LOW ENERGY ELECTRON ATTACHMENT TO COBALT TRICARBONYL NITROSYL MOLECULES AND CLUSTERS AND MIXED CLUSTERS WITH ACETIC ACID

Dušan Mészáros, Peter Papp, Štefan Matejčík

Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina, 842 48 Bratislava, Slovakia
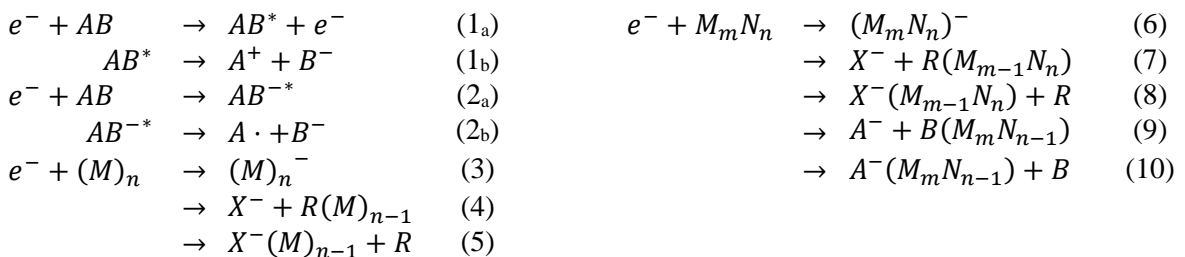E-mail: meszaros44@uniba.sk

We present low energy electron interaction studies of $Co(CO)_3NO$, widely used as a precursor in Focused Electron Beam Induced Deposition (FEBID) and in the alternative Electron Beam Induced Surface Activation (EBISA) technology. The electron attachment (EA) and dissociative electron attachment (DEA) of gas phase $Co(CO)_3NO$ will be compared to the DEA of $Co(CO)_3NO$ clusters and to mixed clusters with acetic acid. New resonances will be revealed in the recent results for pure clusters of $Co(CO)_3NO$, while the mixed clusters with acetic acid has been measured for the first time.

1. Introduction

Interaction of low energy electrons with molecules and molecular clusters is one of the elemental processes in plasma and plasma technologies. In our study we are focusing on electron attachment (EA) and dissociative electron attachment (DEA) on cobalt tricarbonyl nitrosyl ($Co(CO)_3NO$) and mixture of $Co(CO)_3NO$ with acetic acid (CH_3COOH). $Co(CO)_3NO$ is used as precursor gas in Focused Electron Beam Induced Deposition (FEBID) and Electron Beam Induced Surface Activation (EBISA) technology. In previous studies it was shown that deposition of Co layers from $Co(CO)_3NO$ works well with FEBID but not with EBISA [1,2]. The main difference between FEBID and EBISA is the procedure of deposition. FEBID is based on real-time deposition, high energy focused electron beam is used to draw structures on surface via direct interaction with the precursor gas. On the other hand, in EBISA technique the high energy focused electron beam is used to activate the surface and the precursor gas interacts only with the activated surface, not with the electron beam. In EBISA works [1,2] the metal-organic framework (MOF) HKUST-1 was used which consists from metallic atoms (copper) and as linker is used trimesic acid ($C_9H_6O_6$). Therefore in our recent study we focus on interaction of $Co(CO)_3NO$ with the carboxylic group of the MOF, however with acetic acid, considered as a simpler model of trimesic acid.

