

Chapter 3

Introduction

The present thesis deals with reactions initiated in adsorbed and condensed molecules by the interaction of low energy electrons. By low energy we mean in this context the range below the ionization threshold and in particular cases the range below the level for electronic excitation of the respective molecule. It will be demonstrated that electrons below 3 eV may induce a selective bond cleavage in a polyatomic molecule, which in turn can be used to drive a particular reaction in a condensed phase environment.

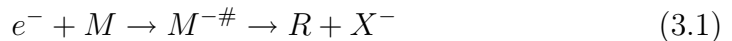
Among the various processes which can be initiated in molecules by the impact of free electrons, the formation and decomposition of negatively charged ions by resonant electron capture is a dominating feature at low energies [1,2]. The cross section for electron capture increases with decreasing electron energy and thus electron capture reactions play a particular role at energies below the level of electronic excitation. At higher energies electron impact can lead to both electronic excitation or ionization. The total cross section for electron impact excitation or ionization varies smoothly with the electron energy reaching a maximum in the energy range between 70 and 100 eV for most molecules [3,4] The absolute value at maximum can come up to the geometrical cross section of the respective molecule. In contrast to that, the cross section for electron attachment behaves reciprocal with energy [5] and it can hence exceed the geometrical cross section by several orders of magnitude at sufficiently low energies.

Capture of low energy electrons by molecules is an important phenomenon

in many fields of pure and applied sciences, in the gas phase as well as in the condensed phase or at interfaces. In the gas phase one can refer to any kind of plasma (used for industrial plasma processing, etc.) where low energy electrons in exceeding numbers are present which can drive ionization, excitation and in particular electron attachment processes [6, 7]. In the condensed phase, energy deposition by high-energy radiation produces electrons as the most abundant secondary species [8]. The interactions of these ballistic secondary electrons within living cells are considered to play a crucial role in the complex reaction sequence leading to genotoxic effects like strand breaks in DNA [9, 10]. At the interface solid/vacuum or solid/gas electron initiated processes play a particular role: (i) the photochemistry of adsorbed molecules can strongly be mediated by the transfer of hot electrons from the surface thereby generating a transient negative ion. Adsorbed molecules can hence be photochemically active already at wavelengths below the threshold for gas phase photoabsorption [11], (ii) tunneling electrons in STM (surface tunneling microscopy) can induce site selective dissociations, or excite selective vibrational modes coupled with surface hopping or desorption [12]. This field, sometimes assigned as single molecule engineering, opens many new and interesting perspectives with respect to both fundamental science and application [13].

Capture of a free electron by a molecule generates a so called transient negative ion (TNI) which can be viewed as a molecular quantum state embedded in the electron - molecule continuum. Such compounds are formed when free electrons of particular energy interact with neutral molecules [1, 2] they are hence also called resonances. In the picture of electron scattering theory a resonance is characterized by constructive interferences of the electron wave in the area of the target. In the time dependent description the electron (characterized by a wave packet) resides in the vicinity of the target for times longer compared to direct (unhindered) propagation across the area of the target. We can thus regard this scattering phenomenon as the formation of a short lived negative ion, also assigned as a negative ion resonance (NIR). Synonymously the term transient negative ion (TNI) is used since such a quantum state is principally unstable towards loss of the extra

electron (autodetachment). In the approach of molecular orbitals (MOs), the extra electron resides temporarily in one of the normally unoccupied MOs. In competition to loss of the extra electron (autodetachment), a NIR can consequently also dissociate into fragments consisting of one ion and one or more neutrals. The overall process is called dissociative electron attachment (DEA), viz.,



where $M^{-\#}$ assigns the TNI formed via a Franck-Condon transition. If DEA channels are energetically accessible at low energies, the cross section for DEA in the gas phase can reach values exceeding 100 \AA^2 (10^{-18} m^2) [5].

The present thesis aims to study the effect of low energy electron interaction with thin molecular films (nanofilms) and molecules adsorbed in submonolayer amounts on a noble gas crystal. The first dissociative electron attachment study to condensed molecules has been performed on an O_2 film two decades ago by Sanche [14]. In the meantime different groups are involved in the field of electron interaction with condensed molecules from both experiment and theory. Such investigations are interesting from the technological point (selective surface modification) but also from a more fundamental view, e. g. the evolution a TNI at a surface as compared to the gas phase or within a gas phase cluster. This concerns solvation shifts of charged compounds and the question of charge and energy distribution on going from single molecules into the condensed phase.

In the gas phase the large cross section for DEA towards low electron energies results from the general energy dependence of the attachment cross section. From very basic principles (Wigner threshold laws [15], scattering of a charged particle from a polarizable target [16]) one expects the capture cross section near threshold to increase with decreasing electron energy ($\sigma \propto \epsilon^{-1/2}$). These threshold laws, on the other hand, are controlled by the dominant electron - target interaction at larger distances. For neutral gas phase molecules this interaction can be approximated by the charge induced dipole potential

$$V(r) = -\frac{\alpha e^2}{2r^4} \quad (3.2)$$

with α the polarizability of the target molecule and r the electron-molecule distance.

For a molecule on a metallic surface the situation changes considerably: The metal electrons are redistributed at the surface to screen the field of the external charge due to the approaching electron. The field created by this charge distribution outside the metal can be represented by the field of a fictitious charge located inside the metal, and having the sign opposite to that of the charge outside the surface (image charge). The associated long-range dipole field is directed perpendicular to the surface and can be expressed as

$$V(d) = -\frac{e^2}{4d} \quad (3.3)$$

with d the distance of the electron from the metallic surface.

In a molecular film the extra electron will generally become localized on an individual molecule, the interaction can therefore (as in a finite cluster system) be viewed on a molecular site. We have then a negative ion coupled to an environment and the initial resonant state (TNI) can decompose or relax into its ground state.

The central part of the present thesis is the electron induced transformation of a 1,2-C₂F₄Cl₂ nanofilm into molecular chlorine and byproducts, possibly perfluorinated compounds which are not yet unambiguously identified. It will be shown that subexcitation electrons (≈ 1 eV) enable a complete transformation while electrons at higher energies can only produce some equilibrium between the initial molecule and the products with a gradual overall degradation of the film. To access possible molecular routes of the underlying reactions, reference is made to electron induced reactions in gas phase 1,2-C₂F₄Cl₂ molecules and clusters of 1,2-C₂F₄Cl₂.

The second part describes DEA to SF₅CF₃, which has recently been identified in the atmosphere [17] and is considered as a very potent greenhouse gas. We have investigated the decomposition of SF₅CF₃ in the gas phase, in clusters and in the condensed phase. These results clearly show the effect of the environment on DEA. Electron induced reactions are directly relevant for the judgment of the tropospheric lifetime of the molecule.

In the appendix some preliminary results are documented without ex-

tended discussion concerning the previously reported giant enhancements of Cl^- and F^- desorption from CF_2Cl_2 on a Ru substrate at coadsorption of ammonia or water following 250 eV impact [18]. The enhancements were interpreted as transfer of secondary electrons from the Ru substrate to traps supported by the polar medium and then tunneling to the CF_2Cl_2 molecules which then decompose leading to desorption of fragment ions. This interpretation caused some controversial discussion. Preliminary experiments on 1,2- $\text{C}_2\text{F}_4\text{Cl}_2$ at coadsorption of NH_3 in fact showed some enhancement in the electron stimulated desorption (ESD) at very low energy.

