

# Chapter 2

## Abstract

The interaction of low energy electrons with condensed molecules is studied by means of electron stimulated desorption (ESD). The molecules are deposited in the ultrahigh vacuum (UHV) on a cryogenically cooled ( $\approx 30\text{K}$ ) metallic substrate in either multilayer amounts (nanofilms) or as submonolayers on a noble gas film acting as a spacer to the metal. The measured quantity is the yield of negatively charged fragment ions desorbing from the adsorbed or condensed molecules as a function of the incident electron energy.

Irradiation of a multilayer film of 1,2- $\text{C}_2\text{F}_4\text{Cl}_2$  generates molecular chlorine and byproducts not yet definitely identified (possibly perfluorinated polymers). However, the presence of  $\text{Cl}_2$  is unambiguously identified from the energy and temperature dependence of the  $\text{Cl}^-$  desorption signal. The cross section for  $\text{Cl}_2$  formation as a function of the electron energy exhibits two pronounced resonant features with maxima near 0 eV and 10 eV, dropping to essentially zero in the energy range between the resonances (near 3 eV). The energy dependence of the reaction cross section qualitatively follows that of  $\text{Cl}^-/\text{C}_2\text{F}_4\text{Cl}_2$  desorption which itself can be correlated to dissociative electron attachment (DEA) from gas phase  $\text{C}_2\text{F}_4\text{Cl}_2$ .

Electron irradiation at elevated dosages demonstrates the potential of slow electrons to act as a soft tool for the control a chemical reaction in the condensed phase. At energies around 1 eV, a complete transformation can be achieved at a sufficiently high dosage while at higher energies (above the threshold for electronic excitation,  $> 5$  eV) some equilibrium composition

between  $\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4\text{F}_2$  can be achieved, however, accompanied by a gradual overall degradation of the film. The effect of complete transformation is based on both the selectivity and particular energy dependence of the initial step of the reaction which is dissociative electron attachment (DEA) to  $\text{C}_2\text{F}_4\text{Cl}_2$  but also the fact that the initial molecule is efficiently decomposed by slow electrons while the products are virtually unaffected.

Strong medium effects in DEA can be demonstrated by the interaction of free electrons with the potent greenhouse molecule  $\text{SF}_5\text{CF}_3$  which was recently discovered in the atmosphere. In the energy range below 2 eV the gas phase molecule decomposes exclusively into  $\text{SF}_5^-$  and the complementary neutral radical  $\text{CF}_3$ . In contrast, electron impact to condensed phase  $\text{SF}_5\text{CF}_3$  exhibits a remarkably strong  $\text{F}^-$  desorption signal appearing from a pronounced resonance located at 11 eV (which in the gas phase is barely visible). Electron induced desorption from sub-monolayers of  $\text{SF}_5\text{CF}_3$  on an amorphous  $\text{H}_2\text{O}$  ice surface is found to be more efficient compared to desorption of  $\text{SF}_5\text{CF}_3$  from a Xe surface. These observations are directly relevant for the judgment of the proposed tropospheric lifetime of the molecule.