The CLUSTER-ILN experiment [3] (Fig. 1) was used to measure the electron molecular and cluster interactions, with a trochoidal electron monochromator (~200 meV measured at FWHM of the Cl^- peak from CCl_4 molecule) and quadrupole mass analyser for identifying the charged products of electron impact, both in a perpendicular orientation. We use external bottles to prepare the mixture of $Co(CO)_3NO$ and Ar gas, in this experiment ~33 mbars of $Co(CO)_3NO$ and ~10 bars of Ar was used. This mixture flows above the surface of liquid acetic acid placed in a container (optional), the mixed gasses are then expanding via 80 μm nozzle into the high vacuum (expansion chamber). The cooling of the gas via supersonic expansion produces a beam of molecular clusters which is then separated with the skimmer (0.8 mm) into the reaction chamber. EA and DEA were measured on $(Co(CO)_3NO)_mAr_k$ and $(Co(CO)_3NO)_m(CH_3COOH)_nAr_k$ clusters, electron molecular or cluster reactions relevant to our experiment are summarized below. With CLUSTER-ILN we can study the electron attachment to molecules (2_a), clusters (3) and (6) and corresponding dissociative electron attachment (reactions (2_b), (4), (5) and (7)-(10)).

$$e^- + AB \quad \rightarrow \quad AB^* + e^- \qquad (1_a)$$
$$AB^* \quad \rightarrow \quad A^+ + B^- \qquad (1_b)$$
$$e^- + AB \quad \rightarrow \quad AB^{-*} \qquad (2_a)$$
$$AB^{-*} \quad \rightarrow \quad A \cdot + B^- \qquad (2_b)$$
$$e^- + (M)_n \quad \rightarrow \quad (M)_n^- \qquad (3)$$
$$\rightarrow \quad X^- + R(M)_{n-1} \qquad (4)$$
$$\rightarrow \quad X^-(M)_{n-1} + R \qquad (5)$$

$$e^- + M_mN_n \quad \rightarrow \quad (M_mN_n)^- \qquad (6)$$
$$\rightarrow \quad X^- + R(M_{m-1}N_n) \qquad (7)$$
$$\rightarrow \quad X^-(M_{m-1}N_n) + R \qquad (8)$$
$$\rightarrow \quad A^- + B(M_mN_{n-1}) \qquad (9)$$
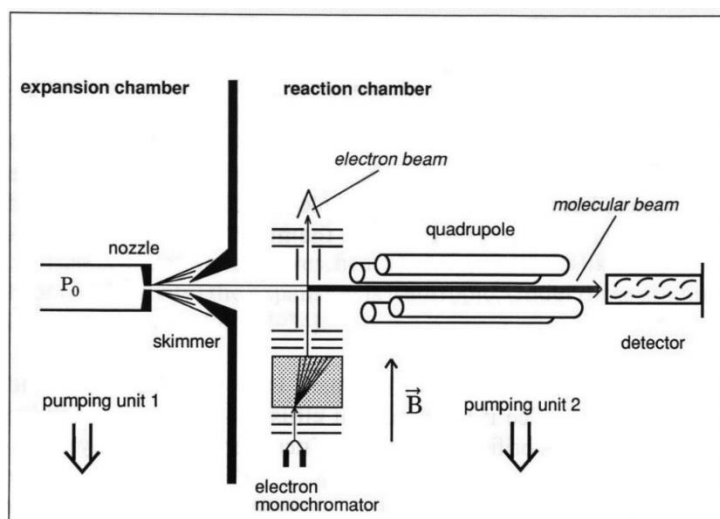$$\rightarrow \quad A^-(M_mN_{n-1}) + B \qquad (10)$$

Fig. 1. The schema of CLUSTER-ILN experiment at the Comenius University in Bratislava (built at the Freie Universität Berlin [3]).

