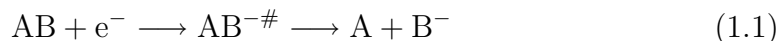


Chapter 1

Introduction

In this work the study of low energy electron induced processes in organic molecules in different states of aggregation is presented. The central step in these processes is the resonant attachment of the electron to the molecule AB that leads to the formation of a temporary negative ion (TNI) $AB^{-\#}$. This TNI can fragment and negative ions are formed by dissociation of the initial target molecule into an anion B^{-} and a radical A. The overall process is called dissociative electron attachment (DEA) and is given by the following reaction mechanism.



The formed anions are detected by means of negative ion mass spectrometry as a function of the electron energy. Thus the obtained spectra provide information on the initial resonant step that leads to the formation of a TNI. Generally, electron-molecule interaction can result in various processes like electronic excitation or ionization, which is for example used in positive ion mass spectrometry for the production of fragment cations. These processes are exclusively operative at higher energy while in many molecules electron attachment is the dominant process below the threshold for electronic excitation of the molecule [17, 41]. In this work the experiments were performed at electron energies below 20 eV with a focus on the resonant processes below the energy of electronic excitation.

To demonstrate the relevance of such low energy electron attachment processes in different states of aggregation some examples for various fields are given in the following. For the gas phase one can refer to any kind of plasma because low

energy electrons are in this case present in high quantity. Thus they can drive excitation, ionization and also electron attachment processes [99, 98]. Especially fluorocarbon molecules are frequently used species in plasma etching, e.g. for the processing of materials in microelectronics [89].

One prominent example for the condensed phase is the role of low energy electrons in radiation damage of living tissue where the interaction can lead to genotoxic effects like single and double strand breaks in DNA [12]. The low energy electrons are produced as secondary species in large quantity ($\approx 4 \cdot 10^4/\text{MeV}$) following high energy irradiation of solids and liquids. Most of the secondary electrons possess an energy below 70 eV, with the most probable energy below 10 eV [91].

At the interface solid/vacuum the interaction with tunneling electrons in STM (scanning tunneling microscopy) can induce site selective dissociation or they can selectively excite particular vibrational modes that are coupled with surface hopping or desorption of the molecule [37, 72, 73, 87].

Low energy electron induced processes can also play an important role in atmospheric chemistry although there are generally no free electrons present in the troposphere. However, after photoexcitation bound electrons of surfaces and particles can be transferred to adsorbed molecules like fluorochlorocarbons [52].

Recent experiments on electron initiated chemical reactions in binary molecular films of CH_3COOD and NH_3 showed the formation of the simplest amino acid glycine following electron irradiation without any need of thermal activation [49]. These results are particularly interesting with respect to extraterrestrial formation of biological matter because low energy electrons are present in the interstellar medium as secondary species [25].

The mentioned examples of electron induced processes describe the subject on isolated molecules in the gas phase or on molecular films. To bridge the gap between these two states of aggregation the study of clusters in the gas phase is of high interest. In this case intermolecular interactions play a particular role and influence the electron attachment process to a considerable extent. As the systems are of reduced complexity in comparison with the condensed phase, the study of such molecular aggregates can help in understanding the observed changes between isolated molecules and molecular films. Therefore an aim of this

work is to compare results of electron induced processes in isolated molecules, clusters and molecular films.

Furthermore, this work analyzes characteristic fragmentation patterns of molecules containing different functional groups like alcohols, carboxylic acids, carboxylic acid esters and ketones. Here it is possible to compare to which extent electron induced chemical reactions are changing when going from the purely σ -bonded alcohols to molecules containing a carbonyl functionality with π -bonding. Within the group of carbonyl compounds of the type R_1COR_2 , the influence of the different substituents for R_2 like $-OH$, $-OR$ and $-R$ is studied. In clusters this comparison is of particular interest as the intermolecular interactions change considerably. While in clusters of organic acids intermolecular hydrogen bonding leads to a stronger bound aggregate (especially the organic acid dimers are complexes of considerable stability), the intermolecular interactions in the other clusters are considered to be weaker. This opens the question if the specific configuration due to hydrogen bonding can drive electron induced chemical reactions in a characteristic way.

Within the different classes of functional groups also the influences of the degree of fluorination is investigated. This can be studied by the comparison of the two substituents for the carbonyl compounds for $R_1 = -CH_3$ or CF_3 and for alcohols of the structure $R-OH$ with $R = -CH_2CH_3$ or $-CH_2CF_3$. Regarding the group of esters and ketones also the fluorination of R_2 is possible which will give additional information on the influence of fluorination.

Thus the main aims of this work can be summarized as follows:

- Comparison of electron initiated processes in different states of aggregation, namely isolated molecules in the gas phase, molecular clusters and molecular films.
- Study of the influence of intermolecular interactions on specific reaction channels.
- Analysis of characteristic fragmentation patterns that can be assigned to specific functional groups.
- Investigation of the effect of fluorination on electron induced reactivity.

