1 Introduction

The severe effects of high energy radiation on living organisms are well-known and range from a simple sunburn up to alterations of the genome possibly leading to cancer. In the meantime it is well-established that electrons having an energy below about 20 eV play a pivotal role for the initial steps in radiation damage [1, 2]. The investigation of low energy electron interactions with biomolecules are hence crucial for a better understanding of the underlying mechanisms at a molecular level thereby also revealing the mode of action of radiosensitisers [3], which are employed in radiation therapy to reduce tumours.

Electrons, radicals and ions are created as secondary particles in the cascade of ionisation events following irradiation of biological material with high energy radiation like x-rays or γ-rays. The final biological effects like cell death and mutations are due to a damage of the genome, that is the deoxyribonucleic acid (DNA). This damage is predominantly caused by the secondary particles rather than directly by the primary radiation. Electrons are the most abundant secondary species and are highly reactive in the low energy regime prior to solvation. Since the energy of the initial radiation quantum is distributed to a large number of secondary particles, about 77 % of the secondary electrons possess an energy below 20 eV [4, 5].

The importance of these electrons for DNA damage was demonstrated in 2000 by the group of Sanche [6, 7], who irradiated plasmid DNA with 3 - 20 eV electrons and found an effective yield of strand breaks below the ionisation threshold. A subsequent investigation at even lower electron energies (< 4 eV) revealed a

sharp maximum of the single strand break yield below 1 eV [8] and a threshold for DNA damage that is basically zero eV [9]. This particular sensitivity of the DNA towards low energy electrons and the characteristic resonant yield curves for single and double strand breaks indicate that the dissociative electron attachment (DEA) mechanism may be the initial step. In other words, an electron is captured by the DNA to form a negative ion resonance, which subsequently dissociates resulting in a strand break. DEA can be a very efficient way to decompose a molecule already at very low, but well-defined electron energies, depending on the electronic structure of the particular molecule.

These findings stimulated many ongoing research efforts [1, 2], which approach the problem from two extremes of complexity: On the one hand electron induced damage in plasmid DNA [7] or model DNA (oligonucleotides) [10, 11, 12, 13] and on the other hand single building blocks of DNA in the gas phase [14, 15]. The investigation of complex systems is closer to the biological situation, but the obtained information is limited. The underlying molecular mechanisms can only be elucidated if the intrinsic properties of all constituents are known. Gas phase experiments on the interaction of low energy electrons with single building blocks of DNA thus can provide vitally important informations for the explanation of the observed electron induced strand breaks. Furthermore gas phase experiments can directly be compared with results of the different theoretical models that have been developed in the meantime [16, 17] describing the fate of a negative charge deposited on a particular site of DNA.

The first isolated building blocks that have been studied with respect to dissociative electron attachment were the nucleobases [18]. It was found that electrons are indeed effectively captured by the nucleobases followed by manifold fragmentation [14, 19]. Very recent investigations on the sequence dependence of electron capture by self-assembled monolayers of DNA confirm that the nucleobases may act as antennas for low energy electrons [13]. However, strand breaks finally occur at the sugar-phosphate backbone and the negative charge must therefore be

transferred from the base to the backbone to induce a strand break.

A *direct* electron attachment to the backbone was barely considered in the past few years; first theoretical studies yielded contradictory results on that scenario [16, 20].

Consequently the work presented here focuses on DEA to different model compounds for the DNA (and RNA) backbone including the sugar and the phosphate unit. At first electron induced dissociation of the isolated sugar D-ribose is extensively studied and presented in chapter 4.1. As became already obvious in the study of the DNA bases [14, 15], the respond towards low energy electrons may substantially be modified, once the base is coupled within the DNA network. In that respect the results from the free sugar D-ribose are compared with peracetylated D-ribose (chapter 4.2), which serves as an essentially improved surrogate for the sugar bound within DNA.

Electron capture by the phosphate group is investigated using organic phosphate esters, which are presented in chapter 4.3 showing fragmentation reactions at low electron energy that can be associated with strand breaks in DNA.

A better understanding of electron induced processes in DNA requires the transfer of larger systems into the gas phase, which are composed of different DNA building blocks, for instance whole nucleotides. While the individual subunits of DNA (nucleobases, sugars and phosphate esters) can usually be transferred into the gas phase as intact molecules by appropriate thermal heating, this technique is no longer feasible for larger systems. Moderate heating of thymidine, e.g. (thymine coupled to 2-deoxy-D-ribose), showed that it is partly subjected to decomposition in the course of the evaporation process. The standard methods matrix assisted laser desorption/ionisation (MALDI) and electrospray ionisation (ESI) are of limited use for DEA since a large number of ions are generated. However, the investigation of DEA requires neutral and intact molecules. A new experimental setup is presented here that utilises laser induced acoustic desorption (LIAD), which was successfully employed previously to desorb only neutral

molecules [21]. To complete the investigation of the DNA backbone the combined sugar-phosphate unit, i.e. ribose-5-phosphate, is studied here using LIAD (chapter 4.4).

DEA to biomolecules can exhibit a remarkable site selectivity as shown in chapter 4.1 for D-ribose. Low energy electrons (near 0 eV) trigger remarkably complex mechanisms yielding to the excission of C-containing units thereby almost exclusively removing C5. It has previously been shown that also DEA to the nucleobases proceeds highly site selective concerning the loss of H [14, 22, 23, 24]. As it was demonstrated with thymine, hydrogen can be released as a neutral H atom or as H^- anion originating either from a C-H or an N-H bond. It turned out that the electron energy can be tuned to abstract only a particular hydrogen from a particular C or N atom, respectively.

A careful study of different organic molecules pointed out that the energy of H^- formation following electron attachment depends on the functional group [25] from which the hydride anion is abstracted. Consequently low energy electrons may serve as a tool for specific modification of molecules at energies below the ionisation threshold [26, 27]. A further example of site selective fragmentation is given in chapter 4.1. To elucidate potential selective electron induced reactions in molecules with increasing complexity DEA of hexafluoroacetone azine is presented in chapter 4.5.