2. Dissociative electron attachment to Co(CO)$_3$NO clusters

At the beginning of the presented studies we have performed the measurements of electron attachment to Co(CO)$_3$NO clusters and compared these results with the previously published gas phase studies [4] and He droplet cluster studies [5], both are summarized in Table 1. All reported molecular fragments are in good agreement with gas phase works of Engmann [4] with few exceptions coming from cluster reactions and few differences with Postler [5]. The recent DEA studies to clusters vs gas phase revealed additional higher energy resonances for fragments [Co(CO)$_2$]$^-$, [CoCONO]$^-$, [Co(CO)$_2$NO]$^-$, and two higher energy resonances for fragment [Co(CO)$_3$]$^-$ (at 9.88 eV has similar shape to the resonance of the [CoCONO]$^-$ fragment at 9.94 eV). However, cluster fragments (>173 amu) reveal some differences from Postler's work [5], we assume it is due to different method of producing the clusters (co-expansion with Ar vs pick up to He droplet). The sensitivity to ionic products is higher in our work, we have nicely resolved the resonances of cluster fragments published previously in Postler's work [5], additionally with electron energies from 0 eV contrary to 2 eV in their work [5]. Common feature of cluster fragments is that multiple processes result in the same fragment. Cluster fragment can be created by several consecutive reactions because of a possibility of interaction between molecules in cluster. This is possible due to self-scavenging electrons. That means electron can scatter on first molecule in cluster, lose some energy and then interact with another molecule. That may result in higher number of resonances, some may be detected at higher energies as the kinetic energy of interacting electron is the sum of the attachment energy and the energy lost in scattering interaction.

We were able to detect cluster fragments up to 3 molecules of Co(CO)$_3$NO in cluster. It is important to note that parent ion does not exist in gas phase and is only visible in cluster measurements. As a consequence of short molecular distances in cluster, energy released at formation of the molecular negative ion, can be distributed more efficiently within a cluster which results in stabilisation of parent ion contrary to the gas phase. Similarities and differences were observed in the energy spectra of cluster fragments in Fig. 2. M$^-$, M$_2^-$, [Co$_2$(CO)$_5$(NO)$_2$]$^-$, [Co$_2$(CO)$_4$(NO)$_2$]$^-$ have similar shapes of the ion yields but also some significant differences. First difference is the slight shift of the low energy resonance position, M$_2^-$ has the maximum at 0.03 eV, [Co$_2$(CO)$_5$(NO)$_2$]$^-$ at 0.15 eV, M$^-$ at 0.32 eV and [Co$_2$(CO)$_4$(NO)$_2$]$^-$ at 0.49 eV. Also the relative intensity of first and second resonance (~4.5 eV) differs for these fragments. While for M$^-$ and M$_2^-$ the first resonance is much more dominant, the second resonance becomes more significant for [Co$_2$(CO)$_5$(NO)$_2$]$^-$ and [Co$_2$(CO)$_4$(NO)$_2$]$^-$. In addition, M$^-$ and M$_2^-$ have one more resonance at higher energy at 10.3 eV and 11.9 eV respectively. [Co(CO)$_2$NO]$^-$ has resonances with similar shape to those of M$^-$, first resonance is split to two at 0.05 eV and 0.52 eV. For fragments with below m/z 145 (smaller than [Co(CO)$_2$NO]$^-$) the main resonance is shifting to higher energies with the increasing number of dissociated ligands. [CoCONO]$^-$ has its main resonance split to two at 2 eV, 2.8 eV and one more at 9.94 eV. [Co(CO)$_2$]$^-$ and [Co(CO)$_3$]$^-$ share second resonance at ~7 eV and [Co(CO)$_3$]$^-$ has one more at 9.88 eV similar to [CoCONO]$^-$. Next similarity is between [Co$_2$(CO)$_5$NO]$^-$ and [Co$_2$(CO)$_6$NO]$^-$. Shape of their resonances is almost identical with two exceptions,

