

5 Summary

To elucidate the molecular mechanisms of low energy electron induced DNA strand breaks, dissociative electron attachment (DEA) to different model compounds of the DNA (and RNA) backbone was investigated in the gas phase including the sugar and the phosphate moiety.

It was found that the free sugar D-ribose efficiently captures electrons close to zero eV and dissociates subsequently into various fragment anions by loss of neutral water and formaldehyde molecules. The use of the isotope labelled analogues 5-¹³C-D-ribose, 1-¹³C-D-ribose and C-1-D-D-ribose enabled an unambiguous assignment of the generated fragment ions. Furthermore it was demonstrated that C5 is selectively excised from the sugar ring as a formaldehyde molecule close to zero eV electron energy. In DNA C5 of the sugar unit is directly connected to a phosphate group. The threshold signals are explained by the initial formation of a dipole bound state that serves as a doorway to dissociation.

An essential question is to which degree the results that are obtained on a single building block of DNA can be transferred to the situation when the corresponding unit is coupled in the DNA/RNA molecular network. In that respect tetraacetyl-D-ribose was investigated, which can be regarded as substantially improved model for the sugar bound within DNA. It was found that the threshold signals of the isolated sugar are preserved leading to an abstraction of all acetate groups following electron attachment. In addition to the signals that are attributed to the sugar ring, a π^* shape resonance was identified at 1-3 eV located on the acetate groups, which results in further fragmentation products.

The response of the phosphate group to low energy electrons was studied by means of phosphate esters, viz., dibutylphosphate and triethylphosphate. It was observed that electron attachment into the π^* orbitals of the phosphate group occurs at energies below 3 eV accompanied with P-O and C-O bond breaking, and a core excited resonance is located at 7-10 eV. The abstraction of a whole butyl group from dibutylphosphate at 2-4 eV and 7-10 eV is due to a C-O bond cleavage, which would correspond to a strand break in DNA.

To judge which resonances and reactions of the individual parts of DNA are preserved in larger systems, it is vitally important to study DEA to molecules such as sugar-phosphates, nucleosides and nucleotides. Due to the thermal fragility of these compounds a new experimental setup was constructed that allows the investigation of DEA to thermal labile biomolecules employing laser induced acoustic desorption (LIAD). To evaluate the performance of the new experiment, DEA to bromouracil and thymidine was studied. Finally, electron attachment to D-ribose-5-phosphate was investigated and an attachment of near 0 eV electrons to both the phosphate group and the sugar unit was found followed by a cleavage of the phosphate-sugar linkage leading to the formation of H_2PO_4^- and $[\text{Ribosephosphate-H}_2\text{PO}_3]^-$, respectively.

In the work presented here it was demonstrated that all building blocks of the DNA backbone capture electrons at 0-12 eV with subsequent dissociation. The highest ion yields were found at subexcitation energies (< 4 eV). Different reaction mechanisms were suggested that could explain the previously determined (*Phys. Rev. Lett.*, 2004, **93**, 068101), well-structured yield functions of low energy electron induced strand breaks in plasmid DNA.