident electron energy; raw data is shown in black while Gaussian smoothing (red) distinguishes the resonance feature around 7.3 eV

Positive ion generation through electron bombardment

Figure 3 portrays a positive ion mass spectrum taken at an incident electron energy of 70 eV. The fragments discernible compare quite well to the ones obtained in electron attachment studies. Six additional fragments can be detected, i.e., the parent cation $Co(CO)_3NO^+$ at 173 amu, CoC^+ at 71 amu, CO^+ and NO^+ at 28 and 30 amu, respectively. The doubly charged fragments $Co(CO)^{++}$ and $Co(CO)_2^{++}$ appear at mass-to-charge ratios of 43.5 and 57.5. $Co(CO)_3^+$, on the other hand, could not be detected. Cross sections for singly charged fragments are summarized in figure 4. For comparison, Ar^+/Ar is included in the plot (black).

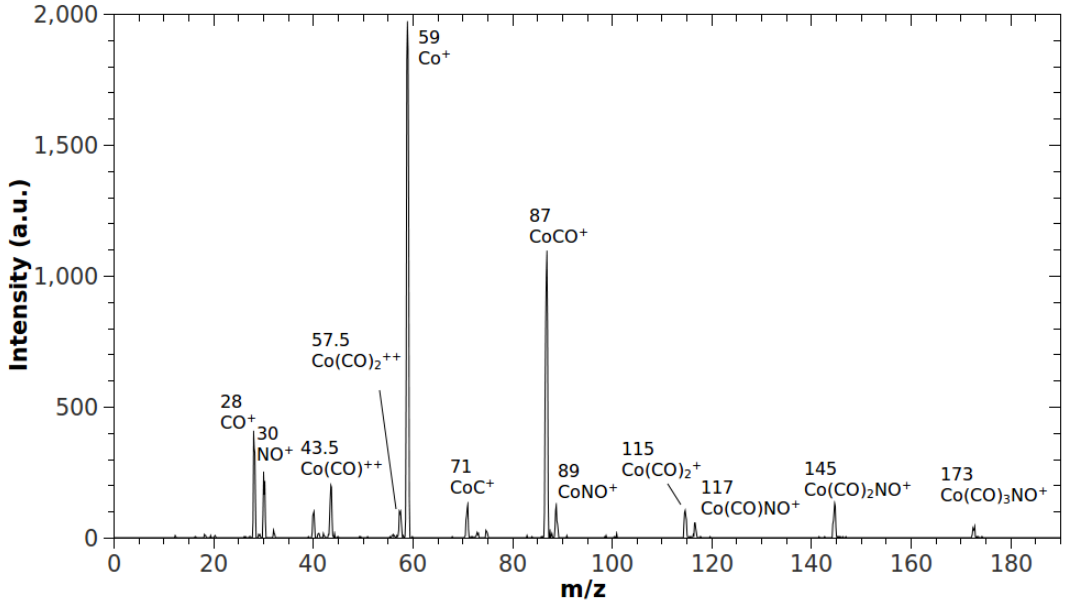

Figure 3: Positive ion mass spectrum of $Co(CO)_3NO$ taken at an incident electron energy of 70 eV

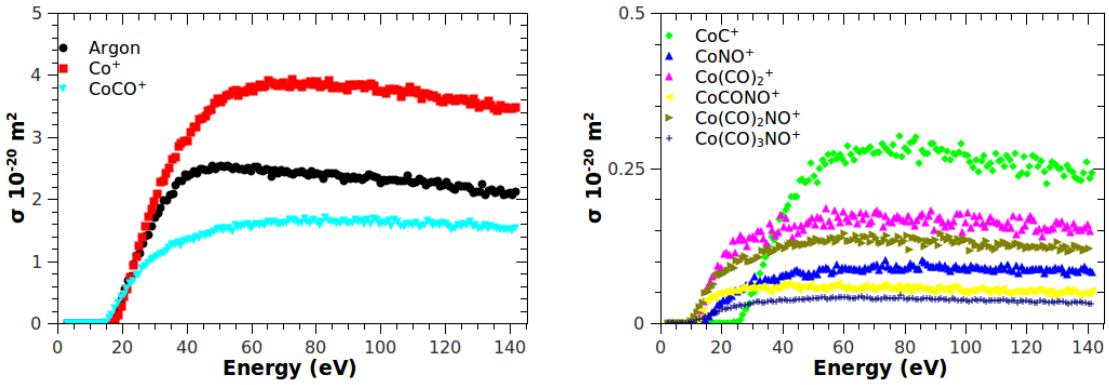

Figure 4: Absolute cross sections for positive fragments of high (left) and low (right) intensity as a function of incident electron energy; Ar^+ (black) is included for comparison

Discussion of the main results

The main objective of this scientific mission was to give some insight into the mechanism of EBI deposition relative to slow (secondary) electrons. A rich fragmentation chemistry is induced by electron attachment, including multiple bond breaks. The cross sections for Co^-, however, are extremely low. On the other hand, the threshold for the abundant Co^+ production lies around 14 eV (detailed data is currently being evaluated) and hence also falls into the low energy regime. It is thus believed, that ionization of the precursor molecule by secondary electrons may also play a major role in the decreasing spatial resolution in EBID deposits.

Future collaboration with host institution

It is expected to continue the collaboration on electron attachment to EBID relevant precursor molecules.

Projected publications resulting from the grant

Work on a joint publication summarizing the results of this STSM is currently in progress.