relative intensity of resonances ~4.5 eV and ~7 eV is different and $[Co_2(CO)_5NO]^-$ have one additional weak resonance at 0.62 eV. $[Co_2(CO)_3NO]^-$ and $[Co_2(CO)_4NO]^-$ like previous pair has similar shape of resonances and $[Co_2(CO)_4NO]^-$ have two more weak resonances close to each other at 2.05 eV and 2.9 eV.
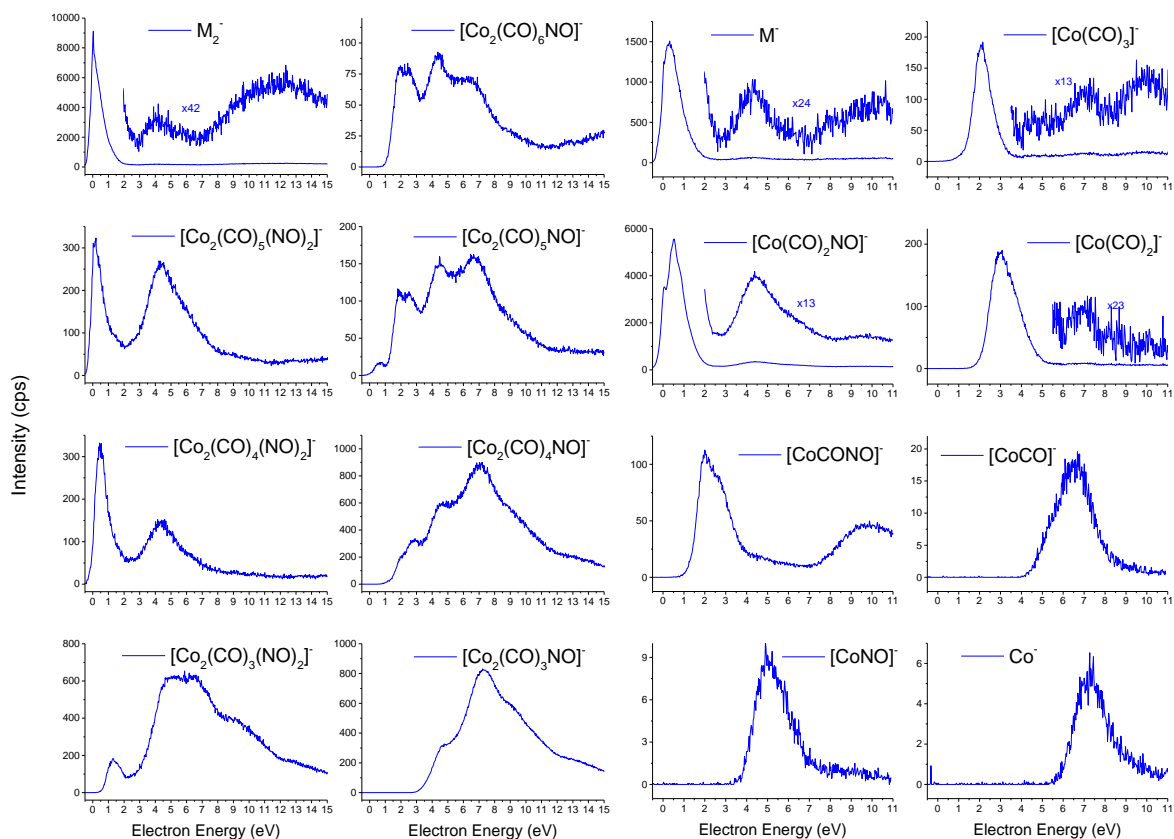
Fig. 2. Ion yield curves of $Co(CO)_3NO$ clusters and its DEA fragments.

Tab 1. Cluster DEA products of $Co(CO)_3NO$, peak positions of the resonances.

Ion	m/z	Peak Position [eV]		
		Gas ph. [4]	Clusters [5]	**CLUSTER-ILN**
Co^-	59	7.30	7.3	**7.30**
$[CoCO]^-$	87	6.50	6.5	**6.55**
$[CoNO]^-$	89	5.11	5.1	**5.07**
$[Co(CO)_2]^-$	115	2.99	2.9	**3.02, 6.96**
$[CoCONO]^-$	117	1.96, 2.55	2.3	**2.00, 2.80, 9.94**
$[Co(CO)_3]^-$	143	1.96	1.7, 2.3, 17.5	**2.05, 7.08, 9.88**
$[Co(CO)_2NO]^-$	145	0.02, 0.53	1.6, 4.1	**0.05, 0.52, 4.44, 9.8**
$[Co(CO)_3NO]^-$	173		5.8, 10.4, 14.9	**0.32, 4.30, 10.3**
$[Co_2(CO)_3NO]^-$	232		~10	**4.72, 7.22, 9.2, 13.1**
$[Co_2(CO)_4NO]^-$	260		~11	**2.05, 2.90, 4.63, 7.06, 9.2, 13.1**
$[Co_2(CO)_3(NO)_2]^-$	262		~11	**1.30, 5.10, 6.41, 9.2, 13.1**
$[Co_2(CO)_5NO]^-$	288		~9	**0.62, 1.94, 2.57, 4.47, 6.68, 8.8**

