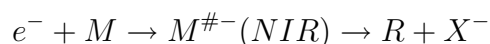


Chapter 7

Summary

We have investigated the behaviour of formation and evolution of the intermediate ion when coupled to an environment by means of monitoring of the anionic fragments ejected from the surface. In the low energy region, the negative fragments are generated via dissociative electron attachment (DEA), which proceeds through the formation of the *negative ion resonance* (NIR). In the gas phase the reaction is expressed as



Concerning the influence of the environment on DEA processes, the desorption resonances observed from condensed $\text{C}_2\text{F}_4\text{Cl}_2$ and SF_5CF_3 nanofilms are directly compared with DEA resonances obtained in the gas phase. In general the observations may be summarized as follows:

1. Both compounds, $\text{C}_2\text{F}_4\text{Cl}_2$ and SF_5CF_3 show intense dissociative channel near 0 eV in the gas phase yielding Cl^{-} and SF_5^{-} , respectively. In condensed phase these resonances are totally suppressed toward the desorption channel as expected from the energy balance of the reaction. On the same basis, the desorption of heavy and polyatomic species is usually suppressed. Ion fragments $\text{CClF}_2^{-}/\text{C}_2\text{F}_4\text{Cl}_2$, $\text{C}_2\text{ClF}_4^{-}/\text{C}_2\text{F}_4\text{Cl}_2$, $\text{SF}_5^{-}/\text{SF}_5\text{CF}_3$ and $\text{CF}_3^{-}/\text{SF}_5\text{CF}_3$ detected in the gas phase were not observed from the condensed phase.
2. Ion desorption in condensed phase basically occurs at higher energies.

At these energies, the particular dissociation channel may even be enhanced with respect to its equivalent in the gas phase. The same tendency is expected from the estimated desorption cross-sections in the case of $\text{Cl}^-/\text{C}_2\text{F}_4\text{Cl}_2$ at 8.3 eV, $\text{F}^-/\text{C}_2\text{F}_4\text{Cl}_2$ at 12.5 eV and $\text{F}^-/\text{SF}_5\text{CF}_3$ at 11 eV. These enhancements are suggested to be activated by polarization effect of the environment on the intermediate ion formation, see section 2.7.

3. The polarization influence on ion desorption (induced polarization of the environment plus image charge in the metal substrate) may be lowered by coadsorbing the compound in submonolayer amounts on top of the rare gas solid as a spacer. Desorption enhancements have been seen for $\text{Cl}^-/\text{C}_2\text{F}_4\text{Cl}_2/\text{Xe}$ near 1.2 eV and $\text{F}^-/\text{SF}_5\text{CF}_3/\text{Xe}$ at 4 eV.
4. When condensed in multilayer amounts both compounds show considerable film charging at very low energies, indicating that the electron attachment processes take place at these energies. From observed film charging, however, it is not possible to identify the negative species solvated at the surface. To the charge accumulated at the surface may contribute fragment ions, parent ions ($\text{C}_2\text{F}_4\text{Cl}_2^-$ and SF_5CF_3^- does exist as was shown by cluster measurements) and possibly trapped electrons.
5. Desorption of the fragments is strongly affected by the orientation of the precursor ion at the surface. The preferable orientation is when the fragment ion is directly ejected into vacuum. Other orientations would lead to the suppression of the desorption. The $\text{C}_2\text{F}_4\text{Cl}_2$ and SF_5CF_3 show very weak intensities of Cl_2^- and F_2^- , respectively, which are suggested to be formed by *post dissociation interactions* PDIs, *i.e.* scattering of the generated anionic fragments on the molecules in the vicinity *prior* to desorption. In the case of $\text{F}_2^-/\text{SF}_5\text{CF}_3$ the fragment was not observed to be formed neither via DEA to gas phase SF_5CF_3 nor to clusters of SF_5CF_3 .
6. The generated fragments which remain at the surface may further initiate the reaction at the surface. In the case of condensed $\text{C}_2\text{F}_4\text{Cl}_2$,

secondary reactions lead to synthesis of the molecular chlorine.

The main part of this work is dedicated to the investigations of secondary reactions at the surface, initiated by the DEA to condensed molecules. Concerning the Cl_2 formation from $\text{C}_2\text{F}_4\text{Cl}_2$, the reaction was possible to study using ESD technique, since both Cl_2 and $\text{C}_2\text{F}_4\text{Cl}_2$ show intense Cl^- desorption. Moreover, the Cl^- yield from Cl_2 as a function of energy does only slightly overlap with that originating from $\text{C}_2\text{F}_4\text{Cl}_2$, which essentially improved the analysis of the reaction behaviour.

Further advantage of using the ESD technique specially in this particular investigations concerns the efficiency of monitoring the modified area, *i.e.* probing desorption scans used for analysis reflect the molecular composition exactly from the irradiated area, since the electron source used for irradiation and energy scans coincide.

We have studied the formation of molecular chlorine at the surface by means of irradiation of condensed $\text{C}_2\text{F}_4\text{Cl}_2$ films with electrons at different energies in the range from 0 to 20 eV. In this energy region Cl_2 synthesis is more pronounced near 10 eV and below 3 eV, as was shown by short time irradiation (120 s, 100 nA). However, extended irradiation near 10 eV leads to an overall degradation of the molecular film, seen by a decrease of the overall Cl^- yield intensity with increasing the electron dosage. On the other hand, irradiation at subexcitation energies (≈ 1 eV) results in complete transformation of $\text{C}_2\text{F}_4\text{Cl}_2$ into Cl_2 (plus byproducts) as was demonstrated by means of Cl^- desorption yield, which changes from that from $\text{C}_2\text{F}_4\text{Cl}_2$ before irradiation to that from Cl_2 after the irradiation.

To identify the perfluorocompounds remaining on the surface, one can compare the F^- yield after the irradiation with that from pure *c*- C_4F_8 (as one of the expected product of the reaction). Since there are no ESD data for *c*- C_4F_8 to date, further investigations would cover the ion desorption from *c*- C_4F_8 nanofilms. However, it is expected that the selection between the different perfluorocompounds using the ESD spectra would not be straightforward and other techniques must be used.

To obtain more information on the composition of the film after the irradiation, we have performed preliminary infrared reflexion-absorption spec-

trospectroscopy IRAS experiments and electron energy loss spectroscopy EELS experiments. The experiments so far did not lead to final conclusions. From EELS experiments the appearance of a C = C double bond was obvious, which may indicate that the perfluoroethen (or polymers) are formed at the surface (see Appendix).