$[Co_2(CO)_4(NO)_2]^-$	290	~10	**0.49, 4.35**
$[Co_2(CO)_6NO]^-$	316	~12	**1.94, 2.56, 4.37, 6.22, 9.1**
$[Co_2(CO)_5(NO)_2]^-$	318	~13	**0.15, 4.37**
$[(Co(CO)_3NO)_2]^-$	346	~4, ~8, ~14	**0.03, 4.05, 11.9**

3. Dissociative electron attachment to mixed clusters of Co(CO)₃NO and CH₃COOH

In this chapter we will discuss the effects of mixed clusters, acetic acid with $Co(CO)_3NO$. Most of the products of interaction between electron and mixed cluster are shown in Fig. 3, in the mass spectrum of this interaction at electron energy 3.9 eV. In the spectrum the same cluster fragments of $Co(CO)_3NO$ as in pure measurements are marked with brown, pure acetic acid clusters (pink) with the maximum 7 acid molecules in cluster are visible. In addition there are cluster fragments of $Co(CO)_3NO$ with number of acetic acid molecules attached (red). Introduction of acid into the mix caused creation of products which contained water (blue). This water originated from water contamination of acid and as by-product of creation of acetic acid clusters as was shown in Ferreira Da Silva's work [6]. Interesting pattern has been detected for the parent ion $(Co(CO)_3NO)^-$ with number of acid molecules attached, from one molecule all the way up to five (green).

Fig. 3. Mass spectrum of mixed clusters of Co(CO)₃NO and acetic acid at electron energy 3.9 eV.

Further investigation result on left side of Fig. 4. On these energy dependence spectra, the effect of increasing number of acid molecules in cluster with the parent ion is visible. Spectra look almost identical with few exceptions, one of which is slight shift of main resonance from 0.46 eV at zero acid molecules to 0.86 eV at one and more. The ~0 eV resonance becomes more significant as the intensity of the main resonance decreases with the number of acids. Second difference is decreasing intensity of resonance at ~4 eV with increasing number of acid molecules in cluster. It seems that the presence of acid in cluster closes that channel of the parent ion. This is evident in the spectrum of fragment $Co(CO)_2NO^-$, we can compare its spectrum of pure Co(CO)₃NO clusters, of mixed clusters and even

more with one molecule of acetic acid attached. Result of this comparison is on the right side of Fig. 4. When acetic acid was present in the chamber but not in the product itself it slightly amplified the resonance at ~0 eV and opened an additional resonance channel at ~8 eV (blue vs red on Fig. 4 right). On the other hand, when acid molecule was part of the product, resonance at ~0 eV was totally suppressed and the main dominant resonance at 0.49 eV was suppressed to level of 4.5 eV resonance and shifted to 0.72 eV.
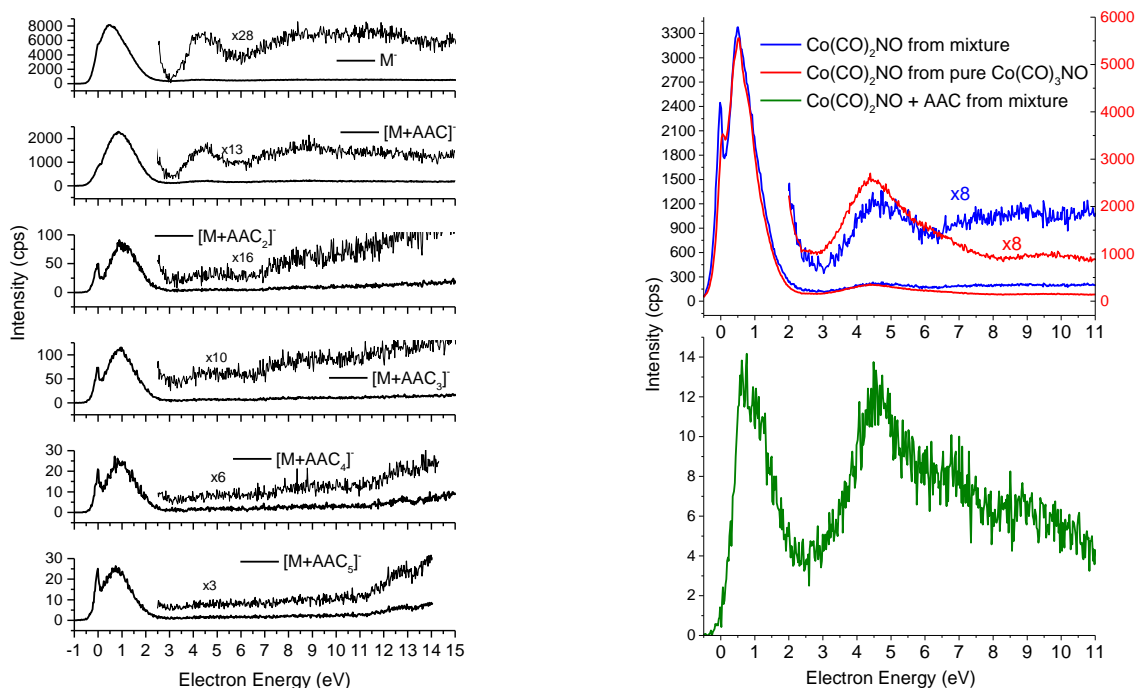
Fig. 4. Evolution of energy dependence of parent ion $(Co(CO)_3NO)^-$ (M) creation with increasing number of acetic acid (AAC) molecules in cluster (left). Difference between energy dependence of $Co(CO)_2NO^-$ fragment creation with (right, blue line) and without (right, red line) presence of acetic acid in chamber and with acetic acid in cluster (right, green line).

4. Conclusion

The electron attachment and dissociative electron attachment to pure $Co(CO)_3NO$ clusters and mixed with acetic acid were performed. We have found a good agreement of the pure $Co(CO)_3NO$ cluster results with previously published gas phase data with few exceptions. Many differences were found in comparison of cluster data with previously published due to different method of cluster creation. Parent ion was seen in cluster measurements which does not exist in gas phase because of excess energy released by negative ion creation. Many resonances were spotted in energy dependence spectra of cluster fragments. This was caused by self-scavenging electrons which one electron will interact with first molecule in cluster, lose some energy and then attach to second molecule in cluster.

The electron attachment and dissociative electron attachment to mixed clusters of $Co(CO)_3NO$ and acetic acid were performed for the first time. Except expecting fragments from both molecules, mixed cluster fragments were detected containing fragments of $Co(CO)_3NO$ with one or more acetic acid molecules or with water molecules. Slight shift of main resonance and decreasing intensity of resonance at ~4 eV of parent ion with increasing number of acid molecules was observed. Similar effect was observed on $Co(CO)_2NO^-$ fragment.

5. Acknowledgments

6. References

[1] Ahlenhoff, K., et al., *J. Phys. Chem. C*, **122**, (2018), Pages 26658-26670

[2] Drost, M., at al., *ACS NANO*, **12**, (2018), Pages 3825-3835

[3] Ingolfsson, O., Weik, F., Illenberger, E., *Int. J. Mass. Spec.*, **155**, (1996), 1.

[4] Engmann, S., et al., *J. Phys. Chem.*, **138**, (2013), 044305.

[5] Postler, J., et al., *J. Phys. Chem. C*, **119**, (2015), Pages 20917-20922

[6] Ferreira Da Silva, F., et al., *Phys. Chem. Chem. Phys.*, **11**, (2009), Pages 11